M.Sc. 4th Semester Examination, 2024

CHEMISTRY

(*Spectroscopy*)

PAPER—CEM-401

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

GROUP – A

Answer any **four** questions : 2 × 4

1. What is Karplus equation ? Show the plot and explain.

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PAPER—CEM-402

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(*Organic Special*)

GROUP – A

Answer any **four** questions : 2×4

1. State the laws of photochemistry.

2. What do you mean by "photosensitized reaction" ? Give the example.

3. What happens when cyclobutanone is subjected to photolysis ?

4. What are coenzymes ? Give examples.

5. What happens when guanine is separately treated with pertrifluoroacetic acid and Br_2/AcOH ?

6. How will you account for the bands at 1515 and 1770 cm^{-1} in the IR spectra of sodium salt of benzylpenicillin ?

GROUP – B

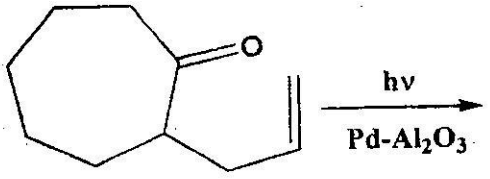
Answer any **four** questions : 4×4

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

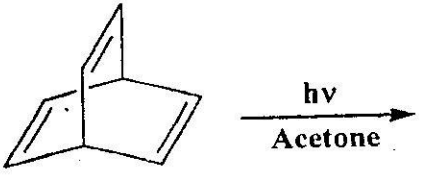
   (*ii*) Draw the structure of NAD and critically discuss its function. $2 + 2$

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

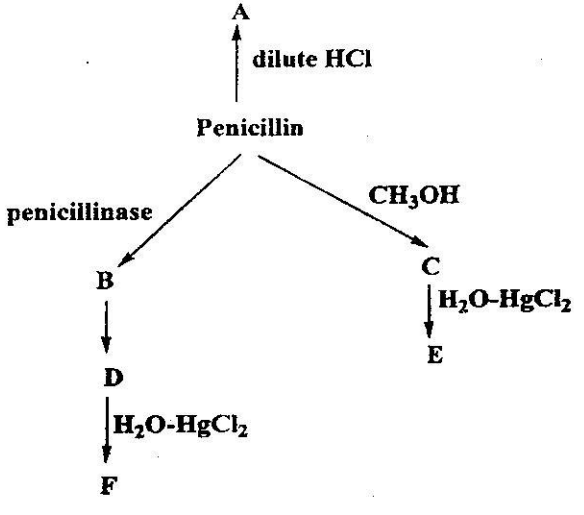
(*i*)



(*ii*)



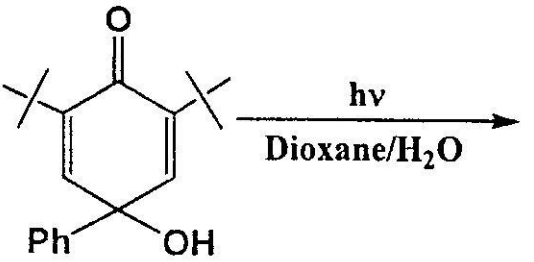
9. Draw the structure of penicillin and identify the products A, B, C, D, E and F. 4



10. What is photochemical equilibrium ? Give an example. Show that the dimer concentration is independent of the monomer concentration at the photostationery state when the monomer is taken in large excess. 2 + 2

11. Write down the steps involved in the synthesis of riboflavin. 4

12. Predict the product(s) of the following reaction with plausible mechanism : 4



GROUP – C

Answer any **two** questions : 8 × 2

13. (*i*) What is Dimorth rearrangement ? Illustrate your answer with a proper example. 3

(*ii*) Why adenine is called a pentamer of HCN ? 3

(*iii*) Write down the Fischer synthesis of xanthine. 2

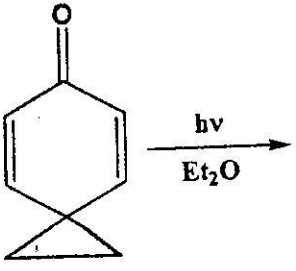
14. (*i*) How will you prepare nicotinamide from β-picoline ? 2

(*ii*) Write down a suitable method for the synthesis of vitamin K_1 and comment on its stereochemical features. 3

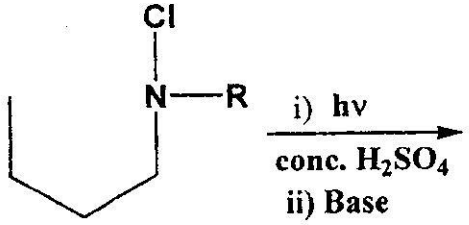
(*iii*) Write down the Traube synthesis of uric acid. 3

15. Predict the products with plausible mechanism for the following reactions : 2 + 3 + 3

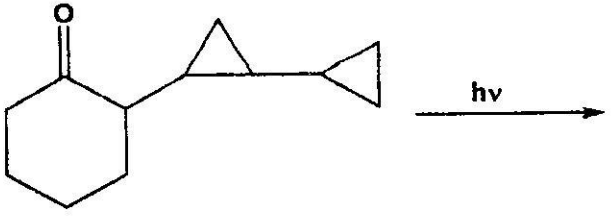
(*i*)



(*ii*)

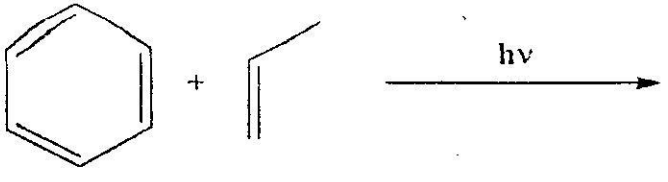


(*iii*)



16. (*i*) What happens when 1, 4-cyclo-octadiene and 1, 5-cyclooctadiene are separately irradiated in presence of acetone ? 2

(*ii*) Identify the product(s) with plausible mechanism : 2



(*iii*) Write down the first successful synthesis of phenoxymethyl penicillin that was carried out by Sheehan et al. 4

[Internal Assessment — 10 Marks]

(*Inorganic Chemistry Special*)

GROUP – A(a)

Answer any **two** of the following questions : 2×2

1. What are the distinguishing features of "antiferromagnetism" ?

2. What do you mean by "spin-orbit interaction" ?

3. What are "magnetically concentrated" substances ? Give an example.

GROUP – A(b)

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

4. *Determine the ground state term symbols,*

Lande' g-factor and total magnetic moment for the following metal ions : 2 + 2

Pm^{3+}, Ho^{3+}

5. Write the magnetic moment equation which is generally used for calculating magnetic moment for lanthanide compounds. Comment on the suitability of this equation for calculating magnetic moments of compounds containing Nd(III) and Eu(III) metal ions. 4

6. Derive an expression for "volume susceptibility" of a diamagnetic material. 4

GROUP – A(c)

Answer any **one** of the following question : 1×8

7. (*a*) What do you mean by "multiplet width" ? Derive the magnetic moment equation for a asystem where the multiplet width is large compared to thermal energy. 1 + 4

(*Continued*)

(*b*) Write note on "intra-molecular antiferro-magnetism". 3

8. (*a*) Explain the magnetic behaviour of bis(diazoaminobenzenato) copper(II). 3

(*b*) Derive the expression for Curie equation for the paramagnetic solid substances. 5

GROUP – B(a)

Answer any **two** of the following questions : 2×2

9. How $Na_2[Fe(CO)_4]$ can be synthesized from $Fe(CO)_5$? 2

10. Write the structure of $[Re_4(CO)_{16}]^{2-}$. 2

11. Calculate the Nb-Nb bond order in $[Nb(Cl)_2(\mu\text{-}Cl)(R_2P\text{-}CH_2\text{-}PR_2)]_2$. 2

GROUP – B(b)

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

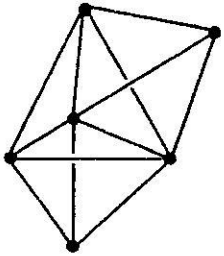
12. (*i*) Write the structure of $[Nb_3(Cp)_3(CO)_7]$. Comment on the types of CO binding in the complex and their electron donation.

(*ii*) How $Re_2(CO)_{10}$ could be synthesized from Re_2O_7 ? $3 + 1$

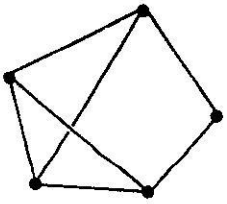
13. What will be the product of the reaction between $Fe_3(CO)_{12}$ and KOH ? Write the structure of the cluster formed. Comment on the ν(C-O) of the cluster compound formed. $1\frac{1}{2} + 1\frac{1}{2} + 1$

14. Confirm the consistency of the structure of the following clusters with their number of valence electrons available. $2 + 2$

(*i*) $Os_6(CO)_{18}$:



(*ii*) $Ru_5C(CO)_{16}$:



GROUP – B(c)

Answer any **one** of the following questions : 8×1

15. (*i*) Draw the possible d-orbital overlap in connection to the bonding in trigonal prismatic structure.

(*ii*) Calculate the Os-Os bond order in $[Os_2Cl_8]^{2-}$ complex. Mention the geometry of this compound.

(*iii*) Confirm that the total valence electron count of $Co_3(CO)_9Ni(\eta^5\text{-Cp})$ is consistent with its tetrahedral cluster network. 3+2+1+2

16. (*i*) Calculate the W-W bond order in $[W(\eta^5\text{-}C_5H_5)(\mu\text{-Cl})(CO)_2]_2$.

(*ii*) Determine the cluster geometry of the following :

(*a*) $Os_5(CO)_{15}C$

(*b*) $Os_5(CO)_{16}$

(*iii*) How $Na_3[V(CO)_6]$ could be synthesized from $Na[V(CO)_6]$? 2+2+2+2

[Internal Assessment — 10 Marks]

(*Continued*)

(*Phy. Special*)

GROUP – A

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

1. Write down the Slater determinant form of wave functions for exited He atom.

2. Write down Hartee Fock equation with the explicit form of the Fock operator.

3. "Hartree-Fock equation is called Integro -differential equation"–Explain.

4. "In multielectron atoms the total energy is always less than the sum of the occupied orbital energy"– Explain.

5. Write down the magnetic interaction Hamiltonian and spin functions for A-X spin system.

6. Evaluate the eigenvalue of $\hat{S}_Z$ operator of two electron system having spin function,

$$\frac{1}{\sqrt{2}}[\alpha(1)\beta(2)-\beta(1)\alpha(2)]$$

GROUP – B

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

7. What is meant by first order and second order NMR spectra ? How do you obtain first order NMR spectra for a two-spin system which shows second order NMR spectra in a 60 MHZ machine ? $2 + 2$

8. Deduce the energy expectation values for the spin system, 4

$$|D_1> = |\Phi_1 \bar{\Phi}_1|$$

9. Write down the procedure to obtain the energy expectation values for multielectron

closed shell system. Hence show that for 2N electron system,

$$E = 2\sum_{i=1}^{N} h_{ii} + \sum_{i=1}^{N}\sum_{j=1}^{N}(2J_{ij} - K_{ij})$$

(Symbols have their usual significances) 2 + 2

10. State and prove Koopman's theorem. 4

11. Define chemical shift (δ) scale in NMR spectroscopy. Show that the separation of two NMR lines in chemical shift scale is independent of the applied magnetic field. 1 + 3

12. Use L-S coupling scheme to obtain the terms of nd^2 electronic configuration. 4

GROUP – C

Answer any **two** questions of the following : 8×2

13. What do you mean by spin relaxation in *NMR spectroscopy ? Why is it so important*

to observe NMR transition ? 'The net effect of spin lattice relaxation in to depopulate the higher level rather than to populate it'– Explain.

14. Write down the magnetic interaction Hamiltonian and spin wave function for A_2 spin system. Deduce the zero order as well as first order correction to energy of each state and hence obtain the frequencies of all possible transitions. 1 + 4 + 3

15. Deduce the pure spin states and indicate their multiplication for a system of three non-equivalent electron with $M_s = \frac{1}{2}$. 8

16. Deduce the expression of spin-orbit interaction energy of electron in an atom. Use J-J coupling scheme to obtain the terms of nf^2 electronic configuration. 4 + 4

[Internal Assessment — 10 Marks]