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

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

PART A

The standard enthalpy of formation of CO_2(g) and H_2O(l) at 25.00 ^oC 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 ^oC. After the reaction is completed, the temperature is observed to be 27.250 ^oC, 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^oC, 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

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

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 ^oC. 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.

Problem 2

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 $^{232}_{90}Th$ and ends with a stable $^{208}_{82}Pb$.

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 (1W = J s^{-1}) produced by 1.00 kilogram of ^{232}Th ($t_{1/2}$ = 1.40 x 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 x 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 masses are :

$^{4}_{2}He$ = 4.00260 u, $^{208}_{82}Pb$ = 207.97664 u, $^{232}_{90}Th$ = 232.03805 u ; and

1u = 931.5 MeV

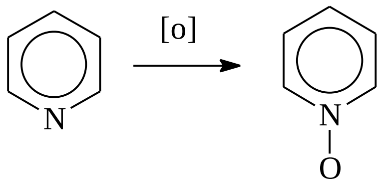
1MeV = 1.602 x 10^{-13} J

N_A = 6.022 x 10^{23} 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

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 ,** m (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

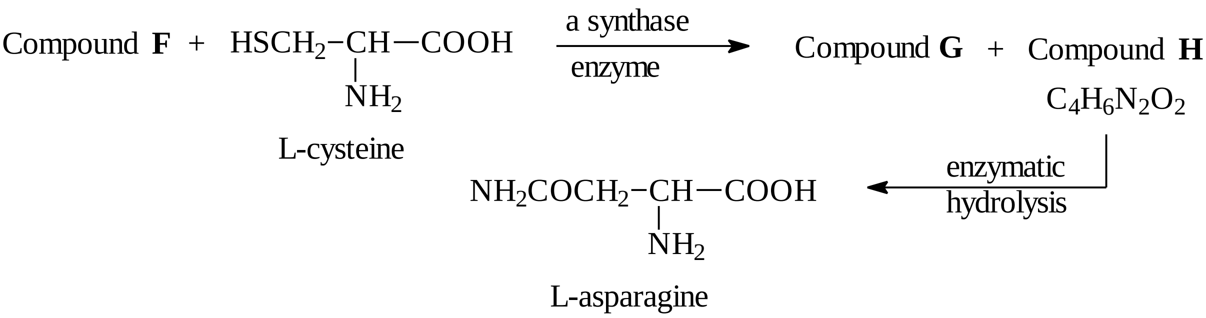
Glycoside **A** ($C_{20}H_{27}NO_{11}$), found in seeds of *Rosaceae* gives a negative test with Benedicts' or Fehling's solutions. Enzymatic hydrolysis of **A** yields (-) **B**, C_8H_7NO and **C**, $C_{12}H_{22}O_{11}$, but complete acid hydrolysis gives as organic products, (+) **D**, $C_6H_{12}O_6$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

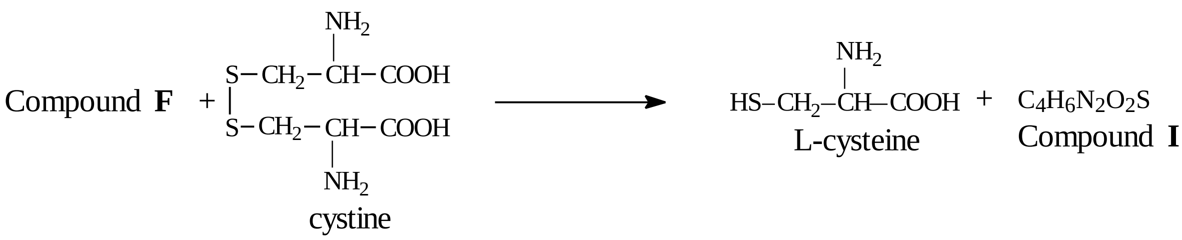
(±) **B** can be prepared from benzaldehyde and $NaHSO_3$ followed by NaCN. Acidic hydrolysis of (±) **B** gives (±) **E**, $C_8H_8O_3$.

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).



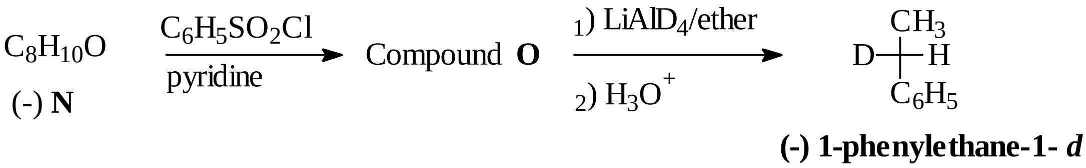
A small amount of compound **F** in human being is believed to be detoxified by a direct reaction with cystine giving L-cysteine and compound **I**, $C_4H_6N_2O_2S$ which is excreted in urine (stereochemistry not shown).



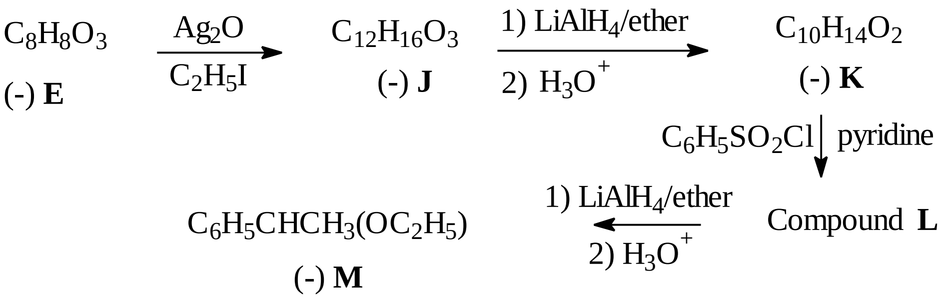
Compound **I** shows no absorption at 2150-2250 cm^{-1} in its IR spectrum but a band at 1640 cm^{-1} and the bands of carboxyl group are observed.

<u>5-2.</u> 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.)

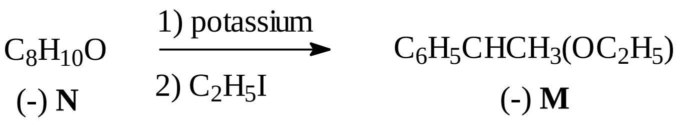
(-) 1-Phenylethane-1-*d*, $C_6H_5CH\mathbf{D}CH_3$ can be prepared in optically active form and the magnitude of its rotation has the relatively high value, $[\alpha]_D$ is equal to -0.6.



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.



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

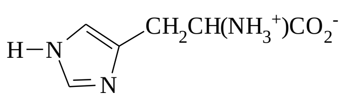
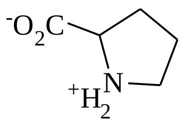
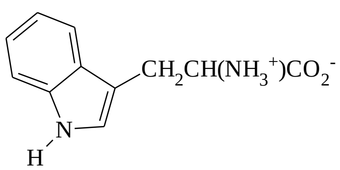
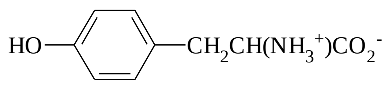
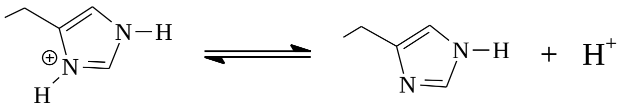
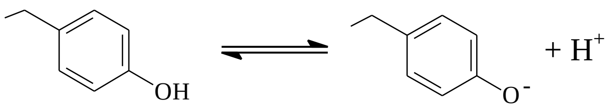
Name	Formula	Three-letter symbol
Alanine	$CH_3CH(NH_3^+)CO_2^-$	Ala
Arginine	$H_2NC(=NH)NH(CH_2)_3CH(NH_3^+)CO_2^-$	Arg
Asparagine	$H_2NCOCH_2CH(NH_3^+)CO_2^-$	Asn
Aspartic Acid	$HO_2CCH_2CH(NH_3^+)CO_2^-$	Asp
Cysteine	$HSCH_2CH(NH_3^+)CO_2^-$	Cys
Cystine	$[SCH_2CH(NH_3^+)CO_2^-]_2$	-
Glutamic Acid	$HO_2CCH_2CH_2CH(NH_3^+)CO_2^-$	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