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 = $\frac{(1.5144)(12.0/44.0)}{12.0} : \frac{(0.2656)(2.0/18.0)}{1.0} : \frac{(0.1575)}{16.0}$

= 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)

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

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

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

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

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

= 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)

6 marks

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

Name:	Student Code:

Problem 1

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

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

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

$= -3079 + (8.314\times10^{-3})(298)(-0.5)$ (1)

$= -3079-1$

$= -3080$ (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)

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

5 marks

ΔH^o_f of Q is [-532] kJ mol^{-1}

Name:	Student Code:

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 $= \dfrac{0.244/244}{(\frac{0.244}{244} + \frac{5.85}{78.0})} = 1.32\text{x}10^{-2}$ (0.01316) (3)

$\Delta T_f = \dfrac{(8.314)(278.55)^2}{9.89\text{x}10^3} \cdot 1.32\times10^{-2} = 0.861$ (2)

$T_f = 5.40\text{-}0.861 = 4.54\ ^oC$ (1)

T_f of solution is [4.54] °C

6 marks

-1 mark for incorrect temperature.

-1 mark for incorrect heat of fusion.

Name:	Student Code:

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

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 x 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

Name:	Student Code:

Problem 2

mmol of Na_2A	=	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

Name:	Student Code:

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.

$$[H^+] \text{ of solution III} = \sqrt{K_a.C}$$
$$= \sqrt{1.75\times10^{-5} \times 1.0}$$
$$= 4.18\times10^{-3}$$

From $HIn \overset{K_{In}}{\rightleftharpoons} In^- + H^+$ (1.0 mark)

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

$$\frac{[In^-]}{[HIn]} = \frac{K_{In}}{[H^+]}$$
$$= \frac{10^{-3.38}}{10^{-2.38}}$$
$$= 0.100$$

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

Whereas $[HIn] + [In^-] = 10^{-5}$
$10[In^-] + [In^-] = 10^{-5}$
$[In^-] = 0.091 \times 10^{-5}$ (1.5 mark)

$\therefore$ Absorbance of solution III $= \frac{0.091\times10^{-5}}{1.00\times10^{-5}} \times 0.300$
$= 0.027$ (1.0 mark)

-0.5 mark for incorrect unit

The absorbance at 400 nm of Solution III = 0.027

5 marks

Name:	Student Code:

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.

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

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

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

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

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

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

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

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

$[In^-] = 0.726 \times 10^{-5}$ (1.5 marks)

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

$= 0.218$

(0.5 mark)

-0.5 mark for incorrect unit

The absorbance at 400 nm of the solution = 0.218

4 marks

Name:	Student Code:

Problem 2

2-9. 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

Transmittance of the solution = 0.605 or 60.5%

1 mark

Name:	Student Code:

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:

$^{232}_{90}Th \rightarrow {}^{208}_{82}Pb + 6\,{}^{4}_{2}He + 4\beta^-$

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)

$= [232.03805\ u - 207.97664\ u - 6 \times 4.00260\ u] \times 931.5\ MeVu^{-1}$

$= (0.04581u)(931.5\ MeVu^{-1}) = 42.67\ MeV$ (2)

4 marks

Energy released = 42.67 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 ^{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

Name:	Student Code:

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:

$^{228}Th \rightarrow {}^{208}Pb + 5\,{}^{4}He$ (1)

The half-lives of various intermediates are relatively short compared that of ^{228}Th.

$$A = \lambda N = \left(\frac{0.693}{1.91\ y}\right)\left[\frac{(1.00\ g)(6.022 \times 10^{23}\ mol^{-1})}{228\ g\ mol^{-1}}\right]$$

$$= 9.58 \times 10^{20}\ y^{-1} \quad (1)$$

Number of He collected

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

$$= 9.58 \times 10^{22}\ particles\ of\ He \quad (1)$$

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

$$= 3.56 \times 10^3 cm^3 \quad (2)$$

5 marks

Volume of He at 0 °C and 1 atm = [3.56×10^3] 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:

$$A = \lambda N;$$

$$t_{1/2} = \frac{0.693}{\lambda} = \frac{0.693\ N}{A} \quad (1.5)$$

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

$$= 3.02 \times 10^6\ min$$

$$= 5.75\ years \quad (1)$$

4 marks

Half-life = [5.75] years

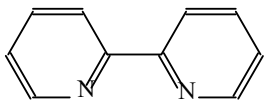
Name:	Student Code:

Problem 4 — 28 points

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

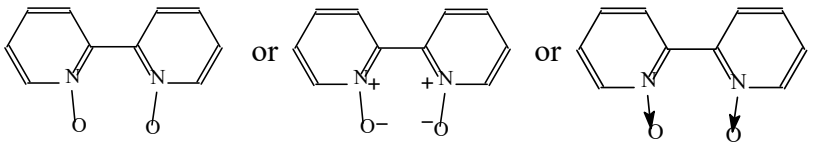
Knowing that L was synthesized from bipyridine and during the reaction bipyridine was simply oxidized to bipyridine oxide. The molecular mass of bipyridine is 156 (for $C_{10}H_8N_2$) while the molecular mass of L is 188. The difference of 32 is due to 2 atoms of oxygen. Therefore , the molecular formula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

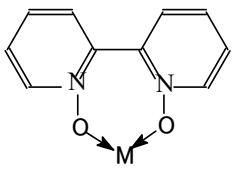
2 marks

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

Name:	Student Code:

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 $FeL_m(ClO_4)_n.3H_2O$?

m = 3 (1 mark) n = 3 (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 $[FeL_3](ClO_4)_3.3H_2O$.

1 mark

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

Name:	Student Code:

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.

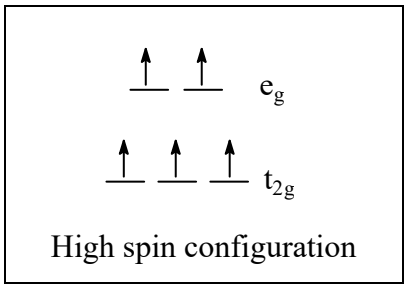
4-6. The oxidation number of Fe in complex **A** is [+3 or III]

0.5 marks

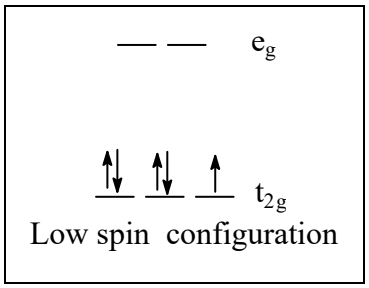
The number of *d*-electrons in Fe ion in the complex = [5]

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

Name:	Student Code:

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.

Name:	Student Code:

Problem 4

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

Calculation:

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

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

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

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

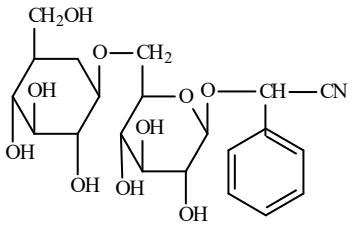
y = 2 1 mark

z = 1 1 mark

Name:	Student Code:

Problem 5 — 23 points

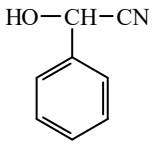
5-1. Write structures of **A - D** with appropriate stereochemistry in Haworth projection, except for **B**.



A

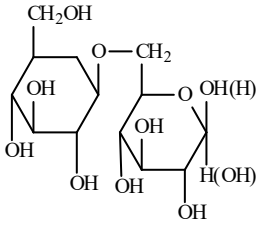
(3 marks)

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



B

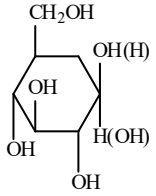
(1 mark)



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

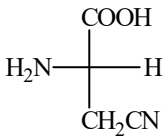
5-2. Write molecular formula each for compounds **F** and **G** and structural formula for compound **H** and **I** and indicate stereochemistry of **H**.

Molecular formula of compound **F** = **HCN**

(0.5 mark)

Molecular formula of compound **G** = **H_2S**

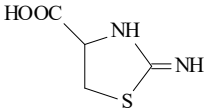
(0.5 mark)



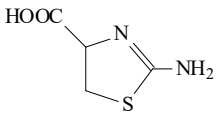
Compound **H**

(2 marks)

Remark:
1 mark for structure
1 mark for correct stereochemistry



or



Compound **I**

(2 marks)

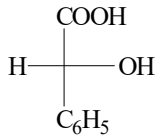
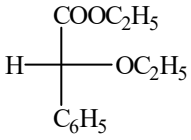
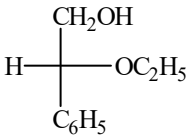
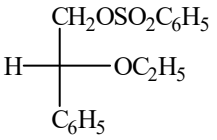
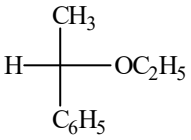
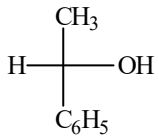
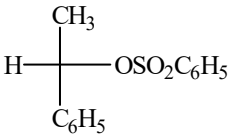
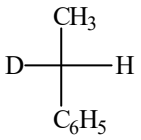
Remark:
2 marks for structure

(5 marks)

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.

 (-) **E** ☑ R or ☐ S (2 marks) Remark: 1 mark for structure 0.5 mark for **R, S** 0.5 mark for correct stereochemistry	 (-) **J** (1.5 mark) Remark: 0.5 mark for ester 0.5 mark for ether 0.5 mark for correct stereochemistry	 (-) **K** (1 mark) Remark: 0.5 mark for structure 0.5 mark for correct stereochemistry	 Compound **L** (1 mark) Remark: 0.5 mark for structure 0.5 mark for correct stereochemistry
 (-) **M** (1 mark) Remark: 0.5 mark for structure 0.5 mark for correct stereochemistry	 (-) **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	 Compound **O** (1 mark) Remark: 0.5 mark for structure 0.5 mark for correct stereochemistry	 (-) **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_N1
√	S_N2
	S_Ni
	E1
	E2

1 mark

Name:	Student Code:

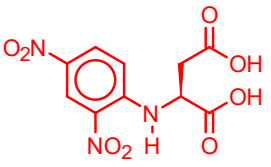
Problem 6 — 16 points

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 |

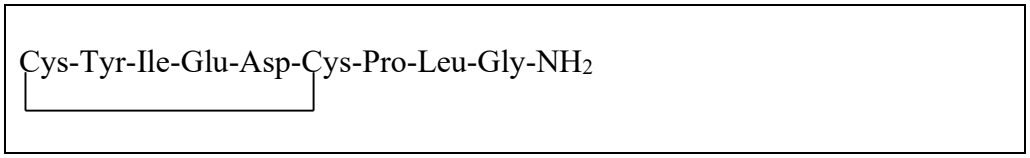
1 mark

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

Name:	Student Code:

Problem 6

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

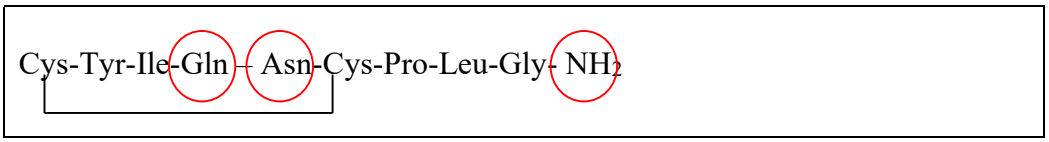


5 marks

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



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