2015

M.Sc. 3rd Seme. Examination

CHEMISTRY

PAPER—CEM-301

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.

(*Physical Special*)

Answer any *five* questions, taking at least *two* from each group.

Group—A

1. (a) Given,

x :	1	2	3	4	5	6	7	8
f(x) :	1	8	27	64	125	216	343	512

Find f(1.5).

(b) Evaluate $\int_0^1 \left(4x - 3x^2\right)dx$

taking 10 intervals by Simpson's $\frac{1}{3}$ rule.   4+4

2. Deduce operator $\hat{p}_x$ and $\hat{H}$ of linear Harmonic oscillator in terms of its raising and lowering operator. Hence obtain the matrix representation of $\hat{p}_x$ and $\hat{H}$.   4+4

3. The Hamiltonian (H) and another observable (A) of a certain three level system is represented by the following matrices.

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

$$A = \lambda \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 2 \end{pmatrix}$$

Where ω and λ are positive real numbers. Find the eigen values and eigen vectors of H and A.   4+4

4. Prove that a non-degenerate Harmitian matrix can be diago-nalized with the help of the matrix of its eigen vectors.   8

5. (a) Four simultaneous eigen kets of operator J^2 and J_z are,

$$|1\rangle = \left|\frac{3}{2}, \frac{3}{2}\right\rangle, \quad |2\rangle = \left|\frac{3}{2}, \frac{1}{2}\right\rangle$$

$$|3\rangle = \left|\frac{3}{2}, -\frac{1}{2}\right\rangle, \quad |4\rangle = \left|\frac{3}{2}, -\frac{3}{2}\right\rangle$$

Find the matrix representation of J^2 and J_z.

(b) Find the eigen values and eigen vectors of the following matrix :

$$\begin{pmatrix} 1 & -2 \\ 1 & 4 \end{pmatrix}$$

     5+3

Group—B

6. Deduce Hartree-Fock equation. Why is it called Integro-differential equation ? What is meant by Hartree-Fock self consistant field ?   3+2+3

7. Obtain the expression for the expectation value of the Hamiltonian for a 2N electron system using a slater determinantal wave function in a closed shell configuration.   8

8. Write down the eigen value equation of S_z and S^2 operator for pure spin state (Say $|D\rangle$) with more than two electrons.

   Deduce the pure spin state and indicate their spin multiplicities for a system of three non-equivalent electrons with

   $$M_s = +\frac{1}{2}.$$ 2+6

9. (a) What is meant by linear function space? Illustrate with an example.

   Obtain the transformation matrix which transforms the n-dimensional base vectors $(e_1, e_2, e_3 \dots e_n)$ in a linear space into its prime set $(e_1', e_2', e_3' \dots e_n')$.

   (b) Show that the set of n-degenerate molecular orbitals form the basis for the representation of an n-dimensional $\mathbb{R}$ of the point group to which the molecule belongs.   (2+3)+3

10. What is meant by accidental degeneracy?

Obtain the symmetry of the splitted d-orbitals of a transition metal ion when it is placed in an octahedral ligand field environment.

Character table of 'O' group is given below :

	E	$6C_4$	$3C_2 (= C_4^2)$	$8C_3$	$6C_2$		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	−1	1	1	−1		
E	2	0	2	−1	0		$(2z^2 - x^2 - y^2)$, $(x^2 - y^2)$
T_1	3	1	−1	0	−1	(x,y,z), (R_x, R_y, R_z)	
T_2	3	−1	−1	0	1		(xy, yz, zx)

1+7

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(Organic Special)

Answer any *five* questions.

1. Write in brief with one example in each case :   8

(a) Allylic 1, 2-strain ;

(b) 2-alkylketone effect ;

(c) α and β-strains ;

(d) Curtin-Hammett principle.

2. Answer the followings :   4×2

(a) What is a symmetry forbidden reaction? Explain by taking the example of ethene under thermal as well as photochemical conditions. ·

(b) How can you account for the opposite stereochemistry in the photochemical cyclization of a 1, 3-butadiene to a cyclobutene than the thermal reaction?

(c) Why thermal [1, 3] sigmatropic migrations of hydrogen are rare?

(d) Predict the product(s) with appropriate reasoning.

3. Write all the possible streoisomers of perhydrophenanthrenes and correlate them with perhydrodiphenic acids by epimerization protocols.   8

4. Write in brief about the following terms : (any *four*)   4×2

(a) ORD ;

(b) CD ;

(Continued)

(c) Cotton Effect (CE) ;

(d) Predict the CE as positive or negative of 9-Methyl-deca-3-ones ;

(e) Cieplak Model.

5. For each of the following transformations, clearly explain the basis for the observed selectivity. For full credit, show reagents, key conformations, transition states, and/or reactive intermediates to support your arguments. Be specific.
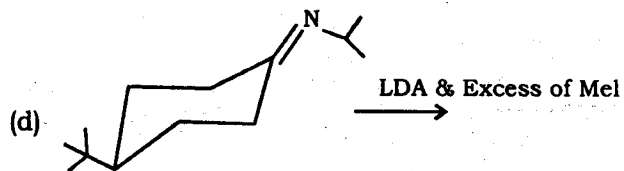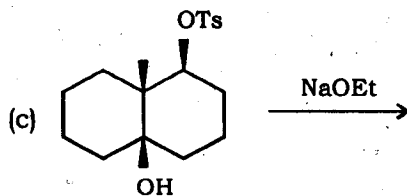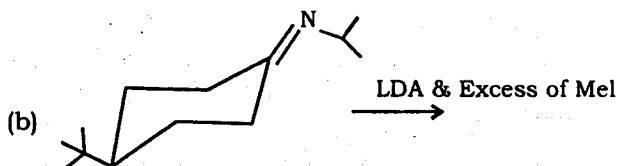
4×2

5. (a)

(b)

(c)

(d)
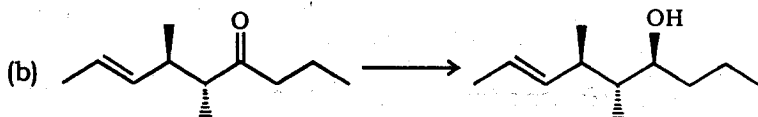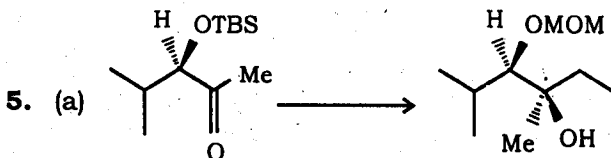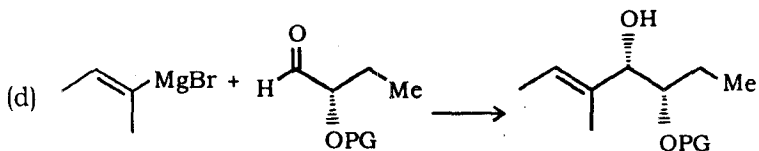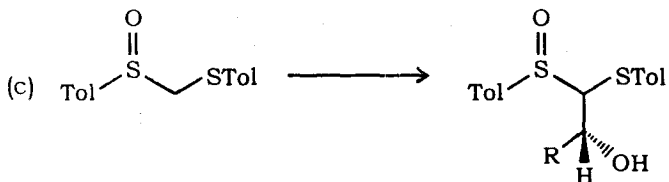
6. Give the products of the following reactions. Where more than one product is likely to be formed in significant yield, indicate which will be the major product and also predict the mechanism of the reaction involved. 8

(a)

(Continued)

(b)

LDA & Excess of MeI

(c)

NaOEt

(d)

LDA & Excess of MeI

(Turn Over)
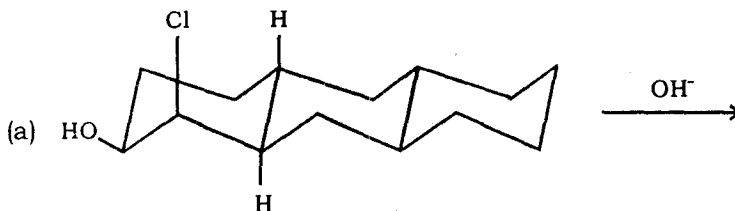
7. Draw the 3d structures for the following conformers and show in them different steric interactions including their optical properties : 8

(i) *cis-transoid-cis* perhydroanthracene ;

(ii) *trans-cisoid-cis* perhydrophenanthrene ;

(iii) 9, 10-dimethyl *cis* decalin ;

(iv) trans-hydrindane.

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(Inorganic Special)

Answer any *five* questions, taking at least *two* from each group.

Group—A

1. (a) Applying group theory justify that the cyclisation of the allyl cation to cyclopropyl cation must occur via disrotatory mechanism under thermal condition but conrotatory mechanism under photochemical condition. (Given below the character table and correlation table).

7

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

		$\sigma(xz)$	$\sigma(yz)$
C_{2v}	C_2	C_s	C_s
A_1	A	A'	A'
A_2	A	A''	A''
B_1	B	A'	A''
B_2	B	A''	A'

(b) Why do the configurations d^n and d^{10-n} give identical ligand field terms in any given field symmetry?   1

2. With the help of group theory determine the symmetries of the group of orbitals of F atoms which are effective for σ-bond formation in PF_5 molecule. Write the appropriate SALCs for these symmetries. Construct a qualitative σ-bonding molecular orbital energy level diagram for PF_5 and from

this energy level diagram comment on the π-acid nature of PF_5 molecule. (Given below the character table for D_{3h} point group) :

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
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)

3. (a) Establish the relation

$$\chi(\alpha) = \frac{\sin\left(1+\frac{1}{2}\right)\alpha}{\sin\frac{\alpha}{2}} \quad (\alpha = 0)$$

Where the term have usual significance. Use group theoretical principle to obtain the splitting of d-orbitals of Pt(II) ion in $[Pt(Cl)_4]^{2-}$ anion. (Given below the character table for rotational subgroup D_4).

4+2

D_4	E	$2C_4$	$C_2(=C_4^2)$	$2C_2'$	$2C_2''$		
A_1	1	1	1	1	1		x^2+y^2, z^2
A_2	1	1	1	-1	-1	z, R_z	
B_1	1	-1	1	1	-1		x^2-y^2
B_2	1	-1	1	-1	1		xy
E	2	0	-2	0	0	(x, y) (R_x, R_y)	(xz, yz) (x^2-y^2, xy)

(b) Use group theoretical principle to determine the symmetry of vibrational mode of cis-1, 2 dichloroethylene molecule using Cartesian coordinate method. Identify the symmetry of IR and Raman active mode in this molecule. (Use the character table of C_{2v} point group given in *Question No. 1*) 2

4. (a) Constuct qualitative π-molecular orbital energy level diagram of trans-butadiene molecule and show that only two $\pi \rightarrow \pi^*$ bands are possible in the electronic spectrum of this molecule. (Given below the character table for C_{2h} point group). 5

C_{2h}	E	C_2	i	σ_h		
A_g	1	1	1	1	R_z	$x^2, y^2, z^2,\ xy$
B_g	1	−1	1	−1	$R_x,\ R_y$	$xz,\ yz$
A_u	1	1	−1	−1	z	
B_u	1	−1	−1	1	$x,\ y$	

(b) Explain why the intensity of $A_2 \rightarrow T_1$ transition around 100 times greater than the intensity of $A_2 \rightarrow T_2$ transition in $[CoCl_4]^{2-}$ anion. (Given below the character table for T_d point group).   3

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
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		
T_2	3	0	−1	−1	1	(x,y,z)	$(xy,\ xz,\ yz)$

Group—B

5. (a) Two peaks in proton NMR spectrum recorded at 500 MHz occurs at 4.2 and 7.9 (δ). What is their separation in Hz?   2

(b) Comment on the proton NMR spectrum of $CH_3 - CH_2 - SPF_2$. Comment on this with a draw of a stick diagram.

3

(c) Indicate the number of signals obtained in ^{19}F NMR spectrum of $PF_2 - S - PF_2$. Draw a stick diagram for this.

3

6. (a) Draw the ^1H, ^{19}F and ^{31}P NMR spectra of HOP(O)FH with proper explanation.

3

(b) Draw the ^1H, ^{19}F and ^{31}P NMR spectra of HP(O)F_2 using stick diagram.

3

(c) Predict the splitting pattern for 1H NMR of $^{11}BH_4$ ion.

2

7. a) Draw the ^{31}P NMR spectra of $[H_2P_2O_5]^{2-}$ and explain. 3

(b) Predict the proton NMR spectrum of $PF_2 - {}^{15}NH - Si\ H_3$.

3

(c) How can you differentiate between terminal and bridging hydrogen in B_2H_6 molecule by ^1H NMR spectrum ?

2

8. (a) How do you characterize the structure of αP_4S_4, βP_4S_4 and βP_4S_5 with the help of ^{31}P NMR.   3

(b) Establish the *cis* and *trans* structure of $PtCl_2(PMe_2Ph)_2$ by ^1H NMR spectroscopy.   3

(c) With the help of stick diagram draw the ^{11}B NMR spectrum of $B_{10}H_{14}$.   2

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