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**Problem 1****15 marks****A. Wave functions and atomic orbitals**

- 1.1** The electronic energy of the hydrogen atom in its ground state, as given by the Bohr theory, is  $-13.6$  eV. Bohr's theory cannot be directly applied to the helium atom. However, consider a hypothetical helium atom in which interelectronic repulsion is 'switched off' (the electrons do not repel each other). What is the total electronic energy of this atom?

**(2.5marks)**

- 1.2** According to the probabilistic interpretation of the wave function (given by Max Born)  $|\psi(x_0)|^2$  is related to the probability of finding the particle at  $x_0$ .

Now consider the wave function  $\psi_1$  for the particle in a one-dimensional

$$\text{box } (0 \leq x \leq 1) \psi_1(x) = \sqrt{2} \sin(\pi x)$$

Evaluate  $|\psi_1(0.5)|^2$

**(1.5marks)**

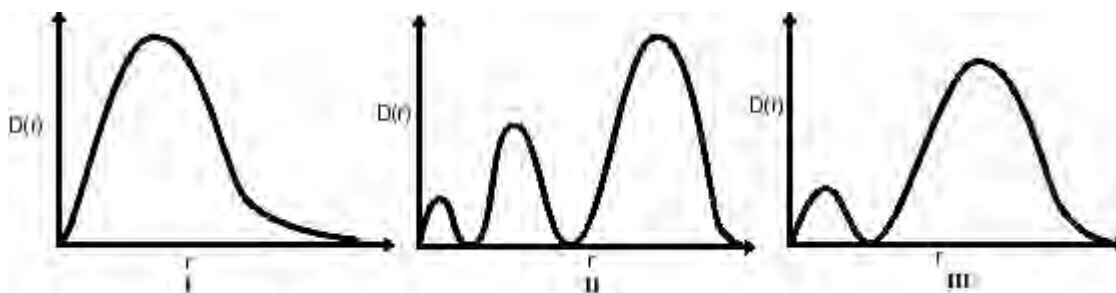
- 1.3** Considering that the probability of an event should never exceed 1, do you think there is a discrepancy in the result of **1.2**?

Yes No **(0.5mark)**

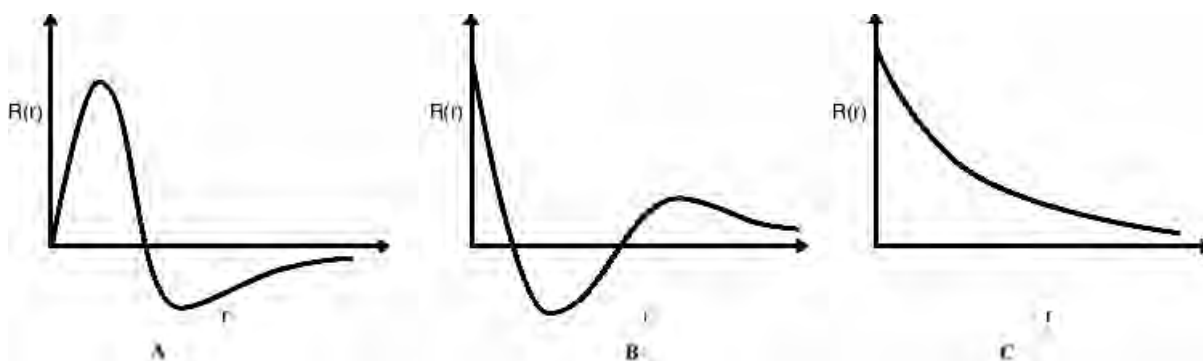
- 1.4** Explain briefly your answer to **1.3**.

**(2.5marks)**

1.5 The radial probability  $D(r) = 4\pi r^2 R^2(r)$  plots of three hydrogenic atomic orbitals (AO's) are shown as I, II and III.



The three qualitative plots of  $R(r)$  versus  $r$  for these three AO's (but not necessarily in the same order) are given below, as A, B and C.



Match I, II, III with A, B and C.

I
II
III

(2marks)

1.6 Identify the corresponding AO's for A, B and C.  
 [Choose your answers from 1s, 2s, 2p, 3s, 3p, 3d, 4d, and 4s].

A
B
C

(2marks)

**B. Properties of oxygen molecule and MO theory**

- 1.7 During the Second World War, there arose a necessity of developing an instrument to determine the amount of oxygen in the air content of a submarine by non-destructive method. Such an instrument was eventually developed and used. Which property of the  $O_2$  molecule do you think was used for this purpose?

(1mark)

- 1.8 What are the bond orders of  $O_2$  and  $O_2^-$  molecules according to qualitative MO energy diagram?

(2marks)

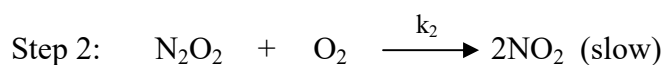
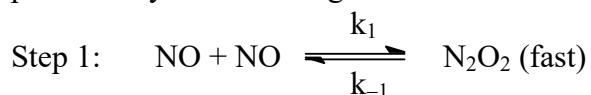
- 1.9 How many unpaired electrons are there in  $O_2$  and  $O_2^-$ ?

(1mark)

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**Problem 2****20 marks****A. Kinetics of the reaction between Nitric oxide and Oxygen**

2.1 The reaction between nitric oxide and oxygen to produce nitrogen dioxide proceeds by the following mechanism:



- Derive the rate law for the reaction on the basis of the above steps.
- What is the order of the reaction as suggested by the rate law?

**(3marks)**

2.2 The rate data for the reaction between NO and O<sub>2</sub> at equal concentration are given below:

	Set I	Set II
Initial concentration of NO/O <sub>2</sub> (mol.dm <sup>-3</sup> )	1.20 × 10 <sup>-2</sup>	2.40 × 10 <sup>-2</sup>
Corresponding rate of reaction (mol.dm <sup>-3</sup> s <sup>-1</sup> )	6.31 × 10 <sup>-3</sup>	5.06 × 10 <sup>-2</sup>

- i) What is the order of the reaction from given data?
- ii) What are the units of the rate constant as per given data?



**(3marks)**

**2.3** At 27°C, the rate of the forward reaction between NO and O<sub>2</sub> to form the intermediate activated complex is 12 times greater than the reverse rate.

- i) What is the free energy change involved?
- ii) Comment on the spontaneity of the reaction.



**(3marks)**

- 2.4 The temperature dependence of the reaction rate ( $k$ ) is given by the Arrhenius equation,  $k = A \times e^{-E/RT}$ , where  $E$  is the energy of activation. Suggest a suitable graph to verify this dependence.



(1mark)

## B. Carbon monoxide

- 2.5 Choose the correct option and Mark **X** in the correct box.

For a spontaneous process,

i)  $\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} < 0$

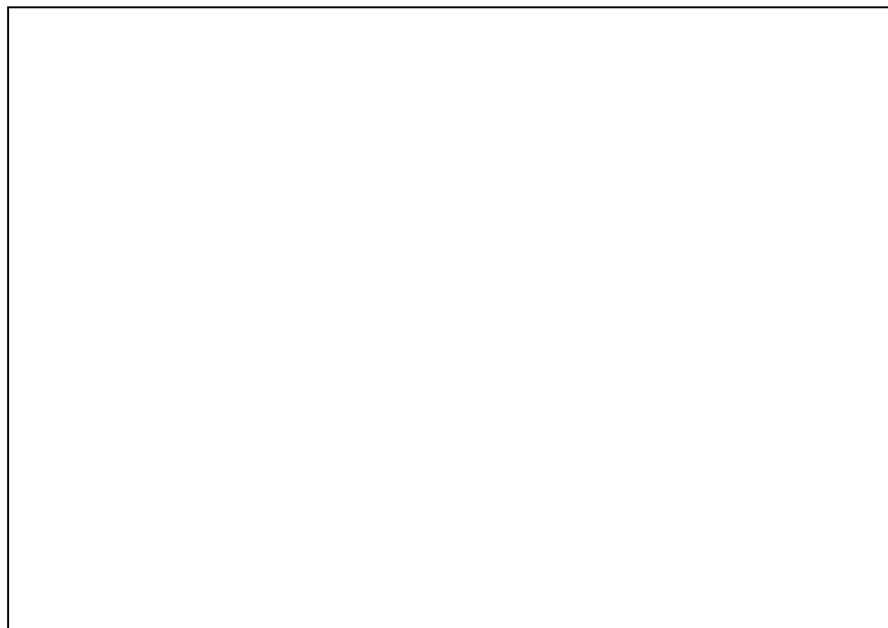
ii)  $\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$

iii)  $\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} = 0$

(1mark)

- 2.6 The combustion of 1 mole of carbon monoxide releases 169.05 kJ of energy into the surroundings.

- Write the balanced equation indicating combustion reaction for 1mole of carbon monoxide.
- Calculate  $\Delta U$  and  $\Delta H$  per mole for the combustion process at  $27^\circ\text{C}$ .  
Given: C = 12, O = 16
- Without performing any calculations, indicate whether the entropy change of the system for the combustion reaction, will be positive or negative (assume that pressure and temperature are constant).
- Give suitable reason for your answer.



(4marks)

- 2.7 2.744g of CO gas was transferred from a cubical container of length  $l$  cm into a bigger cubical container (initially empty), of length  $2l$  cm at  $27^\circ$  C. Assuming that the gas behaves ideally, calculate  $\Delta S$ . Calculate the work done in this transfer if the process is carried out reversibly.



(3marks)

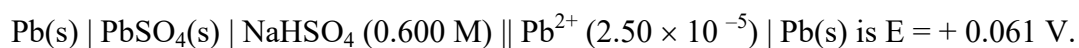
**2.8** Water gas is prepared by mixing CO with hydrogen. A reversible Carnot heat engine employing water gas operates between a water boiler and a sink containing liquid nitrogen at  $-196^{\circ}\text{C}$ .

- i) What is the efficiency of the engine?
- ii) Suggest a method to improve the efficiency.

**(2marks)**



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**Problem 3****10 marks****A. Electrochemical cell****3.1** The voltage of an electrochemical cell at 25°C:

The standard electrode potentials for (at 25°C):



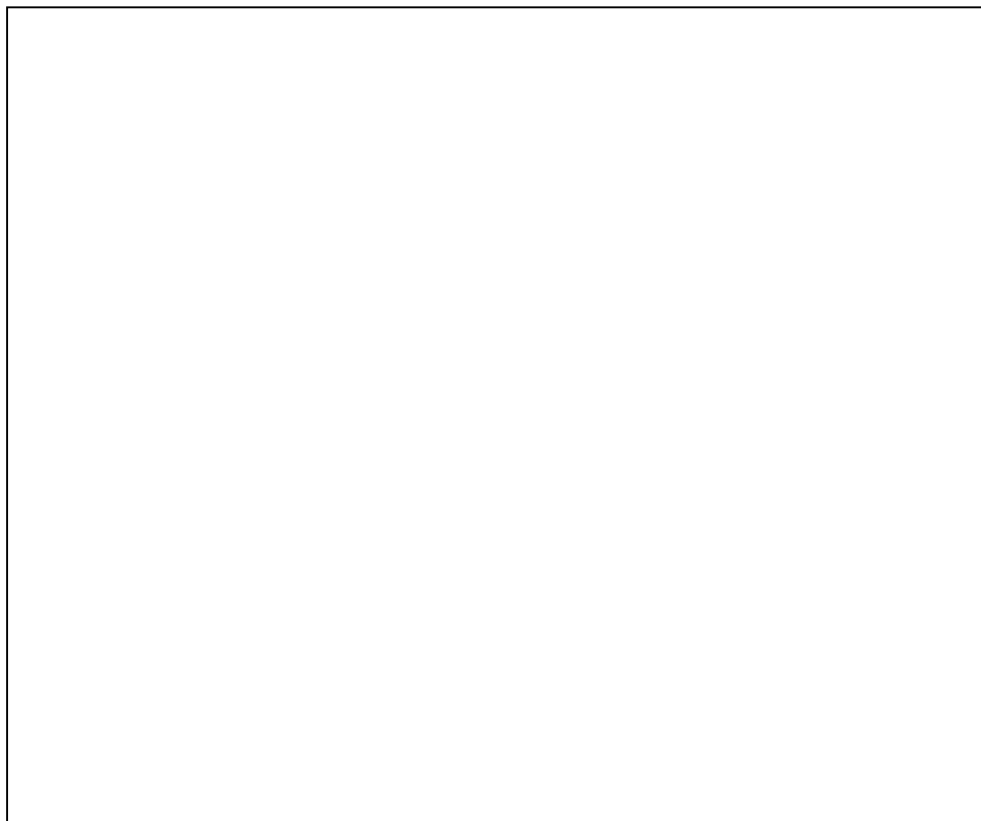
- Write down the overall cell reaction for the above cell.
- Calculate the dissociation constant ( $K_2$ ) for  $\text{HSO}_4^-$ .

**(4marks)**

**B. Mohr's Method**

**3.2** In Mohr's method, solution of  $\text{Cl}^-$  is titrated against standard  $\text{AgNO}_3$ . During the titration, a small quantity of  $\text{K}_2\text{CrO}_4$  solution is added as an indicator. As  $\text{AgCl}$  is less soluble than  $\text{Ag}_2\text{CrO}_4$ , the added  $\text{Ag}^+$  reacts first with  $\text{Cl}^-$  than with  $\text{CrO}_4^{2-}$ . At the equivalence point, when  $\text{Cl}^-$  is precipitated quantitatively as  $\text{AgCl}$ , the slight excess of  $\text{Ag}^+$  reacts with  $\text{CrO}_4^{2-}$  to give intensely red precipitate of  $\text{Ag}_2\text{CrO}_4$ .

- i) 50.0 mL of 0.1 M  $\text{Cl}^-$  solution is titrated against 0.1M standard  $\text{AgNO}_3$ . What must be the theoretical concentration of  $\text{CrO}_4^{2-}$  in the solution so that  $\text{Ag}_2\text{CrO}_4$  will start precipitating at the equivalence-point.
- ii) Solution of theoretical concentration (that is, the concentration calculated by you (i)) is too concentrated and if added, gives distinct deep orange color. This color obscures the  $\text{Ag}_2\text{CrO}_4$  precipitate formed at the endpoint. So a dilute solution of  $\text{K}_2\text{CrO}_4$  is generally used. If the concentration of  $\text{CrO}_4^{2-}$  in the titration flask is 0.002M, then estimate the end point error in percent.  
( $K_{\text{sp}} \text{AgCl} = 1.10 \times 10^{-10} \text{ mol}^2\text{L}^{-2}$ ,  $K_{\text{sp}} \text{Ag}_2\text{CrO}_4 = 1.70 \times 10^{-12} \text{ mol}^3\text{L}^{-3}$ )





**(6marks)**

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**Problem 4****14 marks****A. Carbon dating**

**4.1** During the year 1999, in an archeological excavation of a shelter, a charcoal sample was obtained from a fire pit. It was believed that this sample was formed, when early occupants of the shelter burned wood for cooking. A 100mg of charcoal (containing 87% carbon) had a disintegration rate of 0.25 counts/min. Carbon from a living system is found to give an activity of 15.3counts/min/g of carbon. Calculate:

- When was the wood burnt in the shelter?
- What would have been the activity of this sample in 99A.D.? (half life of  $^{14}\text{C}$  = 5730 years)

**(5marks)**

**B. Power production in nuclear fusion**

4.2 As an energy source, nuclear fusion of light isotopes has several advantages over nuclear fission. Fusion is a clean process in the sense that the products are stable isotopes of [ $^4\text{He}$ ]. In contrast to the hazardous radioactive isotopes formed by fission. Equally important, light isotopes suitable for fusion are far more abundant than the heavy isotopes required for fission.

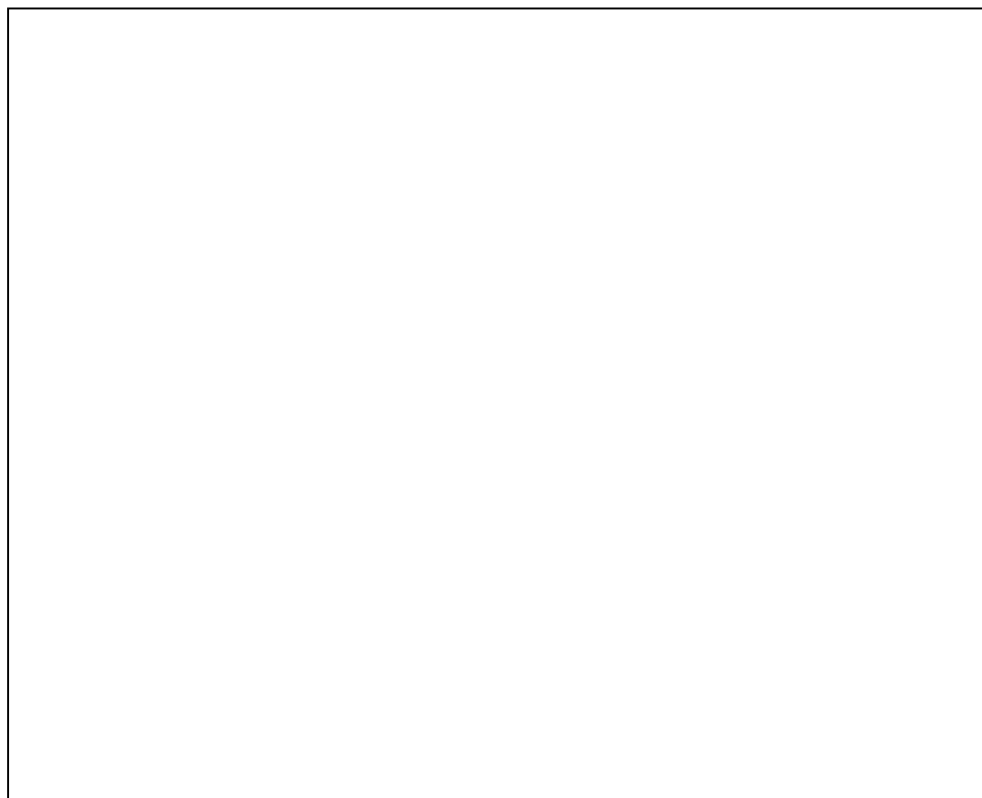
Fusion processes, however, require very high activation energy. One of the fusion reactions currently under study is a two-step process involving deuterium and lithium as the basic starting materials:



Estimate the expected power production in MW, if 1.00 g of  $^6\text{Li}$  per day is completely consumed for the production of  $^4\text{He}$ . Assume 100% efficiency in the process.

Data on masses:  $^6\text{Li} = 6.015120 \text{ u}$ ,  $^2\text{H} = 2.014104 \text{ u}$ ,

$^4\text{He} = 4.00260 \text{ u}$ ,  $^1_0\text{n} = 1.00866 \text{ u}$



(6marks)

**C. Decomposition of Limestone**

- 4.3 A cement-producing factory requires CaO, which is largely obtained by decomposition of limestone. The decomposition reaction for limestone is as follows:



A chemist took 20g of limestone sample and heated it to 800°C in a 10.00L container. Assuming that the limestone contains 100% calcium carbonate, calculate:

- Initial moles of calcium carbonate.
- Number of moles of CO<sub>2</sub> evolved during the decomposition.
- Percentage of unreacted CaCO<sub>3</sub>.

**(3marks)**

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**Problem 5****21 marks****A. Co-ordination chemistry of copper**

- 5.1 The addition of KI to a blue colored solution of  $[\text{Cu}(\text{H}_2\text{O})_6]^{++}$  ( $\lambda_{\text{max}} 12600 \text{ cm}^{-1}$ ) results in the formation of colorless CuI and  $\text{I}_2$ .



The liberated iodine dissolves in water in the presence of excess KI to form  $\text{KI}_3$ .

- i) Consider the dissolution of  $\text{I}_2$  into KI. Assign the acidic and the basic species.

**(1mark)**

- ii) Liberated iodine in equation (1) is estimated with  $\text{Na}_2\text{S}_2\text{O}_3$ . Give equation for this reaction.

**(1mark)**

- iii) In equation (1), which species is oxidized and to what?

**(1mark)**

- iv) Based on the VSEPR theory give the structure of  $\text{I}_3^-$ .

**(1mark)**

v) What is the geometry of the  $[\text{Cu}(\text{H}_2\text{O})_6]^{++}$  ion?

(2marks)

vi) Why is CuI colorless?

(1.5marks)

vii) Calculate the spin only magnetic moments for  $[\text{Cu}(\text{H}_2\text{O})_6]^{++}$  and CuI.

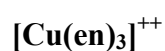
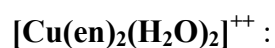
(2marks)

viii) Calculate the  $\Delta_0$  for  $[\text{Cu}(\text{H}_2\text{O})_6]^{++}$  ( $1\text{kJ mol}^{-1} = 83.5\text{ cm}^{-1}$ ).

(1mark)

5.2 The aqua ligands in  $[\text{Cu}(\text{H}_2\text{O})_6]^{++}$  cation are replaced sequentially by ethylenediamine (en,  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ ) to give  $[\text{Cu}(\text{en})(\text{H}_2\text{O})_4]^{++}$ ;  $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]^{++}$  and  $[\text{Cu}(\text{en})_3]^{++}$ .

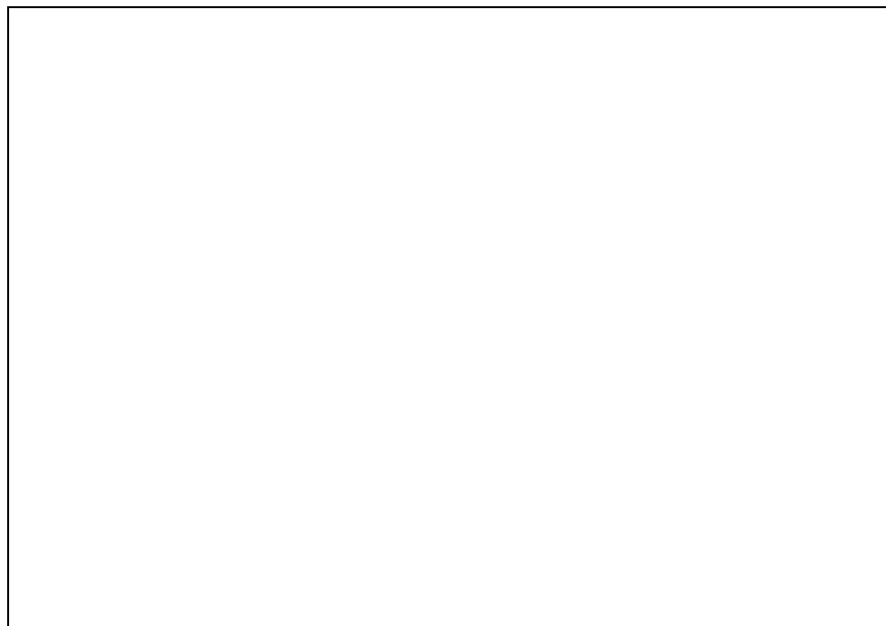
i) Give the IUPAC names of these complexes.



(1.5marks)



- ii) Draw the possible structures of  $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]^{++}$  and assign the configurations.



(3marks)

## B. Complexes of Nickel

- 5.3 Green aqueous solution of Nickel chloride contains  $[\text{Ni}(\text{H}_2\text{O})_6]^{++}$ . This solution on treatment with NaCN yields yellow  $\text{Na}_2\text{Ni}(\text{CN})_4$ . While with  $\text{Ph}_4\text{AsCl}$  it gives blue  $[\text{Ph}_4\text{As}]_2[\text{NiCl}_4]$ .

- i) What are the geometries of the  $[\text{Ni}(\text{H}_2\text{O})_6]^{++}$ ,  $\text{Ni}(\text{CN})_4^{--}$  and

$[\text{Ph}_4\text{As}]_2[\text{NiCl}_4]$ ?

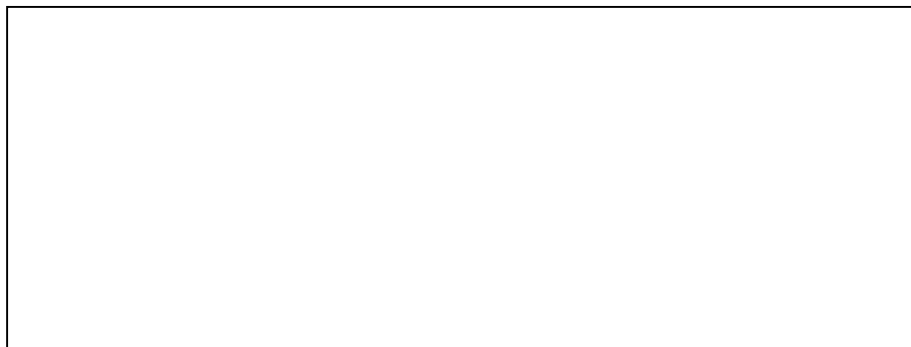
$[\text{Ni}(\text{H}_2\text{O})_6]^{++}$ :

$\text{Ni}(\text{CN})_4^{--}$  :

$[\text{Ph}_4\text{As}]_2[\text{NiCl}_4]$  :

(3marks)

- ii) The electronic spectrum of  $[\text{Ni}(\text{H}_2\text{O})_6]^{++}$  shows a band at  $8500 \text{ cm}^{-1}$  due to d-d transition. Where would one expect such transition for  $[\text{Ph}_4\text{As}]_2[\text{NiCl}_4]$  ?



**(3marks)**

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## Problem 6

25 marks

## A. Structure elucidation of organic compound

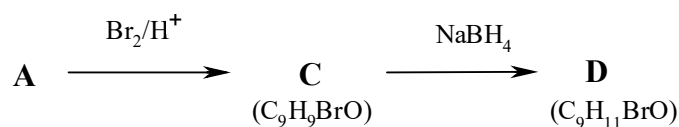
6.1 Compound A ( $C_9H_{10}O$ ) shows a strong IR absorption at  $1690\text{ cm}^{-1}$ . It shows the following signals in its  $^1H$  NMR: 1.25 (3H, triplet), 3.0 (2H, quartet), 7.5 (3H, multiplet) and 8.0 (2H, multiplet). A on oxidation with acidic potassium permanganate gives benzoic acid. [Refer to the Tables 1 and 2 given at the end of the problem]

i) From the IR spectrum, the compound A is expected to have functional group/s:

(1mark)

ii) The structure of A:

(3marks)




6.2 i) Draw the structures of C and D.

C

D

(2marks)

- ii) Draw the Fischer projection formulae of the isomers of **D**.



(2marks)

- 6.3 Compound **B**, isomeric with **A** shows a strong IR absorption at  $1730\text{ cm}^{-1}$  and a medium peak at  $2700\text{ cm}^{-1}$ . It shows the following signals in its  $^1\text{H}$  NMR spectrum: 2.7(2H, triplet), 2.95(2H, triplet), 7.3(5H, multiplet) and 9.7(1H, singlet). [Refer to the Tables 1 and 2 given at the end of the problem]

- i) From the IR spectrum, the compound **B** is expected to have functional group/s:



(1mark)

- ii) The structure of **B**:

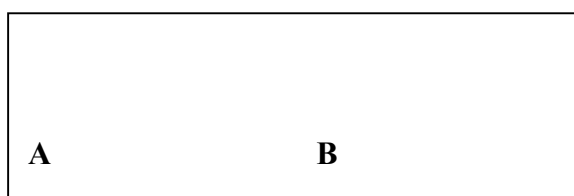


(3marks)

## B. Organic reactions, mechanisms and stereochemistry

- 6.4 The reaction of cyclopentanol with sodium metal gives product **A**. **A** reacts with bromoethane to give **B**.

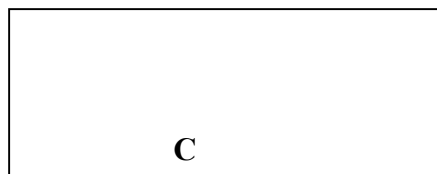
- i) Identify **A** and **B**.



(2marks)

- ii) Bromocyclopentane, on heating with sodium ethoxide, gives C.

Identify C.



**(1mark)**

- iii) In the above reaction (ii), ethoxide functions as :

- |                 |                          |
|-----------------|--------------------------|
| i. Electrophile | <input type="checkbox"/> |
| ii. Nucleophile | <input type="checkbox"/> |
| iii. Base       | <input type="checkbox"/> |
| iv. Lewis acid  | <input type="checkbox"/> |

**(1mark)**

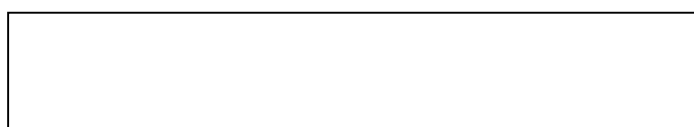
When C is reacted with DBr (in dark), a mixture of products is obtained.

- iv) Draw the structures of the products.



**(2marks)**

- v) What is the relationship between the above products?

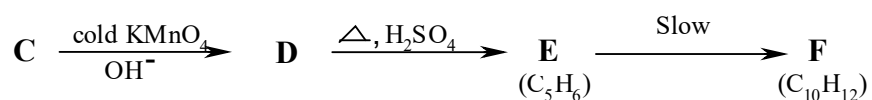


**(1mark)**

vi) When bromocyclopentane is boiled with NaI in acetone, iodocyclopentane is formed. The reaction is possible because:

- a) Sodium bromide is insoluble, and sodium iodide is soluble in acetone.
- b) Bromine is a better leaving group than iodine.
- c) Sodium bromide is soluble, and sodium iodide is insoluble in acetone.
- d) C-I bond is stronger than C-Br bond.

(1mark)



vii) Identify **D**, **E** and **F**.

<b>D</b>	<b>E</b>	<b>F</b>
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(3marks)

viii)  $\text{pK}_a$  value of **E** is found to be 16. Write the equation of the reaction between **E** and a base (Use symbol **B'** for base)

(1mark)

ix) When **E** is treated with a base it shows only one single line in its  $^1\text{H}$  NMR spectrum. Give reason for this observation.

(1mark)

**Table 1: Some characteristic proton chemical shifts**

Type of proton	Chemical shift, $\delta$ (ppm)
p,s,t- C-H	0.9-1.5
C= C-H	4.6-5.9
C $\equiv$ C-H	2.0-2.3
Ar-H	6.0-8.5
Ar-C-H	2.2-3.0
O-C-H	3.3-4.0
O = C-C-H	2.0-2.7
ROOC-C-H	2.0-2.6
O = C-H	9.0-10.0
R-COOH	10-12

**Table 2: Some characteristic Infrared absorption frequencies**

Compound type	Frequency range ( $\text{cm}^{-1}$ )
Alkanes C-H	2850-2960
Alkenes C-H	1350-1470
	3020-3080
Aromatic C-H	675-1000
	3000-3100
Olefin C=C	675-870
	1640-1680
Alkyne C $\equiv$ C	2100-2260
C-O	1080-1300
C=O	1650-1800
O-H	3200-3600
C $\equiv$ N	2210-2260

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## Problem 7

15 marks

## A. Amino acids and proteins

7.1 Diabetes is a disease usually occurring in persons above the age of 40 years. This is caused by the deficiency of a hormone regulating the glucose level in the blood. This hormone is a protein containing two peptide chains cross-linked by two disulfide bonds. In addition, chain **A** has one intrachain disulfide bond between position 6 and 11. The chains **A** and **B** contain 20 and 30 amino acids, respectively.

i) Name this hormone regulating the glucose level in the blood.

(1mark)

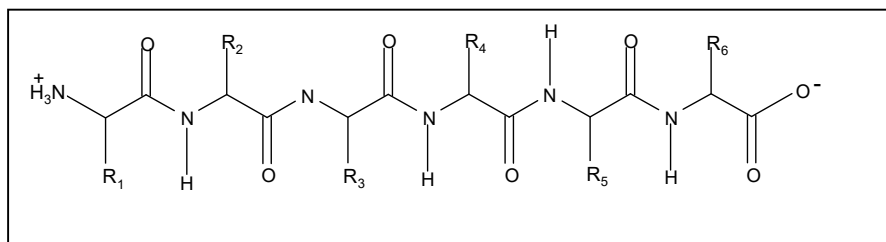
ii) Indicate the amino acid/s present in the positions 6 and 11 of the peptide **A**. Also show the disulphide linkage.

(1mark)

iii) Schematically show the reduction of the above disulfide linkage.

(1mark)

iv) An enzymatic treatment of the chain **A** resulted in a hexapeptide as one of the products. Assuming that the hexapeptide is in  $\alpha$  - helical conformation, indicate the H-bond between the groups using arrows.



(1mark)

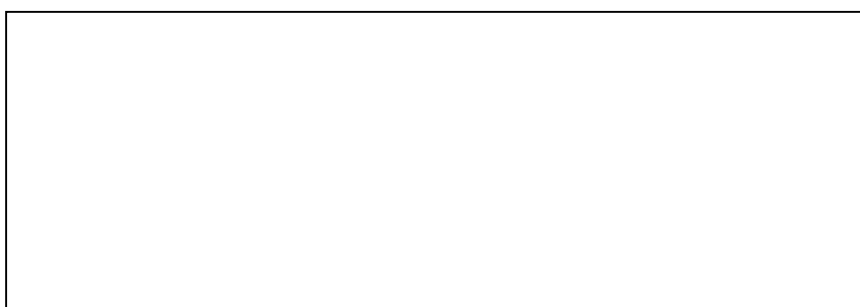


- v) Chemical treatment of the chain **B**, originally in  $\alpha$ -helical form, denatured it. After the treatment, the peptide attained an extended conformation. Find out the length of the peptide before and after treatment.



(2marks)

- vi) Given the average molecular weight of the amino acids to be 128Da. Calculate the molecular weight of the chain **A**.



(2marks)

- 7.2 A protein solution was prepared in a beaker and the pH of the solution was adjusted to the isoelectric point of the protein. The solution was distributed equally in three different containers, **A**, **B** and **C**. Solution in container **A** was kept as control. However in containers **B** and **C**, the pH was adjusted to less and more than that of isoelectric point respectively. Samples from all the three containers were placed on a electrophoresis gel for separation of the protein. State the direction of migration of protein in each of the three samples.



(1.5marks)

**B. Structures and functions of nucleic acids**

7.3 Nucleus of the cell contains the genetic material, DNA. Information stored in the DNA gets decoded and expressed as proteins, via mRNA. DNA is a double helical structure, while mRNA is single stranded. Nucleotides are the basic units of both the nucleic acids. Each nucleotide contains a nitrogen base linked to a pentose sugar, having phosphate at 5' position. Consecutive nucleotides are linked by 3',5' phospho diester bonds. The synthesis of mRNA from the DNA is called transcription and synthesis of protein(polypeptide) chain from mRNA is called translation. Sequence of nucleotides in the mRNA (and therefore in the DNA) determines the sequence of amino acids in the polypeptide.

- i) Find out the number of codons (without start and stop codon) in the mRNA that upon translation would result in synthesis of a protein containing 60 amino acids.

**(1mark)**

- ii) What would be the number of nitrogen bases that will be present in DNA corresponding to above mRNA.

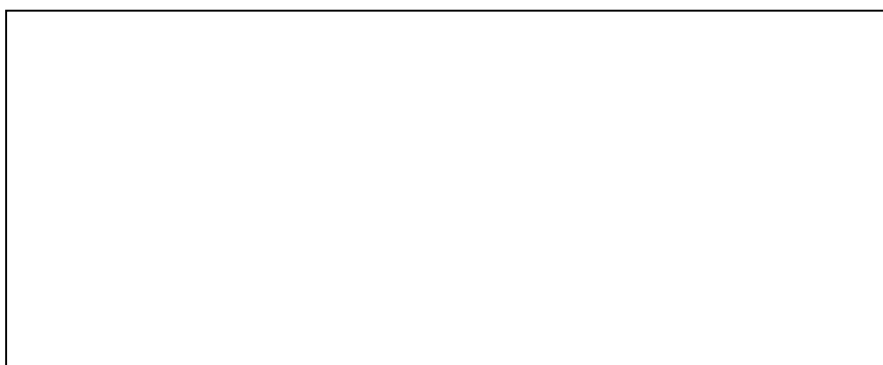
**(2marks)**

- iii) If 20% of bases in the above DNA is adenine, what will be the percentage of other bases?



**(1.5marks)**

- iv) DNA absorbs U.V. radiation at  $\lambda_{\text{max}}$  of 260nm. What structural features of the DNA molecule enable it to absorb U.V. radiation?



**(1mark)**