

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)

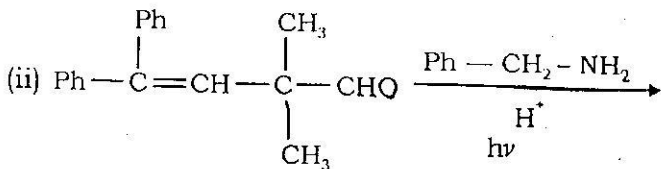
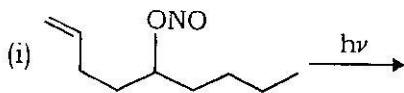
1. Answer any four questions : 4×2
- (a) What are the reasons for high quantum yield of certain chemical transformations ?
- (b) What do you mean by photochemical equilibrium ?
Give an example.

(Turn Over)

- (c) What happens when barrelene is irradiated in presence of a sensitizer like acetone ?
- (d) Write down Isler's synthesis of Vitamin K₂₍₃₅₎.
- (e) What are "polysomes" ? State its function.
- (f) Write down the scheme for Fischer synthesis of guanine.

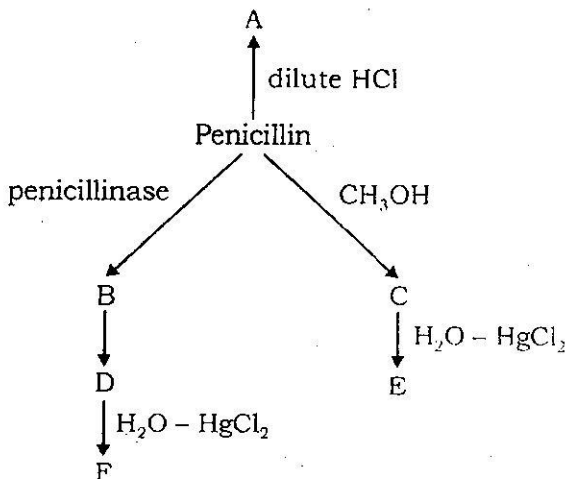
2. Answer any *four* questions : 4×4

- (a) Write an explanatory note on cis-trans isomerization of alkenes.
- (b) What do you mean by "ANRORC mechanism" ? Give an example to illustrate your answer. 2+2
- (c) What are coenzymes ? Draw the structure of NAD and critically discuss its function. 1+3
- (d) Predict the product(s) of the following reactions with plausible mechanism :

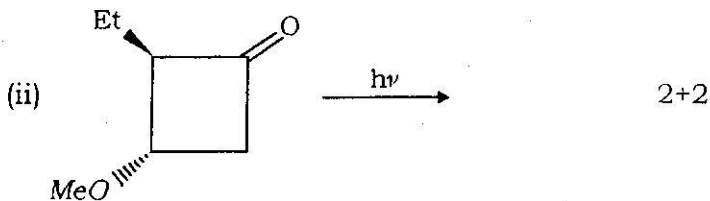
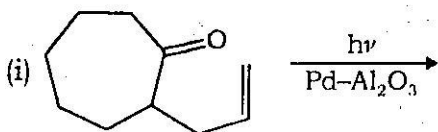


2+2

- (e) Draw the structure of penicillin and identify the products A, B, C, D, E and F.

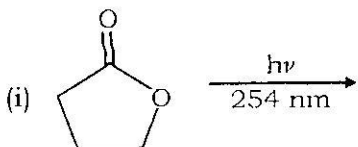


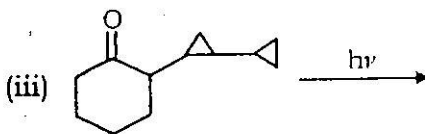
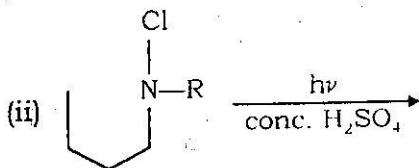
- (f) Predict the products of the following reactions with plausible mechanism :



3. Answer any *two* questions : 2×8

- (a) (i) Discuss the structure and function of tRNA.
- (ii) Adenine is basically a pentamer of HCN — Justify the statement.
- (iii) Write down the commercial method (Traube synthesis) for the preparation of caffeine. 3+3+2
- (b) (i) How will you account for the bands at 3333 and 1770 cm^{-1} in the IR spectrum of sodium salt of benzylpenicillin ?
- (ii) What happens when 1-alkylated purine is treated with NaOH at 80°C ? Give suitable reaction mechanism to illustrate your answer.
- (iii) How will you prepare riboflavin (vitamin B₂) using ethyl chloroformate as a starting material ? 2+2+4
- (c) Predict the products with plausible mechanism for the following reactions :



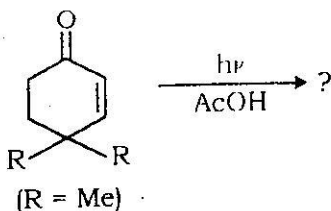


2+3+3

- (d) (i) How will you carry out the following conversion? Give suitable mechanism to support your answer.



- (ii) Identify the product(s) with plausible mechanism:



- (iii) How will you prepare uric acid from thiourea and ethyl cyanoacetate? 2+3+3

(Inorganic Special)**Group—A**

Answer any *two* questions. 2×2

1. What are the distinguishing features of ferromagnetism?
2. Define the term "magnetic susceptibility".
3. State the significance of Weiss constant.

Group—B

Answer any *two* questions. 2×4

4. Number of f-electrons in Eu^{3+} and Am^{3+} are same, but they have different magnetic moment value. Explain.
5. Derive the "magnetic dipole moment" equation associated with the orbital motion of an electron.
6. Write short note on "Landé Interval rule".

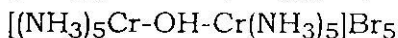
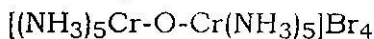
Group—CAnswer any *one* question.

1×8

7. (a) Write the magnetic moment equation which is commonly used to calculate the magnetic moment for 4f metal coordination compounds. Explain why Sm(III) and Eu(III) compounds do not follow this equation.

(b) Determine Lande' g-factor and calculate magnetic moment for Tb^{3+} ion. (1+5)+2

8. (a) Which one of the following two complexes will have more superexchange interaction and why ?



(b) Derive Curie equation for paramagnetic solid material. 3+5

Group—DAnswer any *two* questions.

2×2

9. Complete the following reaction :



10. Schematically show the sigma and pi bonding interaction between CO and metal atom.

11. Write down the synthesis of Collman's reagent by Collman's process.

Group—E

Answer any *two* questions.

2×4

12. (a) How will you synthesize $\text{Na}_2[\text{Fe}(\text{CO})_4]$ from $\text{Fe}(\text{CO})_5$ by reduction? Write down the complete reaction scheme.

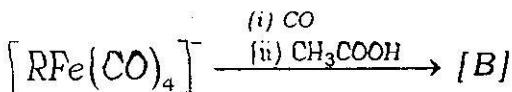
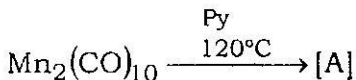
(b) Write the structure of $\text{Os}_5(\text{CO})_{19}$.

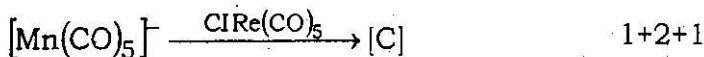
2+2

13. Rationalize why $\text{Os}_6(\text{CO})_{18}$ adopts monocapped trigonal bipyramidal structure rather than octahedral structure.

4

14. Identify [A], [B] and [C] in the following reaction schemes :





Group—F

Answer any *one* question. 1×8

15. (a) How $\text{K}_3[\text{Co}(\text{CO})_3]$ can be synthesized from $\text{K}[\text{Co}(\text{CO})_4]$?

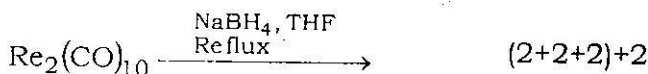
(b) Show the binding mode of 'CO' when it acts as 6 electron donor.

(c) Predict the structure of the cluster core of $[\text{Os}_8(\text{CO})_{22}]^{2-}$. Write down each step of structure determination. Write down the final structure.

2+2+4

16. (a) How $\text{K}[\text{Co}_3(\text{CO})_{10}]$ is synthesized from $\text{Co}_2(\text{CO})_8$? Write down the structure of the synthesized carbonyl complex. Calculate the electron count per 'Co-atom' in $\text{K}[\text{Co}_3(\text{CO})_{10}]$.

(b) Complete the following reaction and write down the structure of the final product :



(Physical Special)

Group—A

Answer any *four* questions. 4×2

1. Write down the Slater determinantal form of wave function of Be atom.
2. Evaluate the eigen value of S_z operator of two electron system having spin function of $\alpha(1)\alpha(2)$.
3. Hartree-Fock equation is called Integro-differential equation. — Explain.
4. What is meant by of Coulomb operator and exchange operator in multi-electron atomic system.
5. Write down the magnetic interaction Hamiltonian of A-X spin system.
6. Write down the spin functions of A_2 spin system.

Group—B

Answer any four questions.

4×4

7. Deduce the eigen value of S^2 operator for two electron system having spin function $1/\sqrt{2}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$.
8. Write down the steps to evaluate the energy expectation value of multi-electron system and deduce the energy expectation value of a $2N$ electron system.
9. Use J-J coupling scheme to deduce the terms for p^2 configuration.
10. 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.
11. Chemical shift in NMR spectra is independent of applied magnetic field — Explain.
12. State the rules for energy ordering of the atomic term and hence find the energy ordering of the atomic terms, 3F_2 , 3F_3 and 3F_4 in d^2 and d^8 configurations respectively.

Group—CAnswer any *two* questions.

2×8

13. Deduce the zero order and first order correction to energies of A-X spin system and hence obtain the frequencies of all possible transitions.
 14. Use L-S coupling scheme for atomic terms and hence deduce Lande's interval rule.
 15. State and prove Koopman's theorem.
 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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