2019

M.Sc.

4th Semester Examination

CHEMISTRY

Paper - CEM 401

(Special Paper)

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.

PHYSICAL CHEMISTRY

Group A

Answer any *four* questions of the following questions: 2×4=8

1. State and explain the parity selection rule for electric dipole transition.
2. Deduce the ground state molecular term of F_2.
3. For an 'N' electron atom, write the expression of $\hat{S}^2$ operator.

[Turn Over]

4. Write the expression for the energy expections value of N-electron system in a closed shell configuration and explain the terms involved in the equation.

5. Hartree-Fock equation is called Integro-differential equation. — Explain.

6. State the rules for energy ordering of molecular terms.

7. Write the matrix representation of $\hat{C}_\theta$ using three Cartesian co-ordinate as base vectors and z-axis as the rotational axis.

8. Write the matrix representation of $\hat{S}_z$ operator.

Group B

Answer any *four* of the following questions: 4×4=16

9. Write down the Slater determinant form of the electronic wave functions for excited Helium atom $\left(1S^1 2S^1\right)$.

10. Deduce the matrix representation of Hamiltonian operator of a Linear Harmonic Oscillator.

11. Find the eigen values and eigen vectors of the following matrix,

$$\begin{pmatrix} 2 & 1 \\ 0 & -1 \end{pmatrix}$$

12. Deduce the possible terms for p^2 configuration using L-S coupling scheme. Find the ground state term for the above.

13. Calculate the spin-orbit interaction energy in the $^3F_2$, $^3F_3$, $^3F_4$ levels in terms of spin-orbit coupling constant (A). And indicate their energy order.

14. $|j,m\rangle$ are the simultaneous eigen kets of operator J^2 and J_z. Obtain the matrix representation of J_z when $j = \frac{3}{2}$.

15. State the rules in determining the molecular term symbols and hence obtain the ground state term for B_2.

16. Lowering operator for total angular momentum operator J_- follows the following equation.

$$J_-|j,m\rangle = C_-(j,m)|j,m-1\rangle$$

Find the value of $C_-(j,m)$.

Group C

Answer any *two* of the following questions : 8×2=16

17. State and proof Koopman's theorem.

18. Deduce the pure spin states and indicate their spin multiplicities for a system of three non-equivalent electron with $m_s = +\frac{1}{2}$.

19. Deduce the possible atomic terms for d^2 and f^2 configuration using j - j coupling scheme.

20. Hamiltonian (H) and some observable (B) of a certain 3D system is represented by the matrix

$$H = \hbar\omega \begin{pmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix}$$

and $B = \mu \begin{pmatrix} 2 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$ respectively

Where ω and μ are real numbers. Find the eigen values and eigen vectors of H and B.

INORGANIC CHEMISTRY

Group - A (a)

1. Answer any *two* questions : 2×2=4

(a) Write down the range of $\gamma_{(c-0)}$ in cm^{-1} for the neutral complexes where

(i) CO is symmetrically μ_2-bridged

(ii) CO acts as $6e'$ donor.

(b) What do you mean by super reduced species ?

(c) What will be the final product when $Fe(CO)_5$ is treated with

(i) sodium hydroxide

(ii) *Na / Hg*

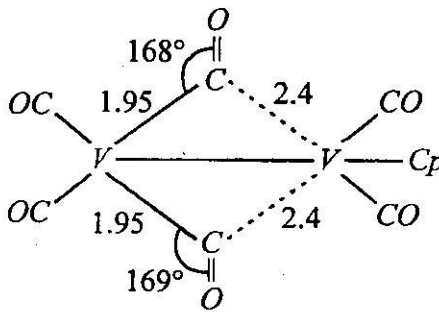
(d) Complete the following reaction

$$Fe(CO)_5 \xrightarrow[\text{reflux}]{\text{pyridine}} ? \xrightarrow{[(Ph_3P)N]Cl} ?$$

Group - A (b)

Answer any *two* questions. 4×2=8

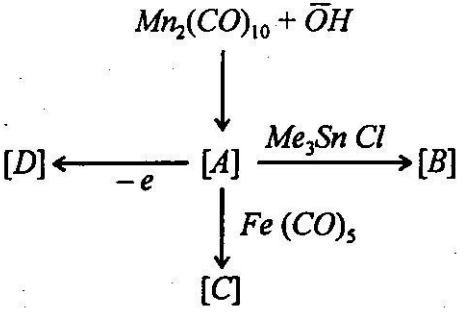
2. (a)



[all bond distance are in Å unit]

Discuss the CO bonding in the above mentioned complex. 4

(b) Complete the following scheme — 4



(c) (i) Write down the probable geometry of the metal carbonyl complex where '*CO*' acts as $6e'$ donor.

(ii) Complete the following reaction 2

$$Fe(CO)_5 + Na^+\left[(MeO)_3\,BH\right]^- \longrightarrow$$

(d) Discuss the bonding in $[W_2Cl_9]^{3-}$ ion. 4

Group - A (c)

2. Answer any *one* questions : 8×1=8

(a) (i) $Os_5(CO)_{19}$ offers 'bow-tie' geometry. Is this geometry consistent with the number of valence electrons available ? 4

(ii) Rationalise why the core structure of $Os_5(CO)_{16}$ is a trigonal bipyramid ? 2

(iii) Predict the geometry of

$Co_3(CO)_9 Ni(\eta^5 - C_p)$ cluster by TVE count. 2

(b) (i) Determine the core geometry of the following cluster molecules — 3+3

(i) $Os_7(CO)_{21}$

(ii) $Ru_6C(CO)_{17}$

(ii) How will you synthesize $[Re_4(CO)_{16}]^{2-}$ from $Re_2(CO)_{10}$. Discuss the structure of this tetranuclear cluster. 2

Group - B (a)

4. Answer any *two* questions : 2×2=4

(a) Calculate the value of magnetic dipolemoment associated with as loop carrying current.

(b) Explain the magnetic nature of bis (diazoaminobenzenato) copper (II) complex.

(c) What do you mean by magnetically dilute system and magnetically concentrated system ? Give one example for each.

(d) Define the terms "magnetic susceptibility" and "magnetization".

Group - B (b)

5. Answer any *two* questions : 4×2=8

(a) Write short notes on "intra and intermolecular antiferromagnetism."

(b) Distinguish between ferromagnetic, ferrimagnetic and antiferromagnetic materials. Give an example for each class of materials.

(c) Explain the Curie law and the Curie-Weiss law. Indicate the significance of the Weiss constant.

(d) Write short note on "super exchange".

[Turn Over]

Group - B (c)

6. Answer any *one* questions : 8×1=8

(a) Establish the volume susceptibility equation for diamagnetism. 8

(b) (i) Explain the following magnetic moment data (at 27°C) : 5

$\left[Sm(acac)_3\right]$: 1.4 *B.M.*

$\left[Eu(acac)_3\right]$: 3.5 *B.M.*

(ii) Determine the ground state Er^{3+} ion. Calculate Lande' *g*-factor and total magnetic moment. 3

ORGANIC CHEMISTRY

Group - A

1. Answer any *four* questions : 2×4=8

(i) What are the reasons for low quantum yield of a photochemical reaction ? 2

(ii) What happens when an aqueous frozen solution of thymine is irradiated at 260 nm ? 2

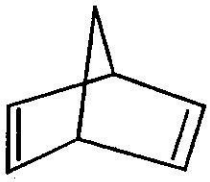
(iii) What happens when quianzoline-3-oxide is treated with 2N sodium hydroxide at room temperature for 24h ? 2

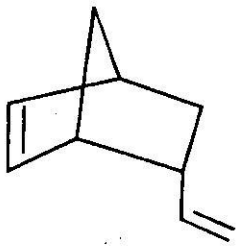
(iv) Discuss the position of helix axis, major and minor groove proportions of B-form DNA ? Also, state the glycosydic orientation in B-form DNA. 2

(v) Outline the steps involved in Traube synthesis of xanthine. 2

(vi) What were the reagents used for Isler's synthesis of vitamin $K_{2(35)}$? Also, give the reaction involved in this synthesis.

(vii) Complete the following reactions : 2

(a) 

(b) 

(viii) What happens when penicillin is treated with methanol followed by $H_2O - HgCl_2$? Give suitable reactions to support your answer. 2

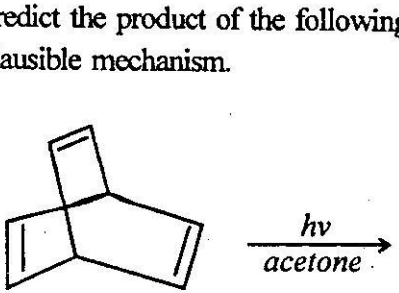
Group - B

Answer any *four* questions : 4×4=16

2. What do you mean by photochemical equilibrium ? Give an example. In this context also show that the dimer concentration is independent of the monomer concentration when the monomer is present in large excess. 4

3. (i) State the composition of cephalosporin C. 2

(ii) Predict the product of the following reaction with plausible mechanism. 2



4. (i) Outline the steps involved in Bredereck synthesis of theobromine. 3

   (ii) State the salient features of the CD spectrum of B-DNA ? 1

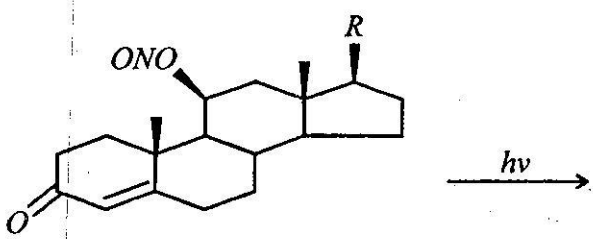
5. How will you carry out the following conversions. 2+2

   (i) Guanidine $\longrightarrow$ Guanine

   (ii) β-picoline $\longrightarrow$ Nicotinamide

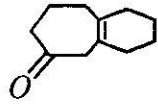
6. (i) Outline the steps involved in Fischer synthesis of theobromine. 2

   (ii) Predict the product with plausible mechanism. 2



7. (i) Outline the steps involved in the synthesis of $(\pm)$-α-tocopherol from phytyl bromide ? 2

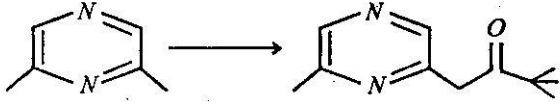
(ii) What happens when the following compound is irradiated ? 2



8. (i) What happens when indene is irradiated in the presence of as acetone ? 2

(ii) When benzene is irradiated with maleic anhydride then compound (A) is obtained which on healing undergoes further reaction with maleic anhydride to give compound (B). Identify the compounds (A) and (B) and complete the reaction sequence. 2

9. How will you carry out the following conversions :

(i) 

1

(ii) Guanine ⟶ 8-bromoguanine 1

(iii) Urea ⟶ 5-aminouracil 2

Group - C

Answer any *two* questions : 8×2=16

10. (i) Discuss the structural features of t-RNA. 3

(ii) What are the physiological functions of vitamin B_1 ? 2

(iii) In photochemistry what do you mean by 'rule of five' ? Illustrate your answer with suitable example. 3

11. (i) How will you prepare D-penicillamine from DL-valine ? 4

(ii) Outline the synthesis of riboflavin using ethyl chloroformate as one of the starting reagents. 4

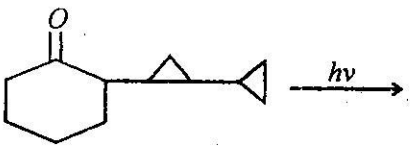
12. (i) What is Zincke reaction ? 3

(ii) Draw the structure of NAD and state its function. 3

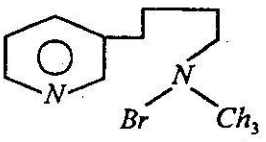
(iii) What happens when 1, 5-cyclooctadience and 1, 4-cyclooctadiene are irradiated separately in presence of acetone ? 2

[Turn Over]

13. (i) Predict the product of the following reaction with plausible mechanism.

(a) 

3

(b) 

2

(ii) What do you mean by haloenzyme and apoenzyme ? What is zymogen ? Give an example. 1+1

(iii) How will you carry out the following conversion. 1