

2018

M.Sc. Part-II Examination

CHEMISTRY

PAPER—V

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.

(Physical Special)

New Syllabus

F.M. - 100

Time : 4 Hrs.

Answer any *five* questions

taking at least *two* from each group (A and B) and answer *five* questions from group C.

Old Syllabus

F.M. - 75

Time : 3 Hrs.

Answer any *five* questions

taking at least *two* from each group (A and B).

(Turn Over)

Group—A

1. (a) State the Huckel approximation for the treatment of π -MO of linear conjugated polyene. 3
- (b) Deduce the energy and wavefunction of π -MO of Allylradical using Huckel theory. 8
- (c) For particle in a 1-dim box problem in $(0, L)$, the approximate wavefunction is given by,

$$\psi = x \sqrt{\frac{2}{L}} (L - x).$$

Show that the average energy \bar{E} for such a system will obey the relation

$$\bar{E} \geq \frac{h^2}{2mL^2}. \quad 4$$

2. (a) Consider a system is subjected to a time independent perturbation H' . Hence deduce the expression of its first order correction and second order correction to energy. 5+5
- (b) Calculate the first order correction to energy for the n th state of Harmonic oscillator whose centre of potential has been displaced from 0 to l . 5
3. (a) Find the eigen value and eigen vectors for the matrix,

$$A = \begin{pmatrix} 2 & 1 \\ 0 & -1 \end{pmatrix}. \quad 5$$

- (b) $|j, m\rangle$ are the simultaneous eigen ket of operator j^2 & J_z . Now for angular momentum quantum number $j = 3/2$, the allowed values of m are $3/2, 1/2, -1/2, -3/2$ and the four basis sets are denoted by,

$$|1\rangle = |3/2, 3/2\rangle \quad |2\rangle = |3/2, 1/2\rangle$$

$$|3\rangle = |3/2, -1/2\rangle \quad |4\rangle = |3/2, -3/2\rangle$$

Find out the matrix representation of operator J_z and its eigen kets. 10

4. (a) Write down the stater determinant form of eigen functions for the excited state of He-atom. 6
- (b) Write down the explicit form of Hustree-Fock equation and the Hartree-Fock operator. 3
"Hustree-Fock equation is called Integro-differential equation" — Explain. 2
- (c) Write down the expression for π -electron density and bond order for π -conjugated system. Hence obtain the π -electron charge density on each carbon atom of Allyl radical. 4

Group—B

5. (a) With the help of group theoretical principle, find the nature of splitting of d-orbitals of a central metal atom when it is placed in an octahedral environment. Following is the character table for 'O' group. 8

O	E	8C ₃	3C ₂ (= C ₄ ²)	6C ₄	6C ₂	
A ₁	1	1	1	1	1	x ² + y ² + z ²
A ₂	1	1	1	-1	-1	
E	2	-1	2	0	0	(2z ² - x ² - y ² , x ² - y ²)
T ₁	3	0	-1	1	-1	(R _x , R _y , R _z) (x, y, z)
T ₂	3	0	-1	-1	1	(xy, xz, yz)

(b) Prove that the representation of a direct product Γ_{AB} , will contain the totally symmetric representation if the irreducible $\Gamma_A =$ the irreducible Γ_B . 5

(c) Why no polarization effect is observed for cubic or higher symmetry group? 2

6. (a) Find out the σ -ligand group orbital (LGO) involved for the construction of SALC in BF₃ molecule. Character Table for D_{3h} is given below : 6

D _{3h}	E	2C ₃	3C ₂	σ_h	2S ₃	3 σ_v	
A ₁ '	1	1	1	1	1	1	x ² + y ² , z ²
A ₂ '	1	1	-1	1	1	-1	R _z
E'	2	-1	0	2	-1	0	(x, y) (x ² - y ² , xy)
A ₁ "	1	1	1	-1	-1	-1	
A ₂ "	1	1	-1	-1	-1	1	z
E"	2	-1	0	-2	1	0	(R _x , R _y) (xz, yz)

(b) Write down the steps involved for the determination of vibrational modes of linear molecules. 3

(c) How does group theory help in determining the zero and non-zero values of spectroscopic transition moment integral? 3

(d) Write the three simple equations for GOT. 3

7. (a) What is polarizability? Show that unit of polarizability in C.G.S. and SI system is same. 1+2

(b) What is meant by magnetic domains? Explain with diagram. 4

(c) For SO₂(g) at 274(K) and 1 atm pressure dielectric constant is 1.00993. This molecule has a permanent dipole moment of 1.63D. Assuming that SO₂ behaves as an ideal gas, calculate —

(a) total (b) orientation (c) induced polarization per mole and (d) distortion polarizability. 2+4

8. (a) Prove $\sigma = \frac{Ne^2\tau}{2m}$ where $\sigma =$ conductivity, N = number of electrons, $\tau =$ relaxation time or mean free time, m = mass of electron. 4

(b) Define f_j and F_{hkl} and also prove that

$$F_{hkl} = \sum_{j=1}^n f_j e^{2\pi i(hv_j + ku_j + lw_j)}$$

$f_j =$ atomic scattering factor for the j th atom ; u_j, v_j and w_j are the indices of the j th atom. 6

(c) Calculate the Schottky defect concentration in an ionic crystal of MX type. 5

Group—C

9. Answer any five of the following :

5×5

(i) According to Huckel theory, the π electron charge density on the central carbon atom in propyl cation $(\text{CH}_2\text{CHCH}_2)^+$ is (in unit of electronic charge) is given by any one of the following :

- (a) $\frac{1}{2}$ (b) $\frac{1}{\sqrt{2}}$ (c) 1 (d) 2

Which one is the correct answer ?

(ii) A particle executing SHM is subjected to an external perturbation cx (where 'c' is const.). Find the first order correction to energy for $n = 1$ state.

(iii) For some one electron system with $l = 0$ and $m = 0$, the function $Ne^{-\sigma}$ and $N_1(2 - \sigma)e^{-\frac{\sigma}{2}}$ refer respectively to the ground state (E_0) and first excited (E_1) energy levels.

If the trial wave function $N_2(3 - \sigma)e^{-\sigma}$ yield and average energy \bar{E} , it will satisfy and of the following relations :

- (a) $\bar{E} \geq 0$ (b) $0 \leq \bar{E} \leq E_0$
 (c) $\bar{E} > E_1$ (d) $E_0 < \bar{E} \leq E_1$

Which one is the correct answer ?

(iv) Choosing some Hamiltonian, H and orthonormal basis, a linear variation is carried out to get approximate energies \bar{E}_j with 2 basis function, one obtained, $\bar{E}_1(2) \leq \bar{E}_2(2)$. Using three basis function, similarly three

order energies $\bar{E}_1(3) \leq \bar{E}_2(3) \leq \bar{E}_3(3)$ are found. The relation which hold from the following is —

- (a) $\bar{E}_1(2) \leq \bar{E}_1(3)$; $\bar{E}_2(2) \leq \bar{E}_2(3)$
 (b) $\bar{E}_1(3) \leq \bar{E}_1(2)$; $\bar{E}_2(2) \leq \bar{E}_2(3)$
 (c) $\bar{E}_1(2) \leq \bar{E}_1(3)$; $\bar{E}_2(3) \leq \bar{E}_2(2)$
 (d) $\bar{E}_1(3) \leq \bar{E}_1(2)$; $\bar{E}_2(3) \leq \bar{E}_2(2)$

(v) Prove that $IC = 2.9979 \times 10^9$ esu.

(vi) What is a projection operator ? Show that it is idempotent.

(vii) What are F-centres ? Why are solids having F-centres are paramagnetic ?

(Organic Special)

New Syllabus

F.M. — 100

Time : 4 Hrs.

Answer any five questions
 taking at least two from each group (A and B)
 and answer group C.

Old Syllabus

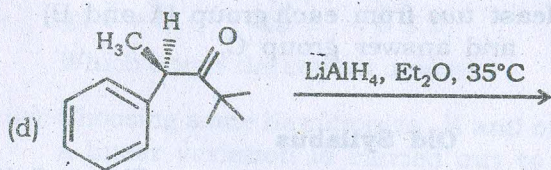
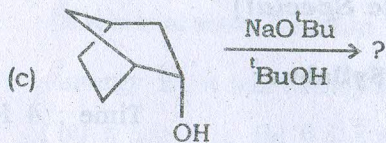
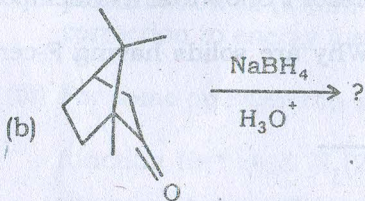
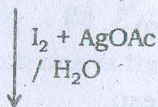
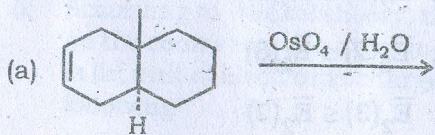
F.M. — 75

Time : 3 Hrs.

Answer any five questions
 taking at least two from each group (A and B).

Group — A

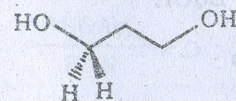
1. Predict the product(s) with plausible mechanisms : 5×3



(e) Can spirans be optically active? Explain with one example.

2. Explain the following : 5×3

- Draw Fisher projections for (2R, 3S)-2-bromo-3-chlorobutane and (2S, 3R)-2-bromo-3-chlorobutane.
- Write the most stable conformation of $\text{OH}-\text{CH}_2-\text{CH}_2-\text{OH}$ in Newman projections. Draw the energy profile diagram with other conformers.
- Explain why ethane is more stable in staggered form.
- Assign Pro-R and Pro-S to the enantiotopic protons of the following compound :



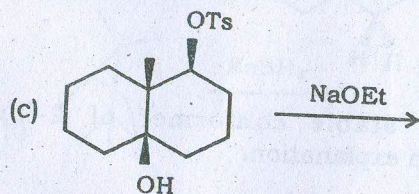
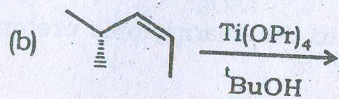
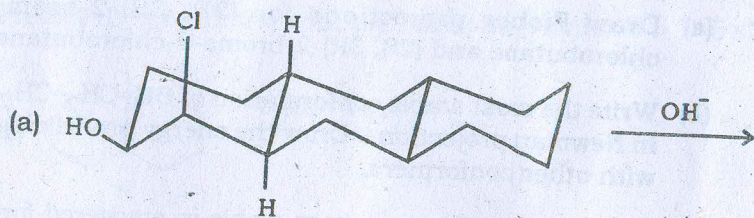
- Write the most stable conformer of 2-^tbutyl cyclohexanone with explanation.

3. Draw the 3d structures for the following conformers and show in them different steric interactions and comment on their optical properties : 5×3

- cis-transoid-cis* perhydroanthracene
- trans-cisoid-cis* perhydrophenanthrene
- 9, 10 dimethyl *trans* decalin
- trans-transoid-trans* perhydrophenanthrene
- cis-cisoid-cis* perhydroanthracene.

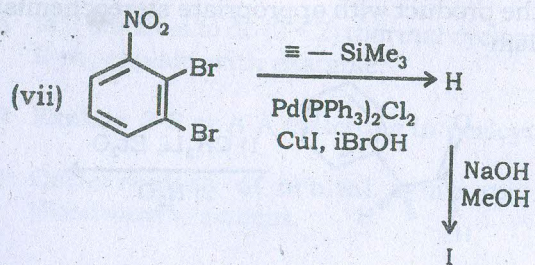
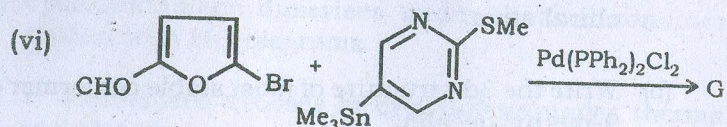
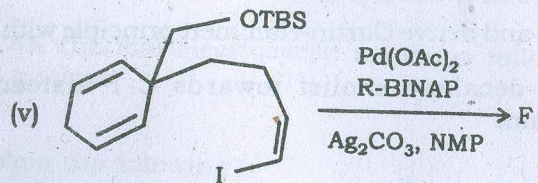
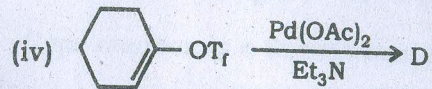
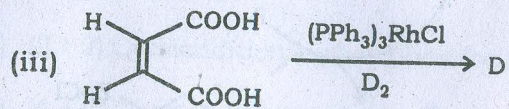
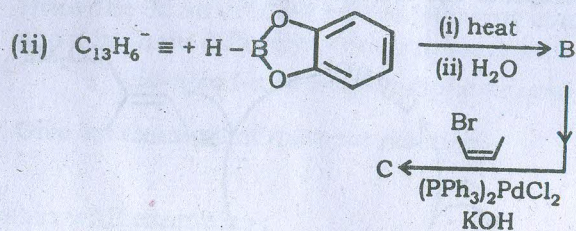
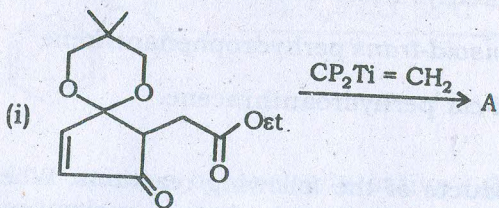
4. Give the products of the following reactions. Where more than one product is likely to be formed in significant yield,

indicate which will be the major product and also predict the mechanism of the reaction involved : 3×5

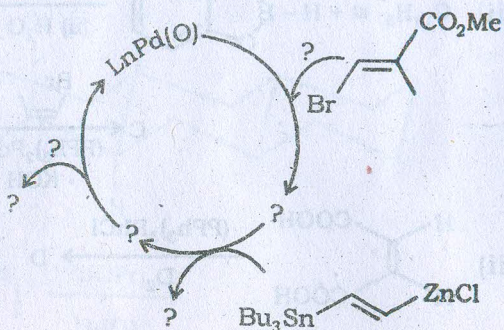


5. (a) What is migratory insertion? Show a migratory insertion with reference to transition metal complex. $1+2$

(b) Write down the structure of products (A \rightarrow I) in the following reactions : 9×1

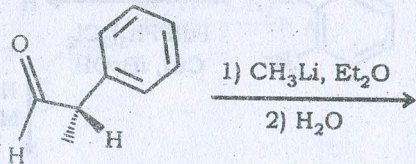


(c) Complete the following cycle :



Group — B

6. (a) State and derive Curtin-Hammett principle with example.
 (b) *cis*-2-decalone enolize towards C-1 instead of C-3. Explain. 12+3
7. (a) Give an example of optically active compound having no chiral atom.
 (b) Write the 3d-structure of most stable conformer of *trans*-9-methyl decalin.
 (c) Predict the product with appropriate stereochemistry and mechanism



(d) Draw the 3d structures for the following conformers and show in them different steric interactions :

cis-cisoid-cis-Perhydrodiphenic acid

(e) Give an example of diatopic reaction.

8. Explain with examples :

3×5

- (a) (2 + 2) Cycloaddition is photochemically allowed process.
 (b) (4 + 2) Cycloaddition is thermally allowed process.
 (c) Cope reaction is a Sigmatropic process.
 (d) Alder ene reaction follows frontier molecular orbitals.
 (e) 4n thermal electrocyclic reactions follow *conrotatory* motions.

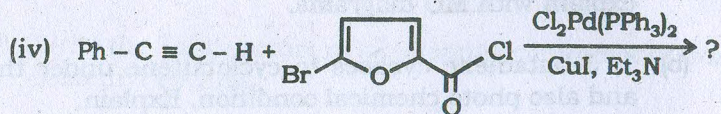
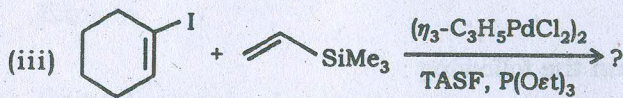
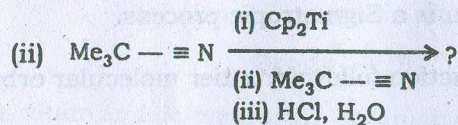
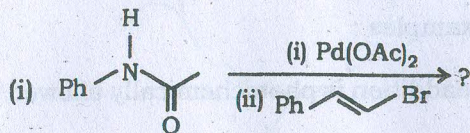
9. Explain the following :

3×5

- (a) Cyclopentadiene dimerises under thermal condition explain with MO diagrams.
 (b) 1, 3-butadiene cyclises to cyclobutene under thermal and also photo chemical condition. Explain.
 (c) Is it possible to do (2 + 2) thermal cycloaddition reaction? If so, explain with example.
 (d) Explain S-S or A-A matching in pericyclic reaction.
 (e) Conservation of orbital symmetry. Explain with Woodward's concept.

10. (a) Transition metal complexes exhibit special bonding explain. 2

(b) Write down the product of the following reaction with mechanism (any three) : 3×3



(c) What is Ziegler Natta Catalyst? Show the mechanism of long chain hydrocarbon formation using Ziegler Natta Catalyst. 1+2

(d) Show a synthetic use of a Rhodium based chiral catalyst. 1

Group—C

11. Write notes on the following (any five) : 5×5

- CD
- ORD
- Octant Rule
- Axial halo ketone rule
- Conformation of Cyclo octanes
- HOMO-LUMO interaction in Diels Alder reaction
- Alder ene Reaction
- Group transfer Reaction