Name of Student	Centre

Problem 1 **14 marks**

Chemical Kinetics

1.1 The mechanism of an enzymatic reaction was given by Michaelis and Menten (1913) and Briggs and Haldane (1925) and is outlined below. Let E, S and P denote the Enzyme, Substrate and Product respectively. ES stands for the corresponding addition complex of E and S.

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES$$

$$ES \xrightarrow{k_2} E + P$$

Denote the concentrations of E, S and ES by [E], [S], and [ES] respectively.

Apply the steady state treatment to calculate [ES].

(2 marks)

1.2 Assume that the initial concentration of the enzyme, $[E]_0$, equals that of the free enzyme during the reaction, [E], *plus* the concentration of the complex, [ES].

Write down the expression for [ES].

(2 marks)

1.3 The rate of the reaction is given by

$v = k_2 [ES]$.

Show that v can be written as $\frac{k_2[E]_0[S]}{K_m + [S]}$.

Express K_m in terms of k_{-1}, k_2 and k_1. What is the unit of K_m?

(3 marks)

1.4 What is the order of the reaction when [S] is small and when it is very large compared to K_m?

(2 marks)

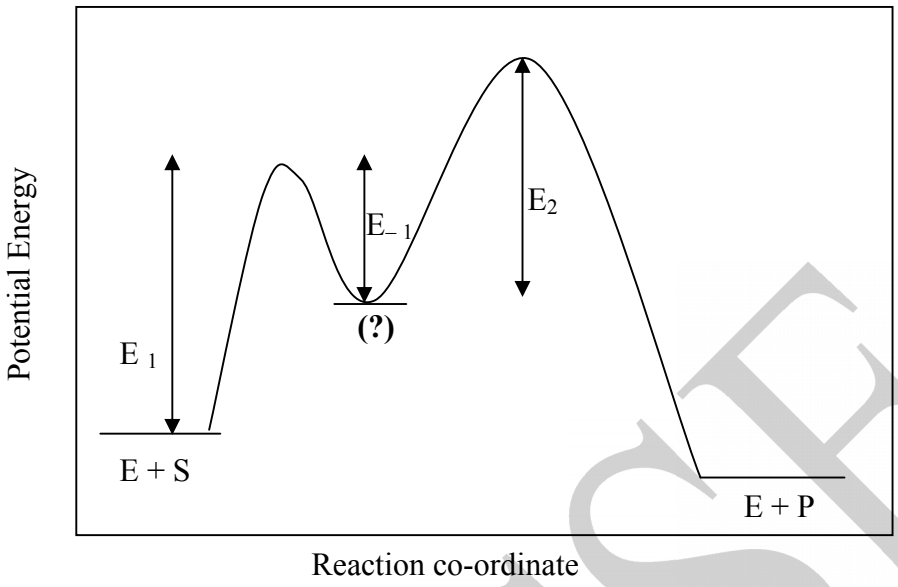
1.5 The hydrolysis of urea is catalyzed by the enzyme *urease*. The half life of urea in this psuedo first-order reaction is doubled, when the temperature is lowered from 27° C to 17 ° C.

Determine the activation energy of the reaction.

.

(3 marks)

1.6 The potential energy diagram corresponding to a particular case of the mechanism given in **1.1** is shown below.



The species marked by **(?)** stands for

Is the reaction represented here, endo/exothermic?

For which reaction is the activation energy represented by E_{-1}?

The activation energy corresponding to the rate determining step is

(2 marks)

Name of Student	Centre

Problem 2 **17 marks**

Ionic Equilibrium and Electrochemistry

A.

2.1 In a titration of a 0.1M solution of a weak acid HX with 0.1M solution of NaOH, the pH of the solution is 5.8 after 10.0 mL of NaOH solution has been added. The pH becomes 6.402 after the addition of another 10.0 mL of NaOH.

Find the volume of the acid taken.

(3 marks)

2.2 Find the ionization constant of the acid HX.

(1 mark)

2.3 Find the pH after the addition of another 10.0 mL (i.e. a total of 30 mL) of NaOH.

(3 marks)

B.

2.4 The standard potentials of the electrodes corresponding to the reactions $Fe^{3+} + 3e^- \rightarrow Fe$ and $Fe^{2+} + 2e^- \rightarrow Fe$ are – 0.02 V and – 0.41 V, respectively. What is the standard potential for the reaction $Fe^{3+} + e^- \rightarrow Fe^{2+}$?

(3 marks)

C.

2.5 When metallic copper is shaken with a solution of $CuSO_4$, the reaction that proceeds is $Cu + Cu^{2+} \rightleftharpoons 2\ Cu^{+}$. When equilibrium is established at 298 K, the concentration of Cu^{2+} and Cu^{+} ions are found to be 0.1M and 2.45×10^{-4}M respectively. Find the equilibrium constant of the above reaction. Find also the EMF of a cell for which the overall cell reaction is given above.

(3 marks)

2.6 If the standard potential of the Cu^{2+}/Cu half cell is 0.337 V, what is the standard potential of Cu^{+}/Cu half cell?

(2 marks)

2.7 Explain why Cu(I)-sulphate does not exist in aqueous solution.

(2 marks)

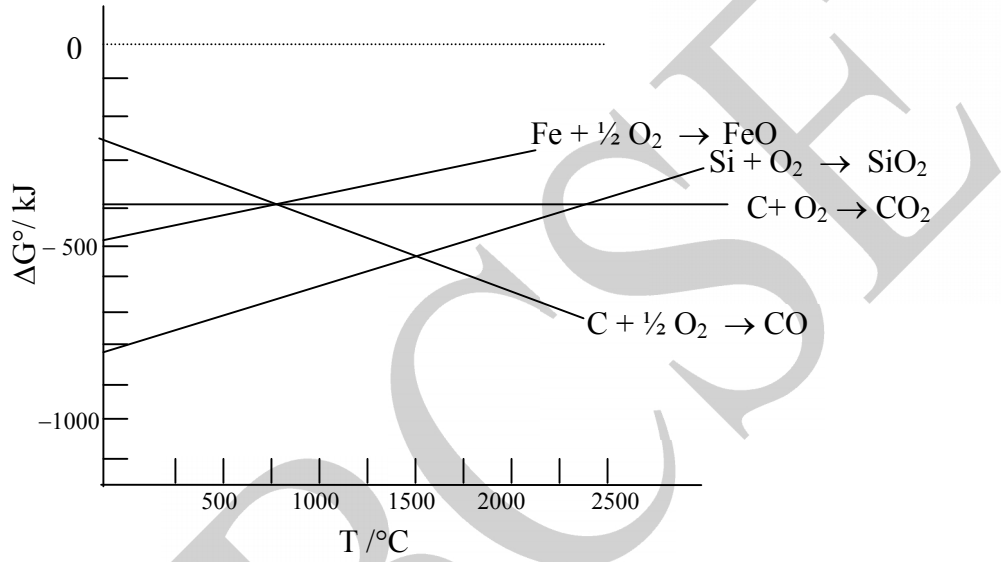
Name of Student	Centre

Problem 3 17 marks

Metallurgy and Chemistry of Iron

3.1 Pyrometallurgy (that is, heating with a reducing agent) is an important technique, which is used for the production of metals from their oxides.

The following graph represents the change in ΔG° (kJ) with temperature for a few important reactions.



If a mixture containing FeO and SiO_2 is heated with coke,

a) State which of the oxides will be reduced first as the temperature rises.

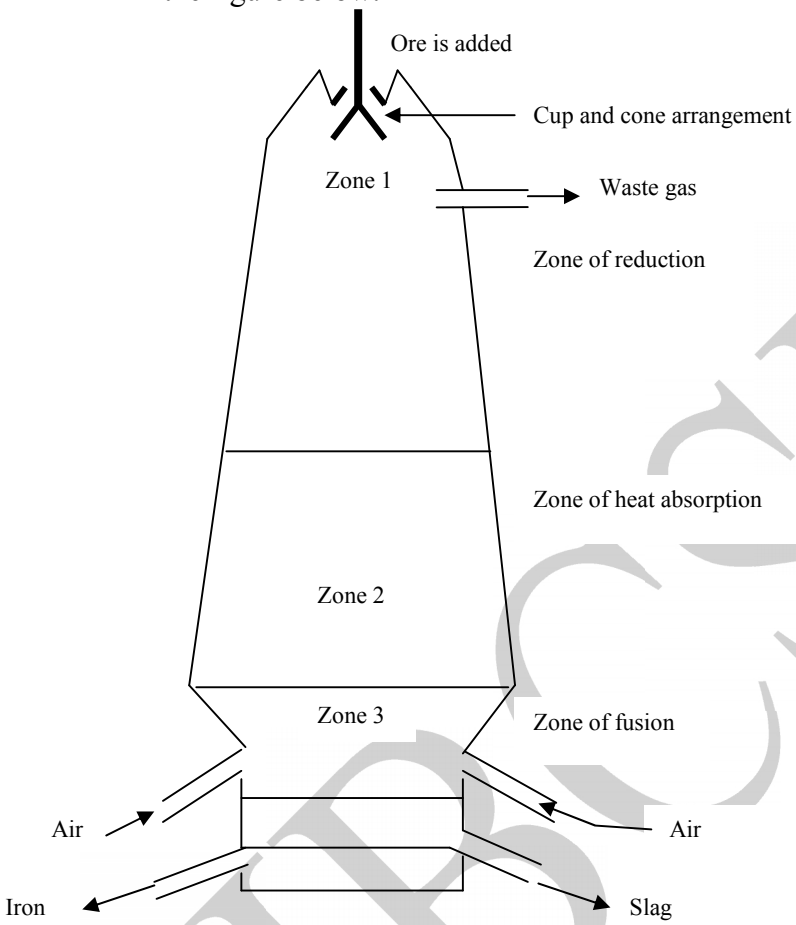
b) State the minimum temperatures at which reduction of FeO and SiO_2 will start.

c) Give the balanced chemical equations for these reduction processes at these temperatures.

(Refer to the above graph for answering these questions).

(5 marks)

3.2 In economical terms, iron ore reduction is the most important application of carbon pyrometallurgy. In the blast furnace the mixture of haematite, coke and limestone is heated with a blast of hot air. A schematic diagram of the blast furnace is shown in the figure below.



The temperature in zone 3 rises from 900^0C to 2000^0C due to an **exothermic reaction** occurring in this zone. Write down its balanced chemical equation.

(0.5 mark)

3.3 In zone 2 (zone of heat absorption), another reaction produces the reagent responsible for the reduction of iron oxides. State the balanced chemical equation that produces this reducing agent.

(0.5 mark)

3.4 In zone 1, the reducing agent reduces the oxides of iron. Write down balanced equations for the reduction of iron oxides.

(3 marks)

3.5 What reaction does limestone undergo in the blast furnace?

(0.5 mark)

3.6 Impurities such as silica present in iron ore react with one of the products (say **A**) produced in the above reaction. This yields a glassy material, called slag.

a) Write the balanced equation for the formation of slag.

b) State and explain whether like silica, iron oxide/s will also react with **A**.

(1.5 marks)

3.7 In the absence of limestone, the yield of iron metal is adversely affected due to a particular chemical reaction. Identify this reaction and give its equation.

(1 mark)

3.8 State the function of the specially designed cup and cone arrangement shown at the top of the blast furnace.

(0.5 mark)

3.9 An aqueous solution of $FeCl_3$ (pale yellow in colour) was taken in 3 test tubes. The reagents added to each test tube are given in the table.
Write your observations and corresponding balanced chemical equations.

Test tube	Reagent added	Observations	Balanced chemical equation/s
1	NaOH		
2	KSCN (under acidic condition)		
3	$K_4[Fe(CN)_6]$		

(4.5 marks)

Name of Student	Centre

Problem 4 7 marks

Coordination Chemistry

4.1 When air is bubbled through a solution of Co(II) chloride and ammonium carbonate, compound **A** having composition $Co(CO_3)Cl.4NH_3$ is formed.

Compound **A** when treated with conc. HCl gives a violet coloured compound **B**, having composition $CoCl_3.4NH_3$.

Compound **A** when treated with a mixture of HCl and H_2SO_4 gives a green coloured compound **C** having composition $CoCl_3.4NH_3$.

Draw structures for compounds **A, B, C** and give their IUPAC names.

Compound A	Compound B	Compound C

(3 marks)

4.2 State the type of isomerism involved in the compounds **B** and **C**.

(1 mark)

4.3 Draw the structures of isomers that are formed when the NH_3 groups of the compounds **B** and **C** are replaced by ethylene diamine (abbreviated as ***en***). Give the IUPAC names for these isomers. State which of these isomers will exhibit optical activity.

(3 marks)

Name of Student	Centre

Problem 5 24 marks

Synthesis of Drug

5.1 A drug Dofetinilide **(1)** is used for the treatment of cardiac arrhythmia, which is a fatal heart disease prominent among the developed countries.

The synthesis of Dofetinilide may require simple starting compounds like 1-bromo-2-phenylethane **(2),** bromobenzene **(3)** and phenol **(4)**.

In the nitration of **(2)** and **(3)** with the nitrating mixture ($HNO_3 + H_2SO_4$), the major product was found to be the *p*-isomer.

State whether the following statements are **True** or **False**.

(i) The rate of nitration of **(2)** is higher than the rate of nitration of **(3)**. ☐

(ii) The rate of nitration of **(3)** is higher than the rate of nitration of **(4)**. ☐

(iii) At a low temperature the *p:o* ratio for **(2)** is higher than the *p:o* ratio for **(3)**. ☐

(3 marks)

5.2 Suggest a method for the preparation of **(2)** starting from benzene.

(2 marks)

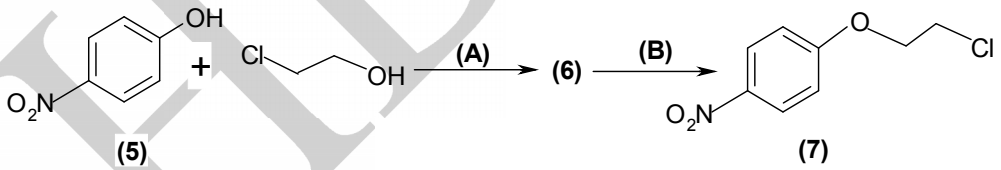
5.3 Phenol is nitrated using $NaNO_3$ and H_2SO_4 in water. In this reaction, significant amount of another compound is formed along with *p*-nitrophenol **(5)**. What is this side product and how is it separated on a large scale from the desired *p*-nitrophenol?

(2 marks)

What is the result if phenol is nitrated using the nitrating mixture?

(1 mark)

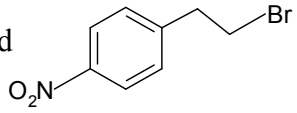
5.4 Compound **(5)** is converted into intermediate **(7)** through the following sequence.

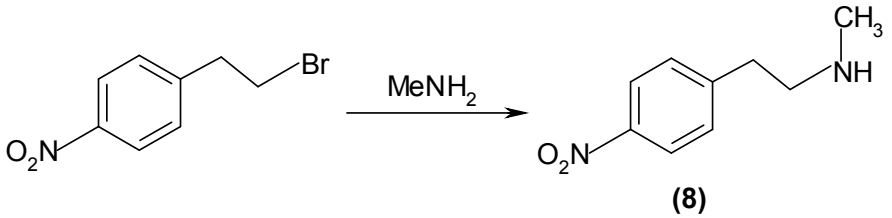


(5) **(7)**

Draw the structure of compound **(6)** and identify the reagents **(A)** and **(B)**.

(3 marks)

5.5 The compound  is reacted with methylamine to form **(8)**.

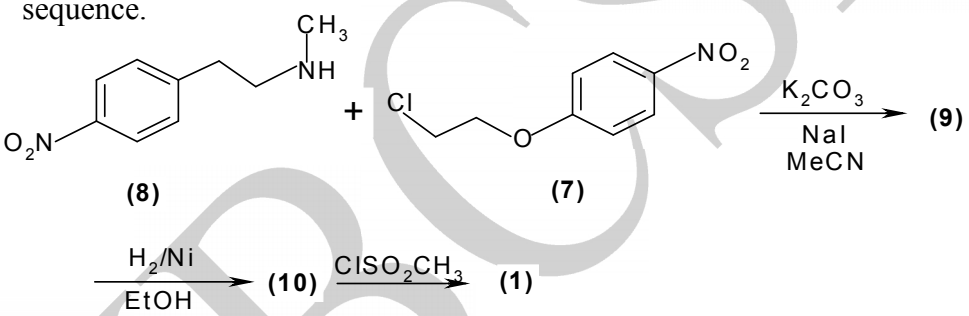


(8)

In this reaction methylamine is taken in excess. Why?

(1 mark)

5.6 Dofetinilide **(1)** is prepared from intermediates **(7)** and **(8)** by the following sequence.

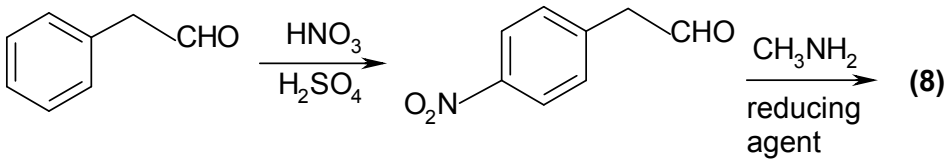


(8) **(7)** **(9)** **(10)** **(1)**

Draw the structures of **(9)**, **(10)** and **(1)**.

(3 marks)

5.7 Synthesis of compound **(8)** may be planned by the following alternative sequence:



(8)

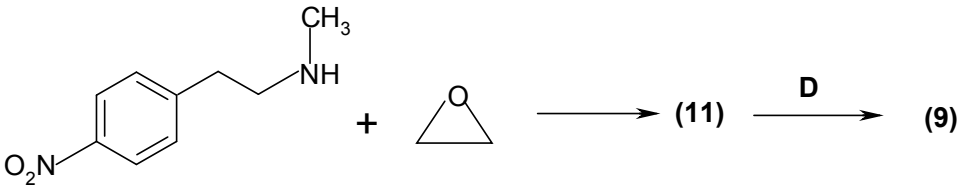
State the drawbacks of this route.

(3 marks)

5.8 In the ^{1}H-NMR spectrum of **1**, two singlets are observed at 2.82 δ and 2.27 δ with an intensity ratio 2:1 and 4 triplets appear at 3.92, 2.78, 2.70 and 2.62 δ. There is also a peak at 4.0 δ which disappears on D_2O exchange. Draw the structure of **1** (that is, dofetinilide) and assign the peaks.

(3 marks)

5.9 Ethylene oxide is an extremely important bulk chemical obtained by the oxidation of ethylene. A researcher planned a synthesis of **(9)** by the following sequence.



Identify **(11)** and compound **D**. Comment on the second step.

(3 marks)

Name of Student	Centre

Problem 6 11 marks

Structure Elucidation

The Compound **A** ($C_5H_8O_2$) exhibits the following spectral data: IR 1710 cm^{-1}.

^{1}H-NMR 1.3(t), 4.2(q), 5.8 (dd, J=4Hz, J=10Hz), 6.2 (dd, J=16 Hz, J=10 Hz), 6.45(dd, J=16 Hz, J=4 Hz)

[t: triplet; q: quartet; dd: doublet of doublet].

6.1 a) What information is obtained from the molecular formula?

(1 mark)

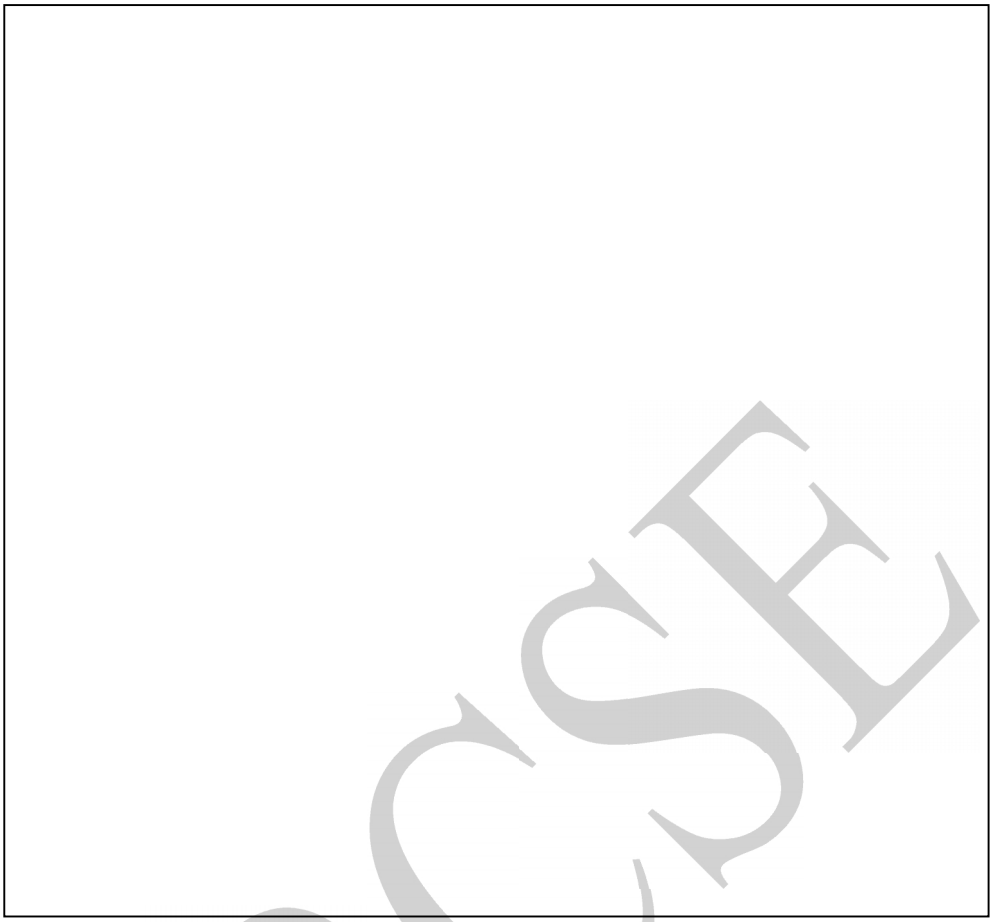
b) Functional group/s in **A** based on the IR data.

(1 mark)

c) Structure of **A**.

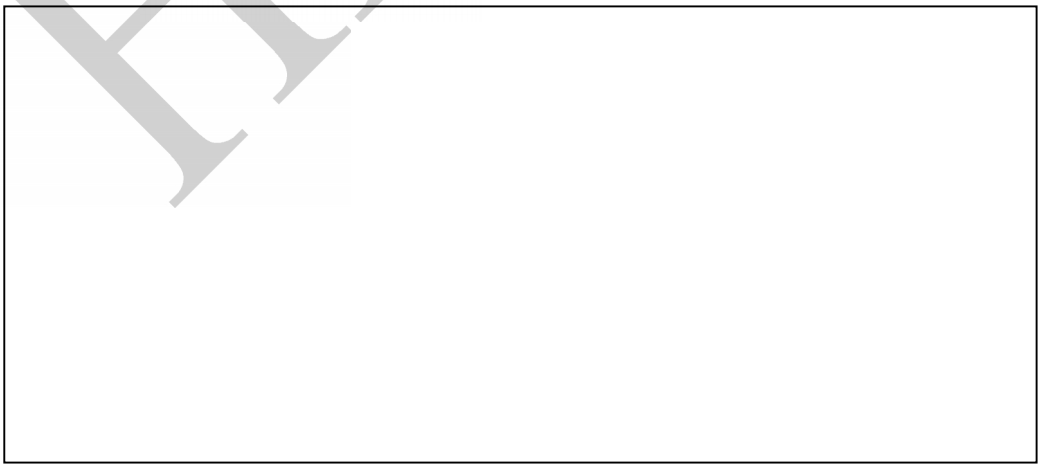
(2 marks)

6.2 Compound **A,** on reaction with potassium persulphate ($K_2S_2O_8$), gives a polymer. Draw the structure of the polymer and show its different stereomeric forms.



(4 marks)

6.3 Compound **A**, on reaction with Br_2, gives compound **B**. Draw the structure of **B**. Draw the Fischer projections for different configurations of **B** and indicate their absolute configurations.



(3 marks)

Name of Student	Centre

Problem 7 **12 marks**

Molecular Spectroscopy

A.

7.1 The photoelectron spectrum of nitrogen molecule shows the peaks: 39.5, 3.7, 1.8, 1.6 and 1.4 MJ mol^{-1}.

Draw the MO energy diagram for nitrogen molecule and identify the MO's corresponding to each peak.

What are the bond orders of N_2, N_2^+ and N_2^- ?

(5 marks)

7.2 Treat σ_{1s} electrons in nitrogen molecule as atomic 1s electrons. Assuming Bohr's theory to be applicable for this case, calculate the corresponding effective nuclear charge.

(3 marks)

B.

7.3 A light of intensity I_0 passes through a medium with the concentration of the absorbing species as c $molL^{-1}$. The intensity (I) after traversing a distance *l* cm, is given by the relation, $\log(I_o/I) = \varepsilon c l$ where ε is the molar absorption coefficient.

A swimmer enters a gloomier world (in one sense) on diving to greater depths. Given that the mean molar absorption coefficient of sea- water in the visible region is 6.2×10^{-5} $Lmol^{-1}cm^{-1}$, calculate the depth at which a diver will experience one tenth of the light intensity at the surface.

.

(4 marks)

Name of Student	Centre

Problem 8 **18 marks**

Nucleic Acids

A.

8.1 Given below are the structures of three nucleic acids.

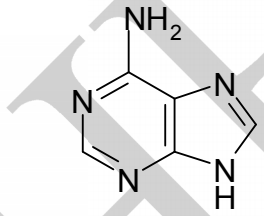
I. 5′-pGGTCCGGATCAATCC-3′
3′ - CCAGGCCTAGTTAGG p-5′

II. 5′-pTCAGGCGAGAATTCA-3′
3′ - AGTCCGCTGTTAAGT p-5′

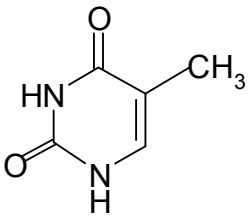
III. 5′-pGGCCAATTCGGGCCC-3′
3′ - CCGGTTAAGCCCGGG p-5′

The structures of different bases present in the nucleic acids **I**, **II** and **III** are given in **Table 1**.

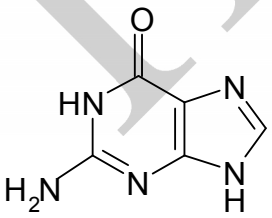
Table 1 : Bases In Nucleic Acids



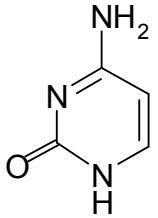
Adenine(A)



Thymine (T)



Guanine (G)

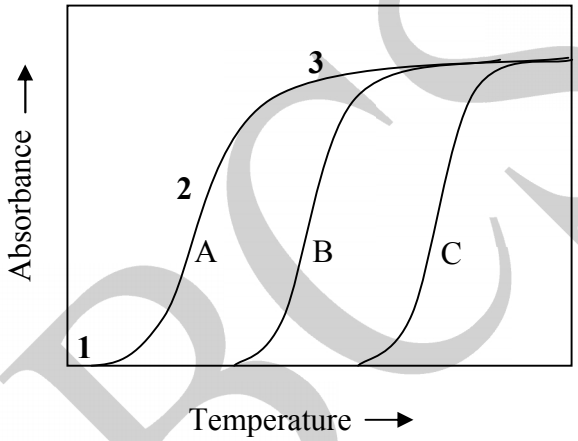


Cytosine (C)

Identify with reason the type/s of nucleic acid/s **I**, **II** and **III** and indicate the direction of each strand.

(3 marks)

8.2 These nucleic acid samples were heated separately and the absorbance of each sample was measured as a function of temperature. The curves obtained are shown below. For each sample, the absorbance initially increases slowly (region **1**), followed by a steep rise (region **2**) and finally attains saturation (region **3**).



a) Based on the structures of bases (**Table 1**) and the above graph, state the region of the electromagnetic spectrum where the absorbance was measured. (Mark X in the correct box.)

Visible ☐

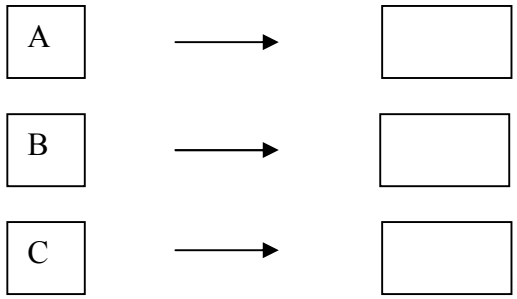
IR ☐

X-ray ☐

UV ☐

(1 mark)

b) Match the curves A, B and C in the above figure with nucleic acids **I**, **II** and **III**, with a brief reasoning.



(4 marks)

c) Why do all the curves in the above figure show the same saturation limit?

(2 marks)

d) Why do all the curves shown in the above graph show a steep rise in the absorbance in region **2**?

(2 marks)

Carbohydrates and Fats

B.

8.3

a) A marathon runner after an exhausting event, was given 200 mL of glucose (10% w/v) solution. Explain in brief the process by which the person will benefit from such a drink.

(1 mark)

b) Instead of glucose solution, the person is given 200 mL of milk, which contains lactose (12% w/v). Will this help the person to recover the same way as in the earlier case?

(2 marks)

c) Carbohydrates and fats are the major sources of energy for the human body. Oxidation of a carbohydrate produces 16.8 kJ/g energy and that of a fat produces 43.62 kJ/g. Calculate the energy content in (kJ) of a solution prepared by mixing 10 grams of a commercial health drink powder in 150 mL of water.

Composition of the health drink powder

Component	%
Carbohydrate	38.2
Fats	21.5
Proteins	30.3
Minerals	9.65
Vitamins	0.35

(3 marks)