Attention!

##### 31st International Chemistry Olympiad

##### Bangkok Thailand



* 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

A compound Q (molar mass 122.0 g mol-1) consists of carbon, hydrogen and oxygen.

**PART A**

The standard enthalpy of formation of CO2(g) and H2O(l) at 25.00 oC are -393.51 and -285.83 kJ mol-1 respectively. The gas constant, R, is 8.314 JK-1mol-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 oC. After the reaction is completed, the temperature is observed to be 27.250 oC, and 1.5144 g of CO2 (g) and 0.2656 g of H2O(l) are produced.

* 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 (Uo) -3079 kJ mol-1.

* 1. Calculate the heat capacity of the calorimeter (excluding the water).
	2. Calculate the standard enthalpy of formation (ΔHf ο) of Q.

# PART B

The following data refer to the distribution of Q between benzene and water at 6oC, CB and Cw 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)** |  |
| **CB** | **CW** |
| 0.01180.04780.0981 0.156 | 0.002810.005660.008120.0102 |

* 1. 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

where Tf is the freezing point of the solution, Tf0 the freezing point of solvent, ΔHf the heat of fusion of the solvent, and XS 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 oC. The heat of fusion of benzene is 9.89 kJ mol-1.

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

### Problem 2


# PART A

A diprotic acid , H2A , undergoes the following dissociation reactions :

 H2A  HA- + H+; K1 = 4.50 x 10-7

 HA-  A2- + H+; K2 = 4.70 x 10-11

A 20.00 mL aliquot of a solution containing a mixture of Na2A 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 ?

1. 2-4. What are the amounts (mmol) of Na2A and NaHA initially present?
	1. 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 (KIn = 4.19x10-4) 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. Ka of CH3COOH is 1.75 x 10-5.

**Table:**

 **Solution I Solution II Solution III**

Total concentration 1.00 x 10-5 M 1.00 x 10-5 M 1.00 x 10-5 M

of indicator HIn

Other reagents 1.00 M HCl 0.100 M NaOH 1.00 M CH3COOH

Absorbance at 400 nm 0.000 0.300 ?

* 1. Calculate the absorbance at 400 nm of Solution III.

2-7. Apart from H2O, 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  and ends with a stable .

3-1. How many beta (-) 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 (1W = J s-1)

 produced by 1.00 kilogram of 232Th (t1/2 = 1.40 x 1010 years).

* 1. 228Th is a member of the thorium series, what volume in cm3 of helium at 0 °C and 1 atm collected when 1.00 gram of 228Th (t1/2 = 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 228Th.

3-5. One member of thorium series, after isolation, is found to contain 1.50 x 1010 atoms of the nuclide and decays at the rate of 3440 disintegrations per minute. What is the half-life in years?

The necessary atomic masses are :

 = 4.00260 u,  = 207.97664 u,  = 232.03805 u ; and

1u = 931.5 MeV

1MeV = 1.602 x 10-13 J

NA = 6.022 x 1023 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 FeLm(ClO4)n.3H2O (**A**) and CrLxCly(ClO4)z.H2O (**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

 Atomic mass : H = 1, C = 12, N = 14, O = 16, Cl = 35.45, Cr = 52, Fe = 55.8

**Table 4b** Physical property

.

|  |  |  |
| --- | --- | --- |
| **Complex** | **Magnetic moment , ** | Colour |
| A | 6.13 |  Yellow |
| B | Not measured | Purple |

Problem 4

**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**.

* 1. 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?

* 1. Draw the structure when one molecule of **L** binds to metal ion (M).
	2. From the data in Table 4a, determine the empirical formula of **A**. What are the values of m and n in FeLm(ClO4)n.3H2O? 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 max (in unit of nm) of **A**.

* 1. Detail analysis of **B** shows that it contains Cr3+ ion. Calculate the ‘spin-only’ magnetic moment of this compound.
	2. Compound **B** is a 1:1 type electrolyte. Determine the empirical formula of **B** and the values of x, y, z in CrLxCly(ClO4)z.H2O.

### Problem 5

Glycoside **A** (C20H27NO11), found in seeds of *Rosaceae* gives a negative test with Benedicts’ or Fehling’s solutions. Enzymatic hydrolysis of **A** yields (-) **B**, C8H7NO and **C**, C12H22O11, but complete acid hydrolysis gives as organic products, (+) **D**, C6H12O6 and (-) **E**, C8H8O3.

**C** has a *β*-glycosidic linkage and gives positive test with Benedicts’ or Fehling’s solution. Methylation of **C** with MeI/Ag2O gives C20H38O11, which upon acidic hydrolysis gives 2,3,4-tri-*O*-methyl-D-glucopyranose and 2,3,4,6-tetra-*O*-methyl-D-glucopyranose.

(±) **B** can be prepared from benzaldehyde and NaHSO3 followed by NaCN. Acidic hydrolysis of (±) **B** gives (±) **E**, C8H8O3.

* 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).



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**, C4H6N2O2S which is excreted in urine (stereochemistry not shown).



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.

* 1. 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.)

Problem 5

**(-) 1-Phenylethane-1-*d***, C6H5CH**D**CH3 can be prepared in optically active form and the magnitude of its rotation has the relatively high value, [α]D is equal to -0.6.



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



Compound (-) **M** can also be obtained from compound **N** as follows.



* 1. 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.
	2. 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 C-H (alkene) 3020-3100C=C 1650-1670C-H (alkyne) 3300C≡C 2100-2260C-H (aromatics) 3030C=C (aromatics) 1500-1600C-H (aldehyde) 2700-2775, 2820-2900C=O 1670-1780 | O-H (free alcohol) 3400-3600 O-H (H-bonded alcohol) 3300-3500O-H (acid) 2500-3100C-O 1030-1150NH, NH2 3310-3550C-N 1030, 1230C=N 1600-1700C≡N 2210-2260 |

### 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 HCO2OH 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-NH2 (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.

* 1. 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.

 Problem 6

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 1: Formulae and symbols of common amino acids at isoelectric point

|  |  |  |
| --- | --- | --- |
| **Name** | Formula | **Three-letter symbol** |
| Alanine | CH3CH(NH3+)CO2- | Ala |
| Arginine | H2NC(=NH)NH(CH2)3CH(NH3+)CO2- | Arg |
| Asparagine | H2NCOCH2CH(NH3+)CO2- | Asn |
| Aspartic Acid | HO2CCH2CH(NH3+)CO2- | Asp |
| Cysteine | HSCH2CH(NH3+)CO2- | Cys |
| Cystine | [SCH2CH(NH3+)CO2-]2 | - |
| Glutamic Acid | HO2CCH2CH2CH(NH3+)CO2- | Glu |
| Glutamine | H2NCOCH2CH2CH(NH3+)CO2- | Gln |
| Glycine | +H3NCH2CO2- | Gly |
| Histidine |  | His |
| Isoleucine | CH3CH2CH(CH3)CH(NH3+)CO2- | Ile |
| Leucine | (CH3)2CHCH2CH(NH3+)CO2- | Leu |
| Lysine | H2N(CH2)4CH(NH3+)CO2- | Lys |
| Methionine | CH3SCH2CH2CH(NH3+)CO2- | Met |
| Phenylalanine | PhCH2CH(NH3+)CO2- | Phe |
| Proline |  | Pro |
| Serine | HOCH2CH(NH3+)CO2- | Ser |
| Threonine | CH3CH(OH)CH(NH3+)CO2- | Thr |
| Tryptophan |  | Trp |
| Tyrosine |  | Tyr |
| Valine | (CH3)2CHCH(NH3+)CO2- | Val |

###  Problem 6

**Table 2: pKa of some important groups in amino acids**

|  |  |  |
| --- | --- | --- |
| **Groups** | **Equilibrium** | **pKa** |
| Terminalcarboxyl | -CO2H  -CO2- + H+ | 3.1 |
| Asp /or Glu side- chain carboxyl | -CO2H  -CO2- + H+ | 4.4 |
| His side-chain |  + H+  | 6.5 |
| Terminal amino | -NH3+  -NH2 + H+ | 8.0 |
| Cys side-chain | -SH-S- + H+ | 8.5 |
| Tyr side-chain |  + H+ | 10.0 |
| Lys side-chainamino | -NH3+  -NH2 + H+ | 10.0 |
| Arg side-chain | -NH(NH2)C=NH2+ -NH(NH2)C=NH + H+ | 12.0 |

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**Problem 1**

## PART A

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

|  |
| --- |
| Calculation  |

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

 Calculation with proper units:

|  |
| --- |
|  |

|  |  |  |
| --- | --- | --- |
|  The heat capacity of calorimeter is |  | J K-1 |

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 **Problem 1**

* 1. Calculate the standard enthalpy of formation (Hof) of Q.

 Calculation with proper units:

|  |
| --- |
|  |

|  |  |  |
| --- | --- | --- |
|  Hof of Q is |    | kJ mol-1 |

## PART B

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

Calculation:

|  |
| --- |
|  Q in benzene is monomer dimer. |

1-5. Calculate the freezing point (Tf) of a solution containing 0.244 g of Q in 5.85 g of

 benzene at 1 atm.

 Calculation

|  |
| --- |
|  |

|  |  |  |
| --- | --- | --- |
|  Tf of solution is |  | °C |

|  |
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**Problem 2**

#### PART A

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

|  |  |
| --- | --- |
| Species which reacts first is |  |
|  |  |
| The product is |  |

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

|  |  |
| --- | --- |
| mmol of product = |  |

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

|  |
| --- |
|  |

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**Problem 2**

* 1. What are the amounts (mmol) of Na2A and NaHA initially present?

Calculation:

|  |
| --- |
|   |

|  |  |
| --- | --- |
| mmol of Na2A = |  |
|  |  |
| mmol of NaHA = |  |

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

 Calculation:

|  |
| --- |
| Total volume of HCl required = mL |

|  |
| --- |
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**Problem 2**

###### PART B

* 1. Calculate the absorbance at 400 nm of Solution III.

Calculation:

|  |
| --- |
|  |

|  |  |
| --- | --- |
| The absorbance at 400 nm of Solution III = |  |

2-7. Apart from H+, OH- and H2O, what are all the chemical species present in the solution resulting from mixing Solution II and Solution III at 1:1 volume ratio?

|  |  |
| --- | --- |
|  |  |

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|  Name: Student Code: |

**Problem 2**

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

Calculation:

|  |
| --- |
|  |

|  |  |
| --- | --- |
| The absorbance at 400 nm of the solution = |  |

|  |
| --- |
|  Name: Student Code: |

**Problem 2**

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

Calculation:

|  |
| --- |
|  |

|  |  |
| --- | --- |
| Transmittance of the solution = |  |

|  |
| --- |
|  Name: Student Code: |

**Problem 3**

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

Calculation:

|  |
| --- |
|   |

|  |  |
| --- | --- |
| Number of beta decays = |  |

* 1. How much energy in MeV is released in the complete chain?

Calculation:

|  |
| --- |
|  |

|  |  |  |
| --- | --- | --- |
| Energy released = |  |  MeV |
|  Name: Student Code: |

**Problem 3**

3-3. Calculate the rate of production of energy (power) in watts (1W = Js-1) produced by

1.00 kilogram of 232Th (t1/2 = 1.40 x 1010 years).

 Calculation:

|  |
| --- |
|  |

|  |  |  |
| --- | --- | --- |
| Rate of production of energy = |  |  W |

|  |
| --- |
|  Name: Student Code: |

**Problem 3**

3-4. What volume in cm3 of helium at 0 °C and 1 atm collected when 1.00 gram of 228Th (t1/2 = 1.91 years) is stored in a container for 20.0 years.

 Calculation:

|  |
| --- |
|  |

|  |  |  |
| --- | --- | --- |
| Volume of He at 0 °C and 1 atm =  |  | cm3 |

3-5. One member of thorium series, after isolation, is found to contain 1.50 x 1010

 atoms of the nuclide and decays at the rate of 3440 disintegrations per minute.

 What is the half-life in years?

 Calculation:

|  |
| --- |
|  |

|  |  |  |
| --- | --- | --- |
| Half-life =  |  |  years |

|  |
| --- |
| Name: Student Code: |

**Problem 4**

4-1. The molecular formula of **L** is

* 1. The structures of bipyridine and **L**

structure of **L**

 structure of bipyridine

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  |
|  |  |  |  |  |  |  |  |  |

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

|  |
| --- |
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 **Problem 4**

* 1. Determine the empirical formula of **A**.

Calculation:

|  |
| --- |
|  |

 The empirical formula of **A** is

 What are the values of m and n in FeLm(ClO4)n.3H2O?

m = n =

The complete formula of **A** is

The ratio of cation to anion is **:**

|  |
| --- |
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 **Problem 4**

4-6.The oxidation number of Fe in complex **A** is

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

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

 High spin configuration Low spin configuration

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

|  |  |
| --- | --- |
|   | High spin |
|  | Low spin |

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

(Please tick):

|  |  |
| --- | --- |
|  | Color |
|  | Elemental analysis data |
|  | Magnetic moment |
|  | Molar conductance |

4-7.max of complex **A** is nm.

|  |
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|  Name: Student Code: |

 **Problem 4**

* 1. Calculate the ‘spin-only’ magnetic moment of complex B.

Calculation:

|  |
| --- |
|  |

|  |  |  |
| --- | --- | --- |
| The ‘spin-only’ magnetic moment of complex **B** = |  |  B.M. |

4-9.

|  |  |  |
| --- | --- | --- |
| The empirical formula of **B** is |  |  |
|  |  |  |
|  x = |  |  |
|  |  |  |
|  y = |  |  |
|  |  |  |
|  z = |  |  |

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**Problem 5**

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

|  |  |
| --- | --- |
| A | B |
| **C** | D |

* 1. Write molecular formula for compounds **F** and **G,** and structural formula for compounds **H** and **I** and indicate stereochemistry of **H.**

|  |  |  |
| --- | --- | --- |
| Molecular formula ofcompound **F** = Molecular formula ofcompound **G** =  | Compound **H** | Compound **I** |
|  Name: Student Code: |

 **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.

|  |  |  |  |
| --- | --- | --- | --- |
|  |  |  |  |
|  |  |  |  |

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

|  |  |
| --- | --- |
|  | SN1 |
|  | SN2 |
|  | SNi |
|  | E1 |
|  | E2 |

|  |
| --- |
|  Name: Student Code: |

**Problem 6 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_**

6-1.

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

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

|  |
| --- |
|  |

6-3.

|  |  |
| --- | --- |
| The sequence of B8 is |  |

6-4.

|  |  |
| --- | --- |
| The sequence of B9 is |  |

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

|  |
| --- |
|   |

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

|  |
| --- |
|   |

6-7.

|  |  |
| --- | --- |
| The isoelectric point of **A** is  |  |

Name: Student Code: …

**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 = (1.5144)(12.0/44.0) : (0.2656)(2.0/18.0) : (0.1575) 12.0 1.0 16.0 = 0.0344 : 0.0295 : 0.00984 = 7 : 6 : 2The formula mass of C7H6O2 = 122 which is the same as the molar mass given ( 2 )C7H6O2(s) +  O2(g) → 7CO2(g) + 3H2O(l) or ( 1 )[2C7H6O2(s) + 15O2(g) → 14CO2(g) + 6H2O(l)] |

3 marks

2 marks for correct formula of Q.

1 mark for correct balanced equation with proper states.

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

 Calculation with proper units:

|  |
| --- |
| Mole Q = 0.6000 = 4.919×10-3 (0.5) 122.0 qv = nUo = 0.6000 ×(-3079) = -15.14 kJ ( 2 ) 122.0Total heat capacity = -qv = 15.14 = 6.730 kJ K-1 (1.5) T 2.250 = 6730 J K-1Heat capacity of water = 710.0×4.184 = 2971 J K-1 ( 1 )Heat capacity of calorimeter = 6730-2971 = 3759 J K-1 ( 1 ) |

 6 marks

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

* 1. Calculate the standard enthalpy of formation (Hof) of Q.

 Calculation with proper units:

|  |
| --- |
| *n*g =  = -0.5 mol (0.5) *H*o = *U*o + *RT* *n*g (0.5) = -3079 + (8.314×10-3)(298)(-0.5) ( 1 ) = -3079-1 = -3080 (0.5)*H*o = (7f*H*o, CO2(g) + 3f*H*o, H2O(l)) - (f*H*o, Q) ( 1 )f*H*o of Q = 7(-393.51) + 3(-285.83)-(-3080) ( 1 ) = -532 kJ mol(0.5) |

5 marks

|  |  |  |
| --- | --- | --- |
| f*H*o of Q is | −532 | kJ mol−1 |

#### PART B

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

 Calculation:

|  |
| --- |
| CB (mol L-1) 0.0118 0.0478 0.0981 0.156√CW (mol L-1) 0.00281 0.00566 0.00812 0.0102either CB/CW 4.20 8.44 12.1 15.3or CB/CW2 1.49×103 1.49×103 1.49×103 1.50×103 ( 2 )(or CB/CW 38.6 38.6 38.6 38.7 )From the results show that the ratio CB/CW varies considerably, whereas the ratio CB/CW2 or √CB/CW 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 (Tf) 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 Q2 = 0.244/244 = 1.32x10-2 (0.01316) ( 3 ) (0.244 + 5.85) 244 78.0 s*T* = (8.314)(278.55)2 . 1.32×10-2 = 0.861 ( 2 ) 9.89x103  *T*s = .40-0.861 = 4.54 oC ( 1 ) |
| *T*s 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 x 0.300 = 0.300 | 0.5 mark |

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

HA- + H2O  H2A + OH-

1 mark

* 1. What are the amounts (mmol) of Na2A and NaHA initially present?

Calculation:

|  |
| --- |
| At pH 8.34 which is equal to (p*K*a1 + p*K*a2)/2 all A2- are protonated as HA—. Therefore no. of A2- initially present in the solution = 0.300 x 10.00 = 3.00 mmolAt pH 10.33 , the system is a buffer in which the ratio of [A2-] and [HA—] is equal to 1. Thus[HA—] initial + [HA—] formed = [A2- ]initial - [HA— ]formedThe amount of initial HA— = 3.00 – 0.300 - 0.300 mmol = 2.40 mmol  |

|  |  |  |
| --- | --- | --- |
| mmol of Na2A = | 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 |

## PART B

* 1. 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 CH3COOHTo 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+] of solution III =  =  = 4.18x10-3 KIn  (1.0 mark)From HIn  In- + H+ KIn =  (0.5 mark)  =  =  = 0.100  = 0.100 (1.0 mark) Whereas [HIn] + [In-] = 10-5 10[In-] + [In-] = 10-5 [In-] = 0.091 x 10-5 (1.5 mark) ∴ Absorbance of solution III =  x 0.300 = 0.027 (1.0 mark) |

-0.5 mark for incorrect unit

|  |  |
| --- | --- |
| The absorbance at 400 nm of Solution III = | 0.027 |

5 marks

2-7. Apart from H+, OH-, and H2O, what are all the chemical species present in the solution resulting from mixing Solution II and Solution III at 1:1 volume ratio?

|  |
| --- |
| CH3COOH , CH3COO- , 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 CH3COO- / 0.45 M CH3COOH is obtained. [H+] of mixture solution = Ka = 1.75 x 10-5 x  = 15.75 x 10-5 (1.0 mark) therefore  =  =   = 2.65 (1.0 mark) Whereas [HIn] + [In-] = 10-5  + [In-] = 10-5 [In-] = 0.726 x 10-5 (1.5 marks)∴ Absorbance of solution =  x 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

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

Calculation:

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

-0.5 mark for incorrect unit

**Problem 3 20 points**

* 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 = 4- emitted. (1) |

2 marks

|  |  |
| --- | --- |
| Number of beta decays = | 4 |

* 1. How much energy in MeV is released in the complete chain?

Calculation:

|  |
| --- |
|   + 6  + 4- Energy released is Q valueQ = [m(232Th)-m(208Pb)-6m(4He)]c2(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 |

3-3. Calculate the rate of production of energy (power) in watts (1W = J s-1) produced by

1.00 kilogram of 232Th (t1/2 = 1.40 x 1010 years).

 Calculation:

|  |
| --- |
| 1.00 kg contains =  = 2.60 x 1024 atoms (1) Decay constant for 232Th =  (1) = 1.57 x 10-18 s-1 A = N = (2.60 x 1024)(1.57 x 10-18) where A is activity = 4.08 x 106 dps (disintegrations s-1)  Each decay liberates 42.67 MeV (1) Rate of production of energy (power) 4.08 x 106 dis s-1 x 42.67 MeV dis-1 x 1.602 x 10-13 J Mev-1 = 2.79 x 10-5 J s-1 = 2.79 x 10-5 W (2) |

5 marks

|  |  |  |
| --- | --- | --- |
| Rate of production of energy = | 2.79 x 10-5 | W |

3-4. What volume in cm3 of helium at 0 °C and 1 atm collected when 1.00 gram of 228Th (t1/2 = 1.91 years) is stored in a container for 20.0 years.

 Calculation:

|  |
| --- |
| 228Th 208Pb + 5 4He (1)The half-lives of various intermediates are relatively short compared that of 228Th. A = N =  = 9.58 x 1020 y-1 (1)Number of He collectedNHe = (9.58 x 1020 y-1)(20.0 y)(5 particles) = 9.58 x 1022 particles of He (1) Vhe =  = 3.56 x 103cm3 (2) |

 5 marks

|  |  |  |
| --- | --- | --- |
| Volume of He at 0 °C and 1 atm =  | 3.56 x 103 | cm3 |

3-5. One member of thorium series, after isolation, is found to contain 1.50 x 1010 atoms of the nuclide and decays at the rate of 3440 disintegrations per minute.

What is the half-life in years?

Calculation:

|  |
| --- |
| A = N;t1/2 =  =  (1.5) =  (1.5) = 3.02 x 106 min = 5.75 years (1) |

 4 marks

|  |  |  |
| --- | --- | --- |
| Half-life =  | 5.75 | years |

**Problem 4 28 points**

4-1. The molecular formula of **L** is C10H8N2O2 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 C10 H8 N2) 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 C10H8N2O2.

* 1. The structures of bipyridine and **L**

|  |  |  |
| --- | --- | --- |
| Structure of bipyridine |  |  or orstructure of **L** |

 2 marks 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

* 1. 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 FeC30H30Cl3N6O21.

3 marks

What are the values of m and n in FeLm(ClO4)n.3H2O?

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 [FeL3](ClO4)3.3H2O

1 mark

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

The three (ClO4)- groups will dissociate as free ion in solution. So the entire complex will be in the ion forms as [FeL3]3+ and 3 (ClO4)- 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

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. where  is the so-called ‘spin-only’ magnetic moment and n is the number of unpaired electrons. Thus , for high spin case ,  B.M.And for low spin case ,  B.MThe measured magnetic moment ,  , 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.  |

450

4-7.max of complex **A** is nm.

1 mark

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

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

Calculation:

|  |
| --- |
| From  For Cr3+ , n = 3 1 mark Therefore,  B.M |

 3.87

 The ‘spin-only’ magnetic moment of complex **B** = B.M.

1 mark

4-9The empirical formula of **B** is CrC20H18N4Cl3O9 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 units0.5 for 1,6-linkage0.5 for β-linkage | D(1.5 marks)Remark: 0.5 for correct structure1 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 ofcompound **F** = **HCN**(0.5 mark)Molecular formula ofcompound **G** = **H2S**(0.5 mark) | Remark: 1 mark for structure1 mark for correct stereochemistry | Remark: 2 marks for structure |

(5 marks)

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.

|  |  |  |  |
| --- | --- | --- | --- |
| Remark:1 mark for structure0.5 mark for **R, S**0.5 mark for correct stereochemistry | Remark:0.5 mark for ester0.5 mark for ether0.5 mark for correct stereochemistry | Remark:0.5 mark for structure0.5 mark for correct stereochemistry | Remark:0.5 mark for structure0.5 mark for correct stereochemistry |
| Remark:0.5 mark for structure0.5 mark for correct stereochemistry | Remark:0.5 mark for structure0.5 mark for **R, S**0.5 mark for correct stereochemistry | Remark:0.5 mark for structure0.5 mark for correct stereochemistry | Remark:0.5 mark for **R, S** |

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

|  |  |
| --- | --- |
|  | SN1 |
| √ | SN2 |
|  | SNi |
|  | E1 |
|  | E2 |

1 mark

**Problem 6 16 points**

6-1.

|  |  |
| --- | --- |
| 2 | sulfonic acid groups are formed from oxidation of a disulfide bond. |

1 mark

* 1. 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"

1. mark for wrong sequence even if Asp and Leu are placed correctly since the information is already provided in the question

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

|  |
| --- |
| Cys-Tyr-Ile-Glu-Asp-Cys-Pro-Leu-Gly-NH2  |

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 "NH2" group at C-terminus.

- 0.5 for using the symbol "Cya" is used in place of "Cys".

0 mark if the sequence wrong.

* 1. 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- NH2 |

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

##### 31st International Chemistry Olympiad

##### Bangkok Thailand



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 Catalysed Reaction Between Acetone and Iodine in Aqueous Solution**

INTRODUCTION

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



 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 I2(aq) has been shown to have the form



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.



Where [ ]0 are the initial concentrations of acetone, I2 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 I2(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 I2 (aq) is determined by titration with sodium thiosulphate, Na2S2O3. As the end point of the titration is approached, starch indicator is added and the titration is continued until the blue colour 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. CH3COONa 80 mL

4. Standard 0.02xxx M Na2S2O3(aq) solution 200 mL

 (the exact concentration will be announced at the beginning of Task 1)

1. Aqueous acetone (50% by volume) 50 mL

 (density of pure acetone; 0.787 g/mL, MW. = 58.08)

1. 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 0.0000. If not, call demonstrator.
2. To start, press **B.**
3. To stop, press **B**.
4. To reset, press **C**.

**Procedure**

A. Standardisation 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.

1. Titrate the iodine with the standard 0.02xxx M sodium thiosulfate solution until the

 colour of the solution is pale yellow.

1. Add 3 - 4 drops of starch indicator and continue the titration until the blue colour disappears.
2. Record the initial and the final volumes of the thiosulfate solution and the volume used in the answer sheet.
3. Repeat the titration as necessary (Steps 1 to 5)
4. Give the titre volume for calculation in the answer sheet.
5. Calculate the iodine concentration.
6. A kinetic study of acid catalysed reaction between acetone and iodine in aqueous solution
7. Label the stoppered flasks as follows: Flask I, II, III and IV.
8. 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.

|  |  |
| --- | --- |
|  | Volume (mL) |
| Flask No. | water  |  0.100 M HCl | 50%acetone |
| IIIIIIIV |  5.000.00.00.0 | 5.005.005.0010.00 | 5.00 5.0010.00 5.00 |

1. Measure out 10 mL of 0.50 M aq. CH3COONa into the graduated cylinder.
2. Set the stop-watch to 0.0000 display.
3. Pipette **5.00 mL** of iodine solution into the stoppered **Flask No. I**. **Start** the stop-watch as soon as the **first drop of iodine solution is added**.
4. Stopper the flask and swirl continuously.
5. 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.**
6. Titrate the remaining iodine with standard thiosulphate solution.
7. Record the volume of the thiosulphate solution.
8. Repeat the above steps (Steps 3 to 9) for Flask II, III and IV but add in step 5 the I2(aq) solution to each flask as indicated:

 **Flask II: 10.00 mL I2 solution**

 **Flask III: 5.00 mL I2 solution**

 **Flask IV: 5.00 mL I2 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



 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.

**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 Na2SO4 (in a plastic vial)

Dichloromethane

Ceric ammonium nitrate solution

2,4-Dinitrophenylhydrazine (labelled as 2,4-DNP)

2% aq. NH3

5% aq. AgNO3

5% aq. HCl

5% aq. NaOH

5% aq. NaHCO3

1% FeCl3 in EtOH

0.2% aq. KMnO4 Decolourised with easily oxidised functional groups.

Acetone (for washing)

#### Equipment’s and Glassware’s

 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

1. Microspatula 1
2. 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 distillate 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 Na2SO4 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 Na2SO4 using the dry cotton plugged Pasteur pipette, then transfer into the vial. Be careful not to transfer any of the Na2SO4 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. AgNO3 in a small test tube followed by 1 drop of 5% aq. NaOH, brown precipitate will appear. Add 2% aq NH3 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 CH3I in the presence of K2CO3 gives compound **X** (C11H14O2). Oxidation of **X** gives unknown **Y** (C10H12O4) as the main product and CO2.

|  |
| --- |
| **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 1H NMR spectra and answer sheet PART II**. 1H 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 1H 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 1H NMR spectra in the same manner as Q.4.** |

RESULTS SHEET

A. Standardisation of Iodine Solution

|  |
| --- |
| Concentration of standard Na2S2O3 in bottle : ............ …………………........... M |

|  |  |
| --- | --- |
|  | **Volume** |
| Titration Number | **1** | **2** | **3** |
| aliquot of I2 (mL) | 5.00 | 5.00 | 5.00 |
| initial buret reading (mL) |  |  |  |
| final buret reading (mL) |  |  |  |
| standard Na2S2O3 (mL) |  |  |  |

The volume of titre used in calculation = mL

Calculation for iodine concentration:

 :

 mol ratio of I2 : S 2O32- =

|  |  |  |
| --- | --- | --- |
| Concentration of I2  |  | M |

1. A kinetic study of the acid catalysed reaction between acetone and iodine in aqueous

 solution

 B-1. Calculation for initial concentrations (M) in the solution mixtures

|  |  |
| --- | --- |
|  | Concentration |
| Flask No. | **I** | **II** | **III** | **IV** |
| [I2], M |  |  |  |  |
| [acetone], M |  |  |  |  |
| [HCl], M |  |  |  |  |

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

|  |  |
| --- | --- |
|  | Volume |
|  | **I** | **II** | **III** | **IV** |
| initial burette reading (mL) |  |  |  |  |
| final burette reading (mL) |  |  |  |  |
| standard Na2S2O3 (mL) |  |  |  |  |
|  |  |  |  |  |
|  [I2] remaining at 7 minutes (M) |  |  |  |  |
|  |  |  |  |  |

B-3. Calculation for initial rate of disappearance of I2  at 7 minutes for Flasks I to IV (in M s-1)

Initial rate of disappearance of iodine (M s-1) = - 

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Flask No.** | **I** | **II** | **III** | **IV** |
| **Calculation for rate**  |  |  |  |  |
| **Initial Rate =** |   |   |  |  |

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

|  |  |  |
| --- | --- | --- |
| **Calculation for x** | **Calculation for y** | **Calculation for z** |
|  |  |  |
| x = (integer) | y = (integer) | z = (integer) |

Write rate equation or rate law

|  |  |
| --- | --- |
| Rate = |  |

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

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Flask No.** | **I** | **II** | **III** | **IV** |
| **Calculation**  |  |  |  |  |
| Rate Constant k = |  |   |  |  |
| **Unit** |  |  |  |  |

 B-6. Mean value of rate constant =

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

|  |  |  |  |
| --- | --- | --- | --- |
| **No.** | Loss Point | **Remark** | **Student’s signature** |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |

|  |  |
| --- | --- |
| RESULTS SHEET:  | Student Copy |

## PART I

|  |
| --- |
| Q.1) Show the distillate (≥5 mL) to your demonstrator and ask for his/her signature.Demonstrator Signature: |

**Q.2) Functional Groups Analysis of the distilled essential oil (S):**

Tick (√) where appropriate.

|  |  |  |
| --- | --- | --- |
| Reagents | Positive test | Negative test |
| 0.2% KMnO4 |  |  |
| 1% FeCl3 |  |  |
| 2,4-DNP |  |  |
| Ceric ammonium nitrate |  |  |
| Tollen’s Reagent |  |  |

|  |  |  |
| --- | --- | --- |
| Functional groups in **S** | Present | Not present |
| -C=C- |  |  |
| -OH (alcoholic) |  |  |
| -OH (phenolic) |  |  |
| -CHO |  |  |
| -CO- |  |  |
| -COOH |  |  |

#### Q.3) Functional Groups Analysis of unknown Y:

 Tick (√) where appropriate.

|  |  |  |
| --- | --- | --- |
| Reagents | Positive test | Negative test |
| 5% HCl |  |  |
| 5% NaOH |  |  |
| 5% NaHCO3 |  |  |
| 0.2% KMnO4 |  |  |
| 1% FeCl3 |  |  |
| 2,4-DNP |  |  |
| Ceric ammonium nitrate |  |  |
| Tollen’s Reagent |  |  |

|  |  |
| --- | --- |
| RESULTS SHEET:  | Student Copy |

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

|  |
| --- |
| **Student signature:**…………………………………………………………….. |

|  |  |
| --- | --- |
| RESULTS SHEET:  | Demonstrator Copy |

## PART I

|  |
| --- |
| Q.1) Show the distillate (≥5 mL) to your demonstrator and ask for his/her signature.Demonstrator Signature: |

**Q.2) Functional Groups Analysis of the distilled essential oil (S):**

Tick (√) where appropriate.

|  |  |  |
| --- | --- | --- |
| Reagents | Positive test | Negative test |
| 0.2% KMnO4 |  |  |
| 1% FeCl3 |  |  |
| 2,4-DNP |  |  |
| Ceric ammonium nitrate |  |  |
| Tollen’s Reagent |  |  |

|  |  |  |
| --- | --- | --- |
| Functional groups in **S** | Present | Not present |
| -C=C- |  |  |
| -OH (alcoholic) |  |  |
| -OH (phenolic) |  |  |
| -CHO |  |  |
| -CO- |  |  |
| -COOH |  |  |

#### Q.3) Functional Groups Analysis of unknown Y:

 Tick (√) where appropriate.

|  |  |  |
| --- | --- | --- |
| Reagents | Positive test | Negative test |
| 5% HCl |  |  |
| 5% NaOH |  |  |
| 5% NaHCO3 |  |  |
| 0.2% KMnO4 |  |  |
| 1% FeCl3 |  |  |
| 2,4-DNP |  |  |
| Ceric ammonium nitrate |  |  |
| Tollen’s Reagent |  |  |

|  |  |
| --- | --- |
| RESULTS SHEET:  | Demonstrator Copy |

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

|  |
| --- |
| **Student signature:**…………………………………………………………….. |

PART II

**Q. 4) Structure Elucidation:**

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

|  |
| --- |
|  |

**NMR Assignment of the main essential oil (S):**

(See peak number in the given 1H NMR spectrum)

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Peak No. | Chemical shift (δ, ppm) | No. of proton(s) | Multiplicity \* | 1H NMR Assignment |
| 1234567 | 3.313.845.0-5.15.65.9-6.06.76.87 | 2H3H2H1H1H2H1H |  | Draw a structure of the essential oil (S) with peak no. assignment at each proton. |

**\* Multiplicity:**

 **s = singlet**

 **d = doublet**

 **t = triplet**

 **q = quartet**

 **m = multiplet**

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

|  |  |  |
| --- | --- | --- |
| **Compound X** |  | **Unknown Y** |
|  |  |  |

**NMR Assignment of Unknown Y:**

(See peak number in the given 1H NMR spectrum, labile proton does not appear in the spectrum)

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Peak No. | Chemical shift(δ, ppm) | No. of proton(s) | Multiplicity | 1H NMR Assignment |
| 1234 | 3.593.863.886.81 | 2H3H3H3H |   | Draw a structure of the unknown Y with peak no. assignment at each proton. |

RESULTS SHEET

A. Standardisation of Iodine Solution

|  |
| --- |
| Concentration of standard Na2S2O3 in bottle : 0.01970 M |

|  |  |
| --- | --- |
|  | **Volume** |
| Titration Number | **1** | **2** | **3** |
| aliquot of I2 (mL) | 5.00 | 5.00 | 5.00 |
| initial burette reading (mL) | 0.00 | 0.00 | 0.00 |
| final burette reading (mL) | 10.00 | 10.05 | 9.95 |
| standard Na2S2O3 (mL) | 10.15 | 10.10 | 10.05 |

10.10

The value of titre = mL

Calculation for iodine concentration:

1:2

 mol ratio of I2 : S2O32- =

 I2 + 2 S2O3 2 2I- + S4O6 2-





 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 I2  | 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.

B. A kinetic study of the acid catalysed reaction between acetone and iodine in aqueous solution

 B-1. Calculation for initial concentrations (M) in the solution mixtures

|  |  |
| --- | --- |
|  | **Concentration** |
| Flask No. | **I** | **II** | **III** | IV |
| [I2], 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 I2 and HCl.

 0.5 mark for each correct concentration of acetone.

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

|  |  |
| --- | --- |
|  | **Volume** |
| Flask No. | **I** | **II** | **III** | **IV** |
| initial burette reading (mL) | 0.00 | 0.00 | 0.00 | 0.00 |
| final burette reading (mL) | 8.35 | 18.55 | 6.75 | 6.85 |
| standard Na2S2O3 (mL) | 8.35 | 18.55 | 6.75 | 6.85 |
|  |  |  |  |  |
| [I2] 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. Calculation for initial rate of disappearance of I2 at 7 minutes for Flasks I to IV (in M s-1)

Initial rate of disappearance of iodine (M s-1) = - 

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Flask No.** | **I** | **II** | **III** | **IV** |
| **Calculation for rate**  |  |  |  |  |
| **Initial rate** | 2.05 x 106 | 1.98 x 106 | 3.95 x 106 | 3.811 x 106 |

4 marks for correct calculation.

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

rate = -  = k[CH3COCH3]x [I2]y [H**+**]z

|  |  |  |
| --- | --- | --- |
| **Calculation for x** | **Calculation for y** | **Calculation for z** |
|  |  |  |
| x = 1 (integer) | y = 0 (integer) | z = 1 (integer) |

 max 1 mark for each correct calculation

Write rate equation or rate law

|  |  |
| --- | --- |
| Rate = | k[CH3COCH3][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**  |  |  |  |  |
| **Rate Constant*****k* =** | 4.85 x 10-5 | 4.68 x 10-5 | 4.66 x 10-5 | 4.51 x 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.

4.68 x 10 -5

 B-6. Mean value of rate constant =

 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.

|  |  |
| --- | --- |
| RESULTS SHEET:  | 28.6 points |

PART I

|  |
| --- |
| Q.1) Show the distillate (≥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 (√) where appropriate.

|  |  |  |
| --- | --- | --- |
| Reagents | Positive test | Negative test |
| 0.2% KMnO4 | √ |  |
| 1% FeCl3 | √ |  |
| 2,4-DNP |  | √ |
| Ceric ammonium nitrate | √ |  | 2.5 marks |
| Tollen’s Reagent |  | √ | 0.5 for each correct result |

|  |  |  |
| --- | --- | --- |
| Functional groups in **S** | Present | Notpresent |
| -C=C- | √ |  |
| -OH (alcoholic) |  | √ |
| -OH (phenolic) | √ |  |
| -CHO |  | √ |  |
| -CO- |  | √ | 3 marks |
| -COOH |  | √ | 0.5 for each correct result |

#### Q.3) Functional Groups Analysis of unknown Y: (7)

 Tick (√) where appropriate.

|  |  |  |
| --- | --- | --- |
| Reagents | Positive test | Negative test |
| 5% HCl |  | √ |
| 5% NaOH | √ |  |
| 5% NaHCO3 | √ |  |
| 0.2% KMnO4 |  | √ |
| 1% FeCl3 |  | √ |
| 2,4-DNP |  | √ |
| Ceric ammonium nitrate |  | √ | 4 marks |
| Tollen’s Reagent |  | √ | 0.5 for each correct result |

|  |  |  |
| --- | --- | --- |
| Functional groups in **Unknown Y** | Present | Notpresent |
| -C=C- |  | √ |
| -OH (alcoholic) |  | √ |
| -OH (phenolic) |  | √ |
| -CHO |  | √ |  |
| -CO- |  | √ | 3 marks |
| -COOH | √ |  | 0.5 for each correct result |

|  |
| --- |
| **Student signature:**…………………………………….……………………….. |

PART II

**Q. 4) Structure Elucidation: (6)**

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

|  |
| --- |
|  |

2 marks

 0.5 mark for OH, 0.5 mark for OCH3, 0.5 mark for CH2CH=CH2,

0.5 mark for 1, 2, 4-trisubstituted benzene

**NMR Assignment of the main essential oil (S):**

(See peak number in the given 1H NMR spectrum)

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Peak No. | Chemical shift (δ, ppm) | No. of proton(s) | Multiplicity | 1H NMR Assignment |
| 1234567 | 3.313.845.0-5.15.65.9-6.06.76.87 | 2H3H2H1H1H2H1H | d (0.25 mark)s (0.25 mark)m (0.25 mark)s (0.25 mark)m (0.25 mark)s (0.25 mark)d or m (0.5 mark)d (0.25 mark) | Draw a structure of the essential oil (S) with peak no. assignment at each proton. |

4 marks

2 marks for multiplicity assignment

 2 marks for chemical shift assignment

 (0.25 mark for each proton assignment)

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

|  |  |  |
| --- | --- | --- |
| **Compound X** |  | **Unknown Y** |
|  |  |  |

1 mark 1 mark

0.5 mark for 2(OCH3) 0.5 mark for 2(OCH3 )

0.5 mark for CH2CH=CH2  0.5 mark for CH2COOH

**NMR Assignment of Unknown Y:**

(See peak number in the given 1H NMR spectrum, labile proton does not appear in the spectrum)

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Peak No. | Chemical shift(δ, ppm) | No. of proton(s) | Multiplicity | 1H NMR Assignment |
| 1234 | 3.593.863.886.81 | 2H3H3H3H | s (0.25 mark)s (0.25 mark)s (0.25 mark) s (0.25 mark)d (0.5 mark)m (0.75 mark) | 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)