

Total number of printed pages-8

14 (CHM-I) CH 106

2017

CHEMISTRY

Paper : CH-106

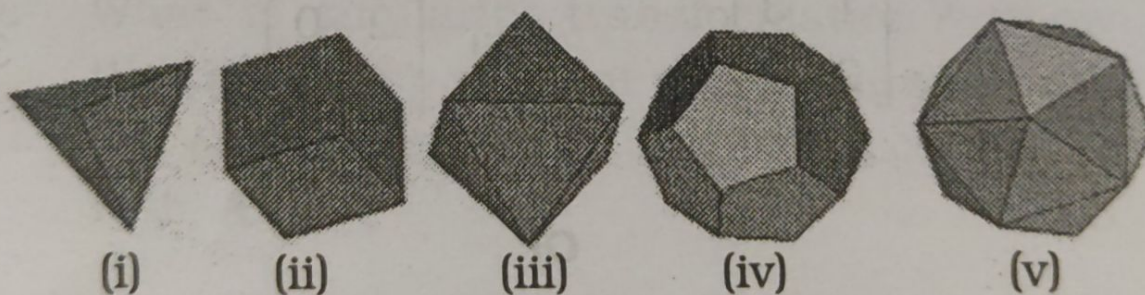
(Symmetry and Group Theory in Chemistry)

Full Marks : 40

Time : Two hours

The figures in the margin indicate full marks for the questions.

1. Observe the following figures of the five regular solids and fill up the table given below. 2



Solids	(i)	(ii)	(iii)	(iv)	(v)
Name					
Vertices					
Edges					
Faces					
Sides of faces					

Contd.

2. Write down all possible symmetry operations of the point group D_3 . 1
3. Determine how many improper rotation operations are generated by the six-fold improper rotation axis S_6 . 1
4. What is the primary difference between a point group and a space group? 1
5. Determine if the multiplication of the following matrices is commutative.

(i) $\begin{bmatrix} 1 & 3 \\ 2 & 2 \end{bmatrix}$

(ii) $\begin{bmatrix} 2 & 0 \\ 1 & 0 \end{bmatrix}$

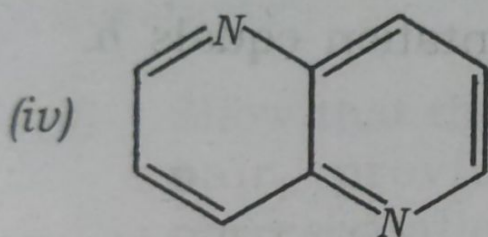
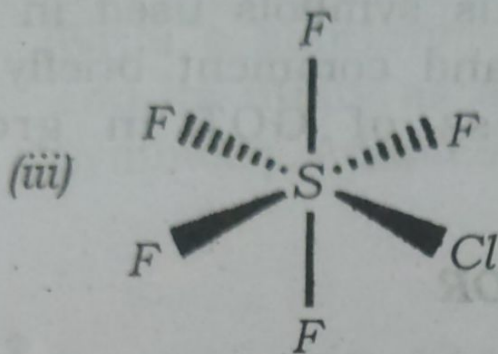
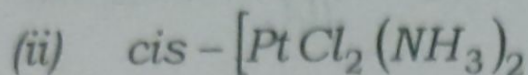
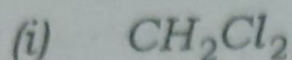
3

Or

What are four essential properties of mathematical groups? Show that the four symmetry elements of C_{2v} conform to the requirements of a mathematical group.

3

6. Determine the point groups of the following molecules : 2



7. What is similarity transformation? Show that if a group element A is conjugate with the group element B , then B is conjugate with A . 3

Or

Work out a representation of the point group C_{2v} by considering the transformation of the Cartesian coordinates x , y and z .

3

8. The statement of the great orthogonality theorem (GOT) is given below :

$$\sum_R [\Gamma_i(R)_{mn}] [\Gamma_j(R)_{m'n'}]^* = \frac{h}{\sqrt{l_i l_j}} \delta_{ij} \delta_{mm'} \delta_{nn'}$$

Explain the various symbols used in the above statement and comment briefly on the usefulness of GOT in group representations. 3

OR

Prove that the sum of the characters in any irreducible representation equals h . 3

9. Find out the inverse of the following matrix which represents the $C_2(z)$ operation in point group C_{2v} . 1

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

10. The Hamiltonian operator in the wave equation for a molecule is invariant with respect to symmetry operations of the relevant molecular point group. Justify this statement. 2

11. Prove that the representation of a direct product, Γ_{AB} , will contain the totally symmetric representation only if irreducible representation $\Gamma_A = \Gamma_B$. 3

12. Write a short note on projection operator and its utility as a tool for construction of Symmetry Adapted Linear Combinations. 3

13. Answer **any three** from the following questions :

(i) Show that the p_x and p_y orbitals, as a pair, provide a basis for the E representation of point group C_{2v} . Eigenfunctions of p_x and p_y may be taken as

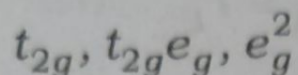
$$p_x = \psi_r \sin \theta \cos \phi$$

$$p_y = \psi_r \sin \theta \sin \phi$$

where ψ_r is not subject to changes by symmetry operations. 5

(ii) Determine the symmetry types of the four sigma orbitals in CH_4 by making use of the appropriate character table given at the end of the question paper. 5

- (iii) In octahedral transition metal complexes the following configurations are conceivable in the limit of very high splitting of d orbitals.



Determine the ligand field states, without spin, that are obtainable from the above configurations. 5

- (iv) Provide answers as appropriate :

(a) Name the seven crystal systems and indicate their essential symmetries.

(b) The seven crystal systems encompass _____ crystallographic point groups, _____ Bravais lattices and _____ space groups.

(c) Give crystallographic (international) symbols to the three crystallographic point groups - C_{2v} , D_2 and D_{2h} — for the orthorhombic crystal system.

2+2+1

- (v) Determine the number of fundamental modes of vibration for NH_3 which will be IR and Raman active. Use the character table of point group C_{3v} given at the end of the question paper.

5

Character tables :

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

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	-1	R_z	
E	2	-1	0	$(x, y) (R_x, R_y)$	$(x^2 - y^2, xy) (xz, yz)$

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	
(43m)						
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	$(2z^2 - x^2 - y^2, \sqrt{3}(x^2 - y^2))$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)
T_2	3	0	-1	-1	1	$(x, y, z) (xy, xz, yz)$

O_h ($m3m$)	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	
	(- C_4^2)										
A_{1g}	1	1	1	1	1	1	1	1	1	1	$x^2 + y^2 + z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1	
E_g	2	-1	0	0	2	2	0	-1	2	0	$(2z^2 - x^2 - y^2, \sqrt{3}(x^2 - y^2))$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1	(xy, xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1	
E_u	2	-1	0	0	2	-2	0	1	-2	0	
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1	