

2022

M.Sc.

4th Semester Examination

CHEMISTRY

PAPER—CEM-402

ORGANIC, INORGANIC AND PHYSICAL SPECIAL

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.

(Organic Special)

Group—A

Answer any *four* questions. 4×2

1. What do you mean by quenching ? What are the major routes of quenching ?

(Turn Over)

2. What are co-enzymes ? Give an example along with its structure.
3. What happens when cyclobutanone is irradiated in presence of a polar solvent like alcohol ?
4. What happens when adenine and guanine are separately treated with pertrifluoroacetic acid ?
5. What are functions of mRNA and rRNA ?
6. What happens when penicillin is subjected to hydrolysis in acidic medium ?

Group—B

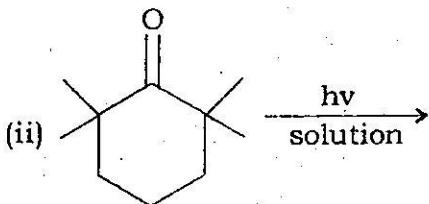
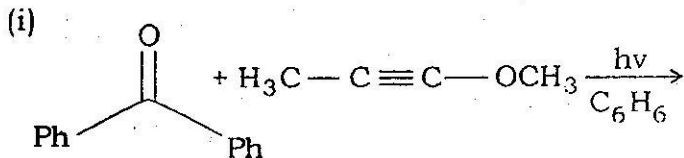
Answer any *four* questions. 4×4

7. How will you prepare uric acid from urea and ethyl actoacetate ? 4
8. How will you prepare nicotinic acid and nicotinamide ? State the physiological functions of vitamin B₅. 2+2

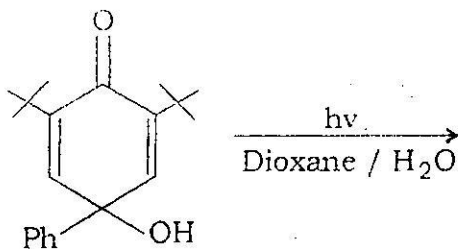
9. (a) Write down the scheme for Fischer synthesis of adenine.

(b) Give an example where an external agent is responsible for mutation of DNA. 2+2

10. Predict the products of the following reactions with plausible mechanism : 2+2



11. Predict the product(s) of the following reactions with plausible mechanism : 4

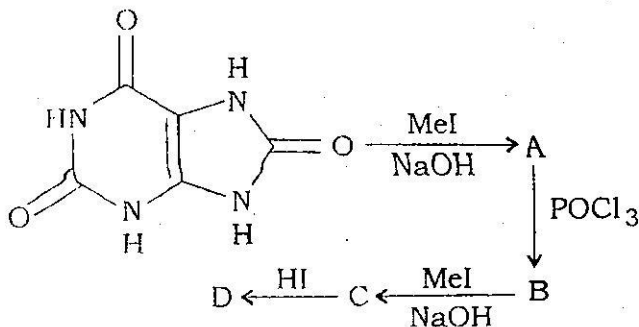


12. Write down the scheme for the synthesis of D-penicillamine from DL-valine ? 4

Group—C

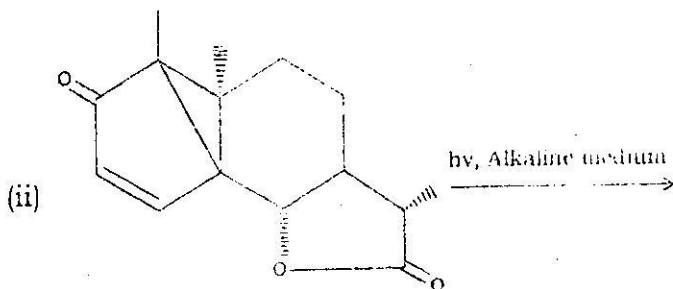
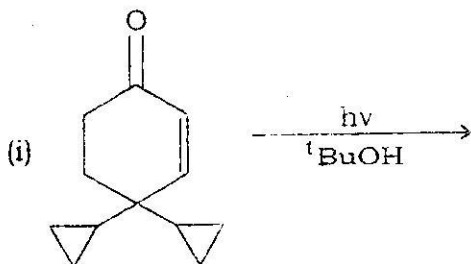
Answer any *two* questions. 2×8

13. (a) Write down the structure, function and synthesis of vitamin K₁ as proposed by Fieser *et al.* 4
- (b) Identify the products A, B, C and D from the following reaction sequence : 4

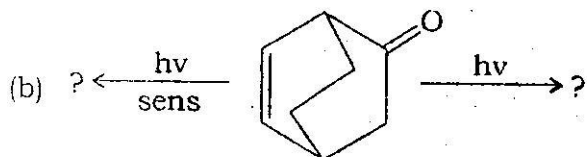
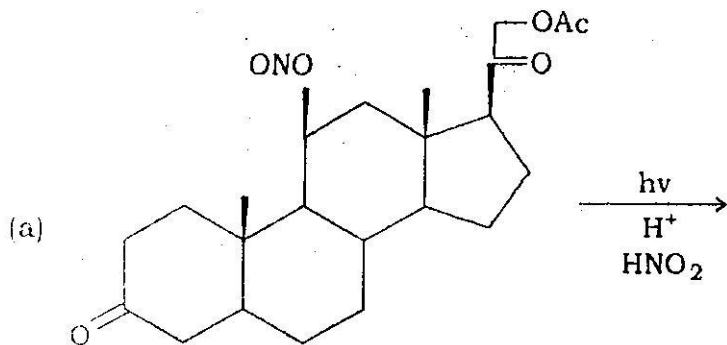


14. (a) What happens when cephalosporin C is treated with nitrosyl chloride in presence of formic acid followed by aqueous hydrolysis and subsequent acylation of the product? 3

(b) Predict the products with plausible mechanism for the following reactions : 2+3

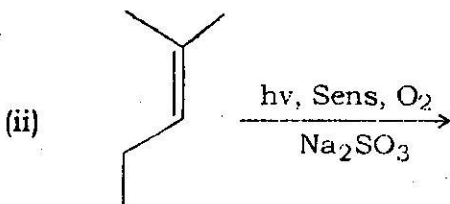
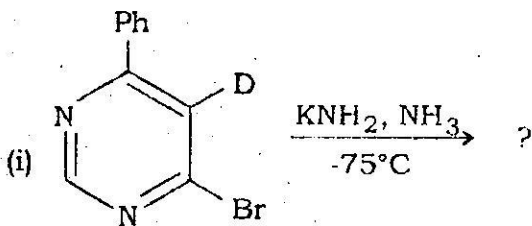


15. Predict the products with plausible mechanism for the following reactions : 4+4



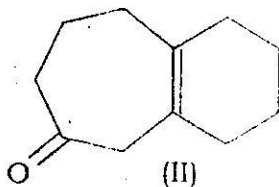
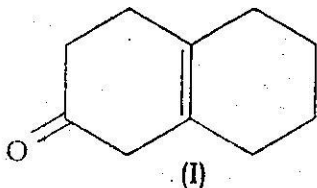
15. (a) Predict the product(s) with proper mechanism :

3+2



(b) Predict the product(s) with proper justification when the following enones (I and II) are irradiated separately.

3



(Inorganic Special)**Group--A**Answer any *four* questions.

4×2

1. The complex $[\text{NiCl}_4]^{2-}$ is paramagnetic but $\text{Ni}(\text{CO})_4$ is diamagnetic. Explain.
2. Explain the term susceptibility in magnetism.
3. What is most likely configuration of an octahedral complex of $\text{Co}(\text{II})$ whose experimental magnetic moment is 4.0 BM?
4. Arrange the complexes according to their increasing magnetic moment (spin only value)
 $[\text{TiF}_6]^{3-}$, $[\text{CrF}_6]^{3-}$, $[\text{MnF}_6]^{3-}$, $[\text{CoF}_6]^{3-}$
5. "Mono-capped octahedral structure of $\text{Os}_7(\text{CO})_{21}$ is in accordance with the nature of available valence electrons" — Justify.

2

6. $[\text{Os}_2\text{C}_{18}]^{2-}$ displays staggered structure' - Explain.

2

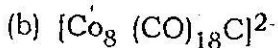
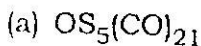
Group—B

Answer any *four* questions.

4×4

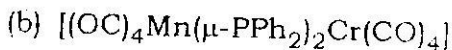
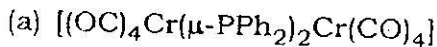
7. Compare the antiferromagnetic interactions of oxido bridged and hydroxido bridged binuclear complexes of Cr(III).
8. How will you determine the magnetic moment of lanthanides? The λ value for $[\text{CoCl}_4]^{2-}$ is -172 cm^{-1} and Δ value for this is 3100 cm^{-1} . Find the μ_{obs} value.
9. Calculate spin-only and effective magnetic moment of $\text{Cr(III)}_{\text{aq}}$ ion.
10. Distinguish among ferrimagnetic, ferromagnetic and antiferromagnetic materials. Give an example of each class of materials.

11. Calculate the total valence electron count (TEC) and polyhedral electron count (PEC) of the following clusters. Also assign each one as *closo*, *nido*, *arachno* or *hypho*.



4

12. Calculate the M-M bond order for the following species:



4

Group—C

Answer any two questions. 2×8

13. (a) (i) Eu^{3+} shows $\mu_{\text{cal}} = 0.0 \text{ BM}$ but $\mu_{\text{obs}} = 3.4\text{-}3.6 \text{ BM}$ at 27°C . Explain

(ii) For high spin d^5 octahedral complexes $\mu_{\text{obs}} \approx \mu_{\text{spin}}$ only -- justify.

(iii) Explain why $\text{Cr}_2(\text{CH}_3\text{COO})_4$ is diamagnetic?

4+2+2

14. (a) Why copper(II) acetate monohydrate shows anomalous magnetic moment?

(b) The λ value for $[\text{CoCl}_4]^{2-}$ is -172 cm^{-1} and Δ value for this is 3100 cm^{-1} . Find the μ_{obs} value.

(c) Determine the Lande' g-factor and total magnetic moment of Er^{3+} .

3+3+2

15. (a) Synthesize $\text{Os}_5(\text{CO})_{18}$ from $\text{Os}_3(\text{CO})_{12}$. Draw the structure of $\text{Os}_5(\text{CO})_{18}$ and discuss.

4

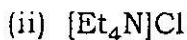
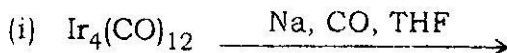
(b) What is isolobal analogy? Find an organic fragment which is isolobal with $[\text{Ir}(\text{CO})_3]$. Using this result suggest an organic molecule isolobal with $\text{Ir}_4(\text{CO})_{12}$.

4

16. (a) How will you synthesize $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ starting from $\text{Fe}_3(\text{CO})_{12}$? Discuss the structure of $[\text{Fe}_3(\text{CO})_{11}]^{2-}$.

4

- (b) Complete the following reaction and predict the structure of the product. 2



- (c) What do mean by 'Super reduced metal carbonyls'? 2

(Physical Special)

Group—A

Answer any four questions. 4×2

1. Write down the Hamiltonian of an N-electron atom.
2. 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.

3. Write down the Slater determinant form of wavefunction of Be atom.
4. Write down the magnetic interaction Hamiltonian of H-atom.
5. Write down the spin functions of A-X spin system.
6. Write down the magnetic interaction Hamiltonian of A_2 spin system.

Group—B

Answer any *four* questions.

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 eigen value of S^2 operator for two electron system having spin function $1/\sqrt{2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$.

9. Deduce the energy of the state described by the Slater wave function, $|D_1\rangle = |\varphi_1\varphi_2|$.
10. Write down the Hartree-Fock equation and hence explain the terms involved in the equation.
11. Use L-S coupling scheme to deduce the terms for d^2 configuration.
12. Chemical shift in NMR spectra is independent of applied magnetic field. - Explain.

Group—C

Answer any *two* questions. 2×8

13. Population difference to observe NMR transition can be obtained through spin-lattice relaxation process. - Explain.
14. Deduce the zero order and first order correction to energies of A_2 spin system.

15. Deduce the zero order magnetic interaction energies of election of hydrogen atom and hence obtain the frequencies of all possible transition.
16. Deduce the pure spin states and indicate their spin multiplicities for a system of three non-equivalent electron with $m_s = -\frac{1}{2}$.
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