2023

M.Sc.

4th Semester Examination

CHEMISTRY (SPECIAL)

PAPER : CEM-402

Full Marks : 40

Time : 2 hours

The figures in the right hand margin indicate marks.

Candidates are required to give their answers in their own words as far as practicable.

Illustrate the answers wherever necessary.

Answer from *any* **one** Section.

SECTION—I

(Physical Chemistry)

Answer from **all** the Groups as directed.

GROUP—A

Answer *any* **four** questions from the following :

2×4=8

1. Write down the Slater determinant form of the wave function of Li atom.

2. Write down the nuclear spin function of $A - X$ spin system and indicate their energy order in presence of an external magnetic field.

3. ^1H NMR chemical shift (δ value) is independent of spectrometer frequency. Explain.

4. Write down the magnetic interaction Hamiltonian for H-atom.

5. State the degeneracy of the state represented by the term $^1D_2$.

6. State Hellmann Feynman theorem.

GROUP—B

Answer *any* **four** questions from the following :

$$4 \times 4 = 16$$

7. State and prove Koopmans' theorem.

8. Use $J - J$ coupling scheme to obtain the terms of d^2 configuration.

9. Spin-orbit coupling mechanism helps to obtain population difference among the magnetic sublevels to observe NMR transition. Explain.

10. Write down the magnetic interaction Hamiltonian and spin functions for A_2 spin system. State the selection rule and the number of transitions to be observed for A_2 spin system.

11. Deduce the eigenvalue of S^2 operator for two-electron system having spin function, $\alpha(1)\beta(2) - \beta(1)\alpha(2)$. Indicate the spin multiplicity of the above spin state.

12. $CH_2Cl — CH_3$ shows two major ^1H NMR transitions, one having triplet with intensity ratio $1 : 2 : 1$ and the other having quartet with intensity ratio $1 : 3 : 3 : 1$. Explain.

GROUP—C

Answer *any* **two** questions from the following :

$$8 \times 2 = 16$$

13. Deduce the pure spin state and indicate their spin multiplicities for a system of three non-equivalent electrons with $M_S = -\dfrac{1}{2}$.

14. Deduce the energy expectation value of two-electron system represented by the following Slater determinant $|D_1\rangle = |\phi_1 \bar{\phi}_1|$ and $|D_2\rangle = |\phi_1 \phi_2|$.

15. Deduce the expression of spin-orbit interaction energy of electron in an atom.

Calculate the spin-orbit interaction energy in the $^3F_2$, $^3F_3$ and $^3F_4$ level of d^2 electronic configuration and hence obtain their energy ordering.

16. Write down the spin functions and magnetic interaction Hamiltonian for H-atom. Obtain the expression of zero order and first order correction to energy for each state.

SECTION—II

(Organic Chemistry)

Answer from **all** the Groups as directed.

GROUP—A

1. Answer *any* **four** questions from the following :

$2 \times 4 = 8$

(a) What are the various units present in the structure of streptomycin? What is it used for?

(b) What are photosensitized reactions? Give an example.

(Continued)

(c) What do you mean by coenzyme, holoenzyme and apoenzyme?

(d) How will you account for bands at 1770 and 1506 cm^{-1} in the IR spectra of methyl ester of benzylpenicillin?

(e) Write down the function of mRNA and rRNA.

(f) Write down the scheme for Fischer synthesis of adenine.

GROUP—B

2. Answer *any* **four** questions from the following :
$$4 \times 4 = 16$$

(a) What are the nucleosides present in DNA? What are 'mutagens'? Give an example.
$$2 + 2 = 4$$

(b) What do you mean by 'ANRORC mechanism'? Illustrate your answer with a suitable example. $2 + 2 = 4$

(c) How will you prepare D-penicillamine from *DL-valine*? 4

(Turn Over)

(d) Predict the products of the following reactions with plausible mechanism :

2+2=4

(i) $\xrightarrow{h\nu}$

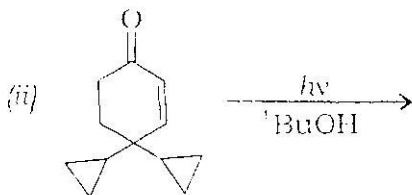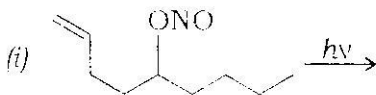*(ii)* $\xrightarrow[\text{Pd Al}_2\text{O}_3]{h\nu}$
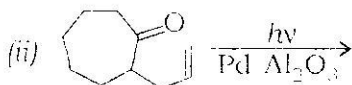
(e) *(i)* How will you prepare nicotinic acid and nicotinamide from 3-methyl pyridine?

2

(ii) Draw the structure of Vitamin K_1 and discuss its stereochemical features. 2

*(f)* Predict the products of the following reactions with plausible mechanism :

2+2=4

(i) $\xrightarrow{h\nu}$

(ii) $\xrightarrow[\text{'BuOH}]{h\nu}$

GROUP—C

3. Answer *any* **two** questions from the following :

$8 \times 2 = 16$

(a) (i) Write down the structure and function of NAD. 3

(ii) Write down the Traube synthesis of caffeine. 3

(iii) What happens when adenine and guanine are treated with trifluoroperacetic acid separately? 2

(b) (i) Write down the Traube synthesis of uric acid. 4

(ii) Outline a scheme for the synthesis of thiamine chloride hydrochloride (Vitamin B_1). 4

(c) Predict the products with plausible mechanism for the following reactions :
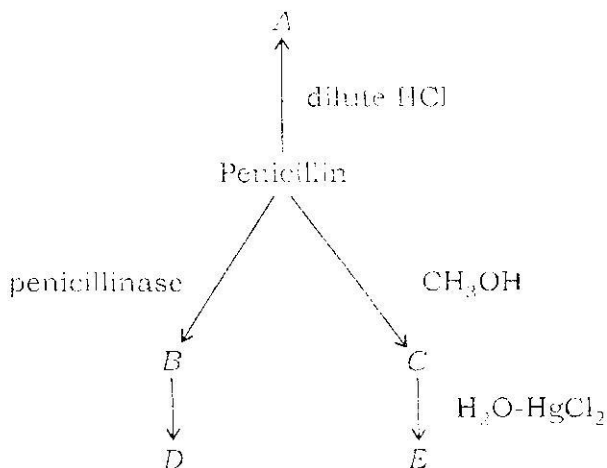
$2+3+3=8$

(i)

(ii)

(iii)
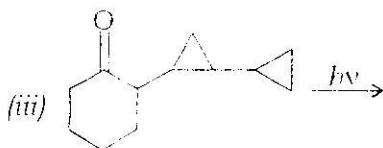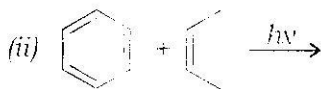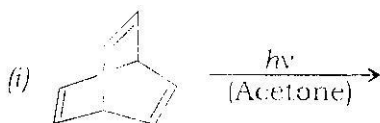
(d) *i)* Identify the product(s) with plausible mechanism :   2

$$\xrightarrow[\text{MeOH}]{h\nu} ?$$
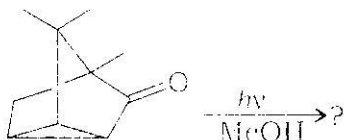
(ii) What happens when 1,5-cyclooctadiene and 1,4-cyclooctadiene are subjected to photolysis separately in presence of acetone?   2

(iii) Draw the structure of penicillin and identify the products A, B, C, D and E.   4

SECTION—III

(Inorganic Chemistry)

Answer from **all** the Groups as directed.

GROUP—A

UNIT—I

Answer *any* **two** questions from the following :

$2 \times 2 = 4$

1. How does an antiferromagnetic substance differ from a diamagnetic substance?

2. What are Neel temperature and Curie temperature? State the significance of these temperatures.

3. Calculate Landé g factor and total magnetic moment for Pr^{3+} ion.

UNIT—II

Answer *any* **two** questions from the following :

$2 \times 2 = 4$

4. How will you synthesize $Ni(CO)_4$ by Mond's process? Why is this method commercially important?

5. Confirm that the mono-capped octahedral of $Os_7(CO)_{21}$ is consistent with the number of valence electrons available.

6. How will you synthesize $[Fe_4(CO)_{13}]^{2-}$ from $Fe(CO)_5$?

GROUP—B

UNIT—I

Answer *any* **two** questions from the following :

$4 \times 2 = 8$

7. Number of f-electrons in Eu^{3+} and Am^{3+} are same, but they have different magnetic moment values. Explain. 4

8. Define the terms 'magnetic susceptibility' and 'magnetization'. $2+2=4$
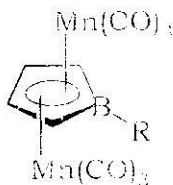
9. Write a short note on 'super exchange'. 4

UNIT—II

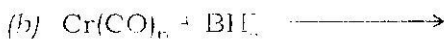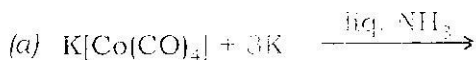Answer *any* **two** questions from the following :

$4 \times 2 = 8$

10. *(a)* How $Cr(CO)_6$ is synthesized from $CrCl_3$ by 'Reductive Carbonylation'? 2

(b) Calculate the total number of valence electrons for 2

$Mn(CO)_3$ (top)

B—R

$Mn(CO)_3$ (bottom)

11. (a) Explain the semi-bridging binding nature of carbonyl as a ligand in $Fe_2(CO)_7(bpy)$ complex by the orbital diagram. 3

(b) What is the range of stretching frequency (in cm^{-1}) for CO (in its neutral complex) for symmetric μ_3 binding? 1

12. Complete the following reactions : 2+2=4

(a) $K[Co(CO)_4] + 3K \xrightarrow{\text{liq. } NH_3}$

(b) $Cr(CO)_6 + BH_3 \longrightarrow$

GROUP—C

UNIT—I

Answer *any* **one** question from the following :

$8 \times 1 = 8$

13. (a) Experimental magnetic moments of tris(acetylacetonato)europium(III) and

tris(acetylacetonato)samarium(III) are 3·5 B.M. and 1·4 B.M. respectively. Comment about the results. 5

(b) Calculate the value of magnetic dipole moment associated with the orbital motion of an electron. 3
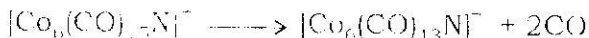
14. Derive an expression for 'volume susceptibility' of a diamagnetic material. State the factors on which the 'volume susceptibility' of a diamagnetic material depends. 6+2=8

UNIT—II

Answer *any* **one** question from the following :

8×1=8

15. (a) Suggest what change in cluster structure might accompany the following reaction :

$$[Co_6(CO)_{15}N]^- \longrightarrow [Co_6(CO)_{13}N]^- + 2CO$$

(b) Synthesize $[Re_4(CO)_{16}]^{2-}$ from $Re_2(CO)_{10}$. Draw the solid state structure of $[Re_4(CO)_{16}]^{2-}$.

(c) Calculate the bond order between 'W' atoms in $[W_2Cl_9]^{3-}$ having face-centered bioctahedral geometry. 3+3+2=8

16. *(a)* Use the capping principle to account for the fact that $[Os_8(CO)_{22}]^{2-}$ has a bicapped octahedral structure.

(b) Using Wade's rule, predict the cluster core geometry of $[HOs_5(CO)_{15}]^-$.

(c) Draw the structure of $[Fe_3(CO)_{11}]^{2-}$.

$$3+3+2=8$$

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