

M.Sc. 4th Semester Examination, 2025

CHEMISTRY

PAPER — CEM-402

Full Marks : 50

Time : 2 hours

Answer all questions

The figures in the right hand margin indicate marks

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

CEM — 402

(Inorganic Chemistry Special)

GROUP — A (a)

Answer any two of the following questions : 2×2

1. State 'Lande interval rule'.

(Turn Over)

2. Why a diamagnetic material is weakly repelled by the external magnetic field ?
3. The number of *f*-electrons in Eu(III) and Am(III) are same, but they have different magnetic moment value. Explain.

GROUP – A (b)

Answer any two of the following questions : 4×2

4. Derive the expression for magnetic dipole moment associated with the orbital motion of an electron.
5. Explain $\frac{1}{\chi_M}$ versus temperature (T) plots for paramagnetic, antiferromagnetic and ferromagnetic materials. (where χ_M = molar magnetic susceptibility). 1 + 1 + 2
6. Write the magnetic moment equation which is commonly used to calculate the magnetic

moment for 4f metal compounds. Explain why Sm(III) and Eu(III) compounds do not follow this equation.

GROUP – A (c)

Answer any one of the following questions : 8×1

7. Derive an expression for “diamagnetic volume susceptibility” of a material. State the factors on which “diamagnetic volume susceptibility” depends. 6 + 2
8. (a) Which one of the following two complexes will have more superexchange interaction and why ? 3
- $[(\text{NH}_3)_5\text{Cr}-\text{O}-\text{Cr}(\text{NH}_3)_5]\text{Br}_4$
- $[(\text{NH}_3)_5\text{Cr}-\text{OH}-\text{Cr}(\text{NH}_3)_5]\text{Br}_5$
- (b) How does an antiferromagnetic substance differ from a diamagnetic substance ? 2
- (c) Write short note “Super exchange”. 3

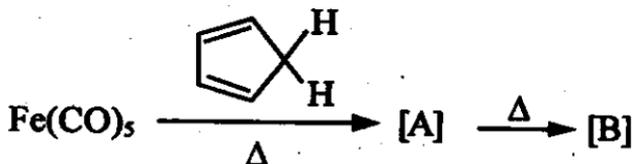
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GROUP – B (a)

Answer any two of the following questions : 2×2

9. Cite one example (with structure) for a μ_4 -CO bridging complex. Write the C-O stretching frequency (in cm^{-1}) for this complex.

10. Complete the following reaction :



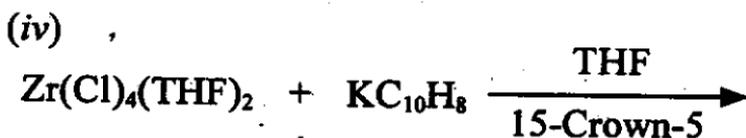
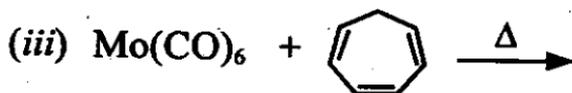
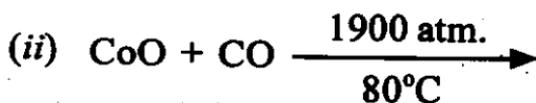
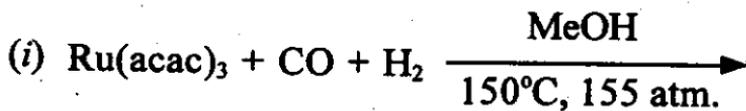
11. Predict the structure of $\text{HRu}_6(\text{CO})_{17}\text{B}$.

GROUP – B (b)

Answer any two of the following questions : 4×2

12. Complete the following reactions :

(5)



13. How will you synthesize $[\text{Fe}_4(\text{CO})_{13}]^{2-}$ from $\text{Fe}(\text{CO})_5$? Discuss the structural features of $[\text{Fe}_4(\text{CO})_{13}]^{2-}$ cluster. 2 + 2

14. (i) Calculate the W-W bond order in $\text{W}_2(\text{OPh})_6$.

(ii) Predict the structure of $[\text{Fe}_4(\text{CO})_{12}\text{C}]^{2-}$ applying Wade's rule. 2 + 2

GROUP – B (c)

Answer any one of the following questions : 8×1

15. (i) $\text{H}_2\text{Os}_7(\text{CO})_{21}$ has a bicapped square pyramidal cluster geometry. Is this consistent with the number of valence electrons available ?
- (ii) $[\text{Os}_8(\text{CO})_{22}]^{2-}$ has an octahedron structure with two metal atoms on the triangular faces, i.e. bicapped octahedron structure—justify.
- 4 + 4
16. (i) Draw the *d*-orbital overlapping in the edge-sharing bioctahera structure. Cite one example of an edge-sharing bioctahera complex. Calculate the bond order between the metal centres in that complex.
- (ii) How will you synthesize $\text{Os}_5(\text{CO})_{19}$ from $\text{Os}_6(\text{CO})_{18}$? Write the structure of $\text{Os}_5(\text{CO})_{19}$.
- (3 + 1 + 2) + (1 + 1)

[Internal Assessment – 10 Marks]

(7)

CEM – 402

(*Physical Chemistry Special*)

GROUP – A

Answer any **four** questions of the following : 2×4

1. Deduce the expression of Hamiltonian of an N-electron atom.
2. Write down the Slater determinant form of wavefunction of Be atom.
3. Write down the eigen value equation of S^2 operator of N electron system having N_1 number of electrons with α spin and N_2 number of electrons with β spin. Hence obtain the eigen value of S^2 operator for the following function, $|D_1\rangle = |\phi_1 \bar{\phi}_1 \phi_2 \bar{\phi}_2|$.
4. What is meant by Coulomb operator and exchange operator in multi-electron atomic system ?

5. "Energy ordering of nuclear and electron spin in presence of an external magnetic field are opposite to each other." – Explain.
6. Write down the magnetic interaction Hamiltonian and the nuclear spin functions for A_2 spin system.

GROUP – B

Answer any four questions of the following : 4×4

7. Write down the Slater determinant form of wavefunctions of excited Helium ($1s^1 2S^1$) and indicate their spin multiplicities.
8. Deduce the energy of the state described by the slater wavefunction, $|D_1\rangle = |\phi_1\phi_2\rangle$.
9. Write down the steps to evaluate the energy expectation value of multi electron system and deduce the energy expectation value of $2N$ electron system.

10. Use L-S coupling scheme to deduce the terms for d^2 configuration.
11. Calculate the population ratio of β and α spin in a uniform magnetic field of 5.50 T. (Given, $g_N = 5.5854$, $\beta_N = 5.051 \times 10^{-27}$ J/T, $h = 6.626 \times 10^{-34}$ J.S). Comment on your result.
12. What is meant by AX, AB and A_2 spin system in ^1H NMR spectra? Give the schematic plot of energy of each of the spin system and show the possible transitions of spin states stating the selection rules of transition.

GROUP - C

Answer any two questions of the following : 8 × 2

13. Deduce the zero order and first order correction to energies of A-X spin system and hence obtain the frequencies of all possible transition.

14. Use L-S coupling scheme for atomic terms to deduce Lande's interval rule. Calculate the spin-orbit interaction energy of 3F_2 , 3F_3 and 3F_4 levels in terms of spin-orbit coupling constant.

15. Deduce the following expression of total energy (E) for 2N closed electron system.

$$E = 2 \sum_i \epsilon_i - \langle G \rangle$$

Where ϵ_i is the energy of the i^{th} orbital and $\langle G \rangle$ is the total electron-electron repulsion energy of the system.

State and proof Koopman's theorem to obtain the energy of the k^{th} atomic orbital.

3 + 5

16. Deduce the pure spin states and indicate their spin multiplicities for a system of three non-equivalent electron with $M_s = -1/2$.

[Internal Assessment – 10 Marks]

CEM - 402

(*Organic Special*)

GROUP - A

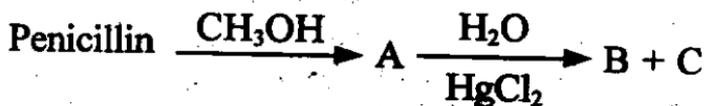
Answer any four questions : 2 × 4

1. What happens when 1,5-cyclooctadiene and 1,4-cyclooctadiene are subjected to photolysis separately in presence of acetone ?
2. What do you mean by photochemical equilibrium ? Give an example.
3. What happens when barrelene is irradiated in presence of a sensitizer like acetone ?
4. Write down Isler's synthesis of Vitamin K₂₍₃₅₎.
5. How will you prepare nicotinamide from 3-methyl pyridine ?
6. What happens when adenine and guanine are treated with trifluoroacetic acid separately ?

GROUP – B

Answer any four questions: 4 × 4

7. Write the structure of penicillin and identify the products A, B and C.



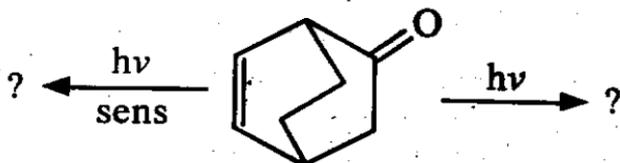
8. (i) Suggest a suitable mechanism for the conversion of 4-phenyl-6-bromopyrimidine to 4-phenyl-6-aminopyrimidine.

(ii) Outline a scheme for the synthesis of uracil.

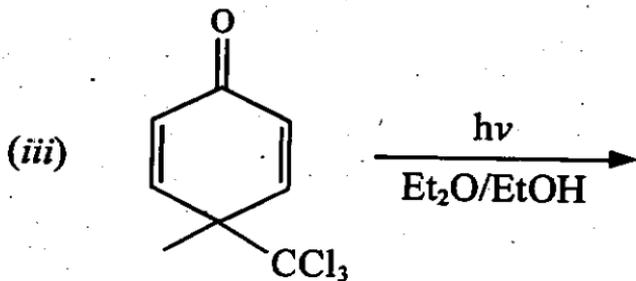
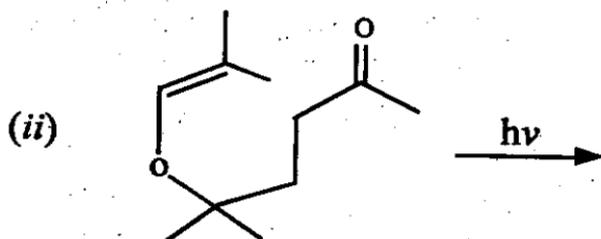
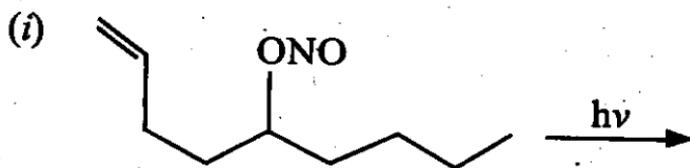
2 + 2

9. Predict the product(s) with proper mechanism :

2 + 2



10. Predict the products of the following reactions with plausible mechanism (any two): 2 + 2



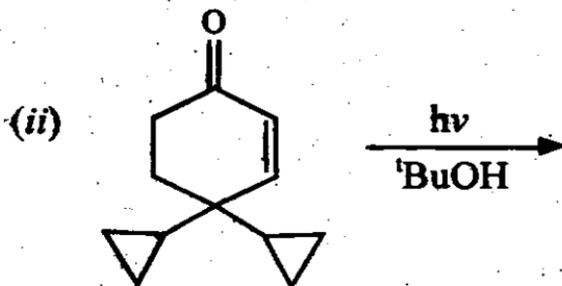
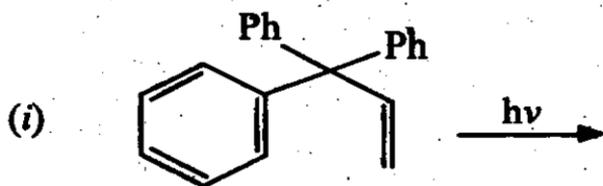
11. Write down the Traube synthesis of uric acid. 4

12. What are coenzymes, holoenzyme and apoenzyme? Draw the structure of NAD and state its function. 2 + 2

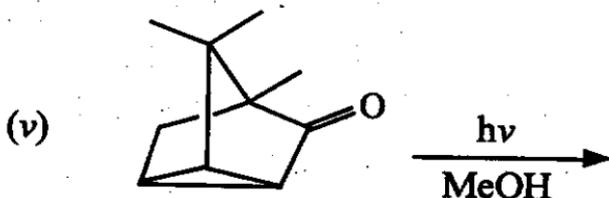
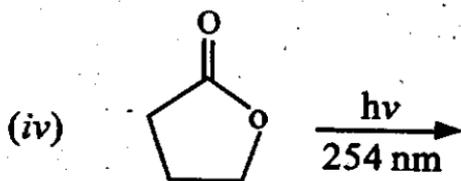
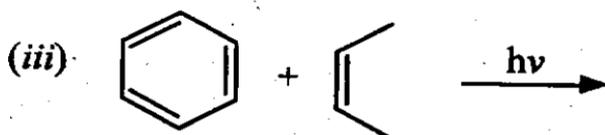
GROUP – C

Answer any two questions : 8 × 2

13. Predict the products of the following reactions with plausible mechanism (any four) :

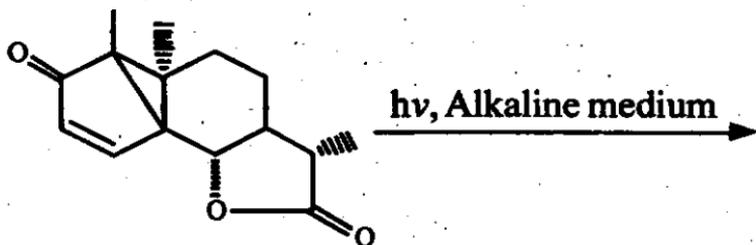


(15)



14. (i) Write down the scheme for the synthesis of D-penicillamine from DL-valine. 4

(ii) Predict the product of the following reaction with plausible mechanism : 4



15. (i) How will you account for the bands at 3333, 1770 and 1506 cm^{-1} in the IR spectra of methyl ester of benzyl penicillin? 3
- (ii) Suggest a suitable scheme for the synthesis of thiamine chloride hydrochloride (vitamin B1). 5
16. (i) Write down the scheme for the Fischer synthesis of hypoxanthine. 2
- (ii) Write down the Traube synthesis of adenine. 3

(17)

(iii) What is Hoffmann-Loeffler-Freytag reaction? Give proper mechanism to illustrate your answer. 3

[Internal Assessment – 10 Marks]

