

2017

**M.Sc. 4th Semester Examination****CHEMISTRY****PAPER—CEM-401**

Full Marks : 40

Time : 2 Hours

*The figures in the margin indicate full marks.**Candidates are required to give their answers in their own words as far as practicable.**Illustrate the answers wherever necessary.***(Physical Special)**Answer any *five* questions,  
taking *two* questions from each group.**Group—A**

1. (a) Imagine a system in which there are just two linearly independent kets.

$$|1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Hamiltonian matrix of the system has the following form,

$$H = \begin{pmatrix} h & g \\ g & h \end{pmatrix}$$

*(Turn Over)*

Where  $g$  and  $h$  are real constant. If the system starts out at  $t = 0$  in state  $|1\rangle$ , then find out the state at time,  $t$ .

- (b) Find the eigen values and eigen vectors for

$$A = \begin{pmatrix} 1 & -2 \\ 1 & 4 \end{pmatrix}$$

5+3

2. Obtain the matrix representation of the following angular momentum operator when  $J = 1$ .

$$J_+, \quad J_-, \quad J_x \text{ and } J_y \quad 2 \times 4$$

3. Deduce the pure spin states and indicate their spin multiplicities for a system of three non-equivalent electron

with  $M_s = \frac{1}{2}$ . 8

4. Write down the steps involved for the determination of molecular term symbols. Deduce the possible term symbols for  $O_2$  and hence obtain its ground state terms. Write the ground state wavefunctions,

$$(\Psi = \Psi_{\text{spatial}} \cdot \Psi_{\text{spin}}) \text{ of } O_2 \quad 2+4+2$$

### Group—B

5. (a) State and Proof Koopman's theorem to obtain the energy of atomic orbital.

- (b) Use j-j coupling scheme to obtain the terms for  $d^2$  configuration. 4+4

6. Deduce Hartree-FOCK-Roothaan equation. How do you obtain energy of HF orbital using this equation ?
7. Write down the spin-orbit interaction Hamiltonian for L-S coupling scheme. Obtain the expression of spin-orbit interaction energy ( $E_{50}$ ).  
Calculate the spin-orbit interaction energy of  ${}^3F_2$ ,  ${}^3F_3$  and  ${}^3F_4$  levels. Comment on your results. 2+3+3
8. Write down the perturbation operator corresponding to Zeeman effect in many electron atom and hence obtain the first order correction to energy. Give a schematic diagram with appropriate term symbols for  $1s \rightarrow 2p$  transition in H-atom (i) in the absence, (ii) in the presence of an external magnetic field. 5+3

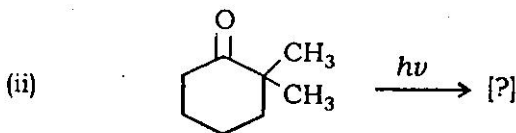
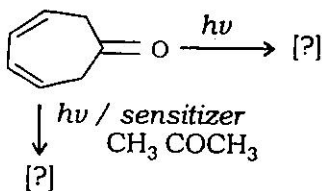
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**(Organic Special)**

Answer any *five* questions,  
taking at least *two* from each group.

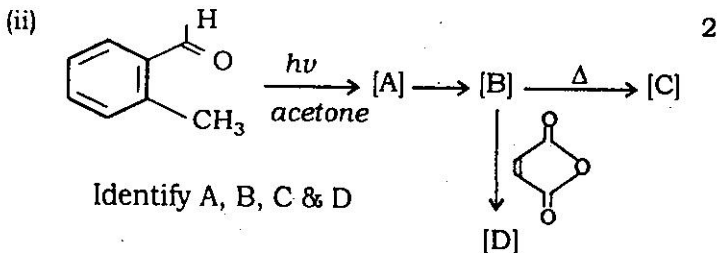
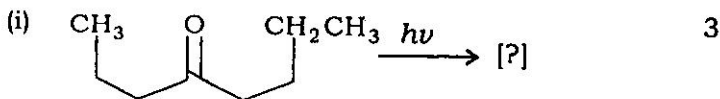
**Group—A**

1. (a) Define Norrish type - 1 reaction and explain the cleavage reaction with example along with the mechanism.
- (b) (i) Predict the products of the following reaction giving proper explanation in each case : 3+2×2½

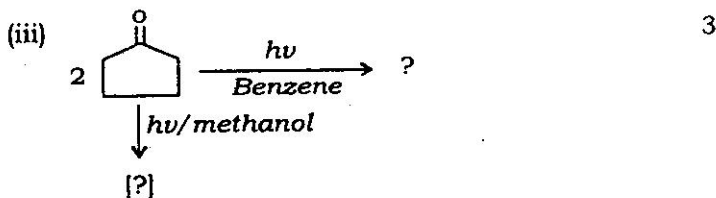
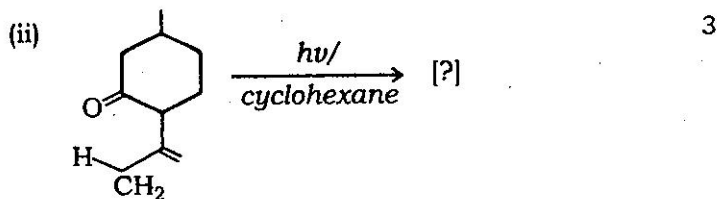
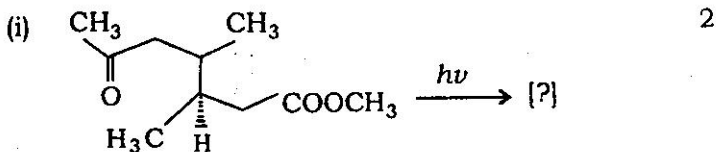


2. (a) What are the minimum conditions for occurring Norrish type - II Cleavage reaction? Explain the mechanism with reference to an example. 3

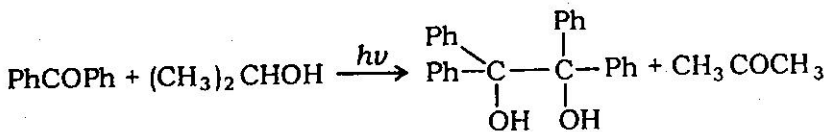
(b) Predict the products of the reactions :



3. (a) Predict the products of the following reaction indicating mechanism in each case :

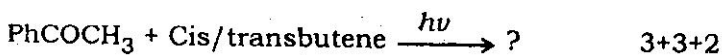


4. (a) The following reaction gives the products as follows :



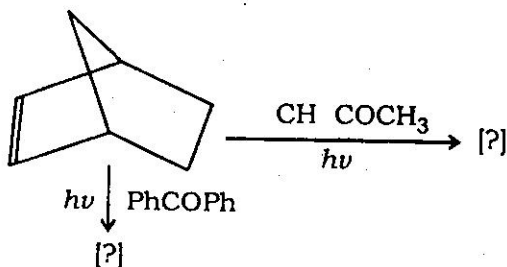
The quantum yield for the reaction was investigated nearly as,  $\phi = 1$ . Establish this observation showing mechanism of the reaction.

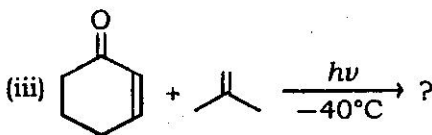
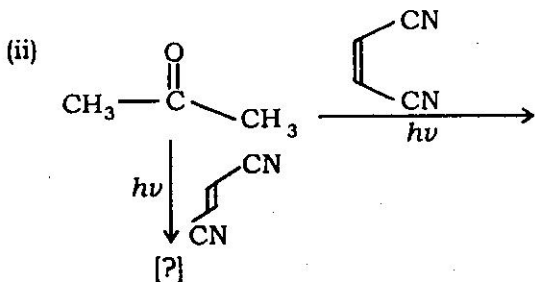
- (b) Mischler's Ketone does not undergo photo reduction under the same condition at which benzophenone absorbs. Explain with proper reasoning.
- (c) Predict the products of the following reaction



5. Predict the products of the following reaction with proper explanation :

(i)

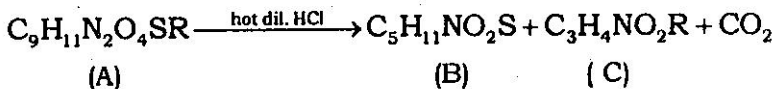




3+2+3

### Group—B

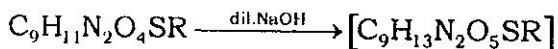
6. (a) Write the names with chemical formula of different types of natural penicillin isolated from the fungus, genus penicillium.
- (b) The following compound (A) on hydrolysis yields to product as :



Identify (B) and (C) and establish their structures.

3+3+2

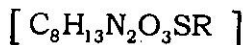
7. (a) Penicillin undergoes the conversion as follows :



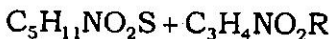
(Penicillin)

(D)  $\downarrow \Delta$  (Heating) -  $\text{CO}_2$

Draw backwards and write the possible structures of Penicillin.



(E)  $\downarrow$  aq.  $\text{HgCl}_2$



(F)

(G)

- (b) Establish the exact structure of penicillin from IR spectroscopic evidences. 3+5

8. Write all the synthetic steps for the synthesis of phenoxy methyl penicillin starting from phthalinide as applied by Sheehan et. al. Indicate the synthetic methodologies where applicable. 8

### (Inorganic Special)

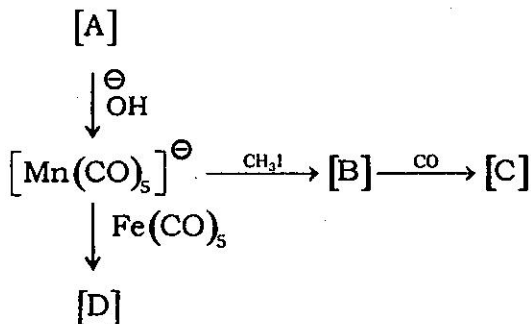
Answer any four questions.

1. (a) In a Carbonyl complex having linear  $(\text{OC}) - \text{M} - (\text{CO})$  group, indicate how  $\nu_{\text{CO}}$  will change when
- (i) One CO is replaced by  $\text{Et}_3\text{N}$
  - (ii) a positive charge is placed on the complex.

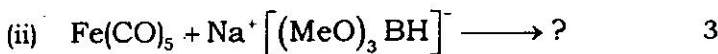
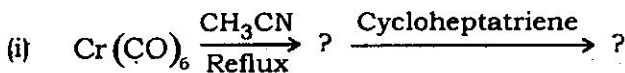


(iii) a negative charge is placed on the complex. 3

(b) Predict [A] to [D]. 4



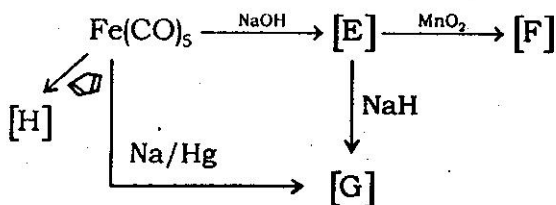
(c) Cite the products of the following reaction :



2. (a) "Removal of all CO ligands is rarely possible"—Justify or Criticize. 2

(b) Complete the following reaction :

4



(c) In  $L_nM - CO$  complexes, if CO gets coordinated to a Lewis acid (A) and becomes  $L_nMCO - A$ .

What will happen to its  $\nu_{CO}$  value? [ $L_n$  = non  $\pi$ -acid ligand]. Justify your answer. 2

(d) Write down the complete reaction when Chromium hexacarbonyl is treated with sodium borohydride. 2

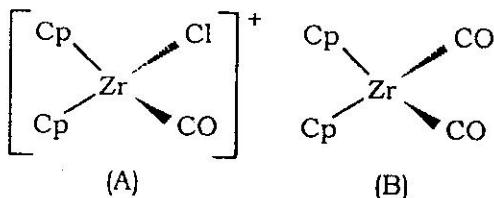
3. (a) Deduce the expression for volume susceptibility of diamagnetism. 7

(b) Write a short note on natural types of supramolecular interactions. 3

4. (a) What is the structure of the cluster core of  $Os_6(CO)_{18}$ ? Upon adding two electrons, what will be the change in the geometry of the cluster core? Explain on the basis of Wade's rule.

- (b) How will you synthesize  $[\text{Fe}_4(\text{CO})_{13}]^{2-}$  starting from  $\text{Fe}(\text{CO})_5$ ? Discuss the structure of this tetrametallic cluster compound. 3
- (c) Write down the synthesis procedure of synthesizing  $\text{Co}_4(\text{CO})_{12}$  and  $\text{Ir}_4(\text{CO})_{12}$ . Discuss the structure. 3
5. (a) Elucidate and draw the geometry of the metal core structure for the following clusters.
- (i)  $[\text{Co}_6(\text{CO})_{15}]^{2-}$
- (ii)  $[\text{Os}_7(\text{CO})_{21}]$  4
- (b)  $\text{Os}_5(\text{CO})_{18}$  has metal framework consisting of three edge sharing triangles (raft structure). Show that the valence electron count for this raft is consistent with the number of electrons available. 3
- (c) Predict the geometry of the following metal clusters based on total valence electron count — 3
- (i)  $\text{Co}_3(\text{CO})_9 (\mu_3 - \text{CCl})$
- (ii)  $\text{HRu}_6(\text{CO})_{17}\text{B}$
- (iii)  $\text{Co}_3(\text{CO})_9\text{Ni}(\eta^5 - \text{Cp})$
6. (a) What do you mean by Neel and Curie temperature? Discuss the significance of Neel and Curic temperature. 4

- (b) What do you mean by "multiplet width"? Establish the magnetic moment equation for a system having large multiplet width compared to  $kT$ . 2+4
7. (a)  $N_2$  and CO are iso-electronic molecules but  $M - N_2$  Complexes are much weaker compared to  $M - CO$  complexes. Offer reasonable explanations.
- (b) What happens to  $\nu_{CO}$  when CO gets coordinated to  $BH_3$  or  $Ni(CO)_3$ ?
- (c) Among the given two complexes (A) and (B), which will show a lower carbonyl stretching frequency? Give reasons for your answer.



- (d) Which of the given complexes (A) and (B) will undergo ligand substitution faster with  $PPh_3$ ? Why?

