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14 (CHM-1) 106

2022

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. Answer **any one** of the following questions :

3

- (a) Construct the group multiplication table
for a non cyclic group of order 4.

C_4 v E A R e

E E A B e

A A B e E

B B e E e
e e E A B

Contd.

- (b) Find the classes present, from the group multiplication table of order 6 given below.

$G_6^{(2)}$	E	A	B	C	D	F
E	E	A	B	C	D	F
A	A	E	D	F	B	C
B	B	F	E	D	C	A
C	C	D	F	E	A	B
D	D	C	A	B	F	E
F	F	B	C	A	E	D

- (c) Identify the subgroups in the group of order 8. Group multiplication table given.

G_8	E	A	B	C	D	F	G	H
E	E	A	B	C	D	F	G	H
A	A	C	E	B	H	G	D	F
B	B	E	C	A	G	H	F	D
C	C	B	A	E	F	D	H	G
D	D	G	H	F	E	C	A	B
F	F	H	G	D	C	E	B	A
G	G	F	D	H	B	A	E	C
H	H	D	F	G	A	B	C	E

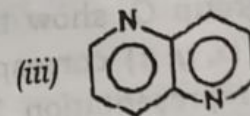
2. Answer **any one** of the following questions :
5

(a) Define symmetry elements and operations. Why the operations generated by three σ_v planes in ammonia molecule belong to same class?
2+2+1=5

(b) Considering the operations generated by S_5 symmetry element show that S_5 is not a valid point group.

(c) Identify the point groups of the following molecules :
3+2=5

- (i) Chlorobenzene
(ii) SF_5Cl



- (iv) $BIClF$
(v) $OPCl_3$

3. Answer **any two** of the following questions :
4×2=8

(a) Derive a matrix representation for C_n symmetry operation.

- (b) The great orthogonality theorem is stated as

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

Identify the terms in it.

- (c) Complete the character table given below and identify the point group.

	E	C ₂	i	σ _h		
Γ ₁	1	1	1	1	R _z	x ² , y ² , z ² , xy
Γ ₂	1	-1	1	-1	R _x , R _y	
Γ ₃					z	
Γ ₄	1	-1	-1	1	x, y	

- (d) For the point group O, show that the set of function (x, y, z) correspond to the irreducible representation T₁.
[Hint: Use the matrices for the operations showing transformation of x, y and z function.]

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

Answer **any three** of the following questions :
5×3=15

- (a) Part of the character table for C_{4v} point group is given below. Find the direct products A₂ ⊗ B₂, E ⊗ B₁, E ⊗ A₂ ⊗ B₁. Which of the direct products will have the totally symmetric representation in it?

C _{4v}	E	C ₂	2C ₄	2σ _v	2σ _d
A ₁	1	1	1	1	1
A ₂	1	1	1	-1	-1
B ₁	1	1	-1	1	-1
B ₂	1	1	-1	-1	1
E	2	-2	0	0	0

3+2=5

- (b) Considering the eigenfunctions for 2p_x and 2p_y

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

$$p_y = \Psi_r \sin \theta \sin \phi$$

show that these two eigenfunctions indeed form the basis for the E irreducible representation in C_{4v} point group.

- (c) Using the projection operators P_{11}^E and P_{22}^E project out the part of the arbitrary function, $x+y+z$, in the group C_{3v} that from the basis for the E irreducible representation.

Matrices for the E Representation of the Group C_{3v}

Operation	Matrix	Operation	Matrix
E	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\sigma_v(xz)$	$\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$
C_3	$\begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$	σ'_r	$\begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix}$
C_3^2	$\begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix}$	σ''_r	$\begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix}$

- (d) Identify the irreducible representations to which the normal modes of vibration of CO_3^{2-} ion belong. Comment on the IR and Raman activity of the normal modes of the same.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		x^2+y^2, z^2
A_1'	1	1	1	1	1	1	R_z	$(x^2 - y^2, xy)$
A_2'	1	1	-1	1	1	-1	(x, y)	
E'	2	-1	0	2	-1	0		
A_1''	1	1	1	-1	-1	-1	z	(xz, yz)
A_2''	1	1	-1	-1	-1	1	(R_x, R_y)	
E''	2	-1	0	-2	1	0		

- (e) Find the symmetry adapted linear combination for sigma bonding in $PtCl_4^{2-}$ ion.

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		x^2+y^2, z^2
A_{1g}	1	1	1	1	1	1	1	1	1	1	R_z	$x^2 - y^2$
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1		xy
B_{1g}	1	-1	1	1	-1	1	-1	1	-1	1	(R_x, R_y)	(xy, yz)
B_{2g}	1	-1	1	-1	1	1	0	-2	0	0		
E_g	2	0	-2	0	0	2	-1	-1	-1	-1	z	
A_{1u}	1	1	1	1	1	-1	-1	-1	1	1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	-1	1		
B_{1u}	1	-1	1	1	-1	-1	1	-1	1	-1	(x, y)	
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0		

C_4	E	C_4	C_2	$2C_4^3$		x^2+y^2, z^2
A	1	1	1	1	z, R_z	$x^2 - y^2, xy$
B	1	-1	1	-1		
E	$\begin{Bmatrix} 1 & i \\ 1 & -i \end{Bmatrix}$	$\begin{Bmatrix} i & -1 \\ -i & 1 \end{Bmatrix}$	$\begin{Bmatrix} -1 & -i \\ 1 & i \end{Bmatrix}$	$\begin{Bmatrix} -i & 1 \\ 1 & i \end{Bmatrix}$	$(x, y)(R_x, R_y)$	(yz, xz)

- (f) Discuss how group theory can be helpful in solving the problems of molecular quantum mechanics with suitable examples.

5. Answer the following multiple choice questions : $1 \times 6 = 6$

- (a) Which of the following statements is correct for a set of elements forming a group? A, B, C, D...etc are the elements of a group of order h

(i) There will always be a non cyclic group independent of the order of the group.

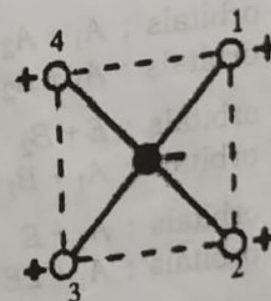
(ii) There will always be subgroups of all the orders g that are integral divisor of h .

(iii) If the elements A and B, then B and C are conjugate to each other, A and C are conjugate to each other.

(iv) Even if the element A is conjugate with B, B not necessarily be conjugate with A.

- (b) If a molecule has S_n axis the molecule
- is achiral
 - is chiral
 - always has a C_n axis
 - always has a σ_h plane perpendicular to C_n axis

- (c) The 'out of plane' bending vibrational mode for a square planer complex shown below, belongs to the irreducible representation



(i) A_{1g}

(ii) B_{1g}

(iii) A_{2u}

(iv) B_{2u}

- (d) For an MX_4 molecule having a flattened tetrahedral structure of D_{2d} symmetry, identify the splitting pattern of p and d orbitals.

D_{2d}	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$		
A_1	1	1	1	1	1	R_z	$x^2 + y^2, z^2$
A_2	1	1	1	-1	-1		
B_1	1	-1	1	1	-1	z	$x^2 - y^2$
B_2	1	-1	1	-1	1		xy
E	2	0	-2	0	0	$(x, y);$ (R_x, R_y)	xz, yz

- (i) p orbitals : $A_1 + A_2 + B_2$
 d orbitals : $A_1 + A_2 + B_1 + E$
- (ii) p orbitals : $E + B_2$
 d orbitals : $A_1 + B_1 + B_2 + E$
- (iii) p orbitals : $A_1 + E$
 d orbitals : $A_1 + 2E$
- (iv) p orbitals : $A_1 + B_1 + B_2$
 d orbitals : $A_1 + 2B_2 + E$
- (e) Number of point and space groups one can find in two dimension
- (i) 10 and 17 respectively
- (ii) 5 and 8 respectively
- (iii) 32 and 230 respectively
- (iv) 7 and 14 respectively

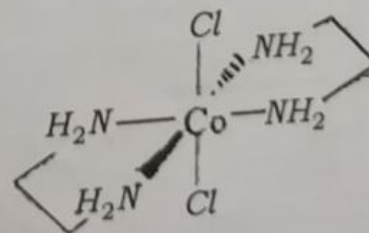
- (f) Considering the diagram below, the linear combination of atomic orbitals for the π bonding molecular orbital in an octahedral complex (AB_6) matching the d_{xy} orbital of central metal atom is

- (i) $1/2(p_x^1 + p_x^2 + p_x^3 + p_x^4)$
- (ii) $N_1[d_{xy} + 1/2(p_x^1 + p_x^2 + p_x^3 + p_x^4)]$
- (iii) $N_1[d_{xy} - 1/2(p_x^1 + p_x^2 + p_x^3 + p_x^4)]$
- (iv) $1/2(p_x^1 - p_x^2 + p_x^3 - p_x^4)$



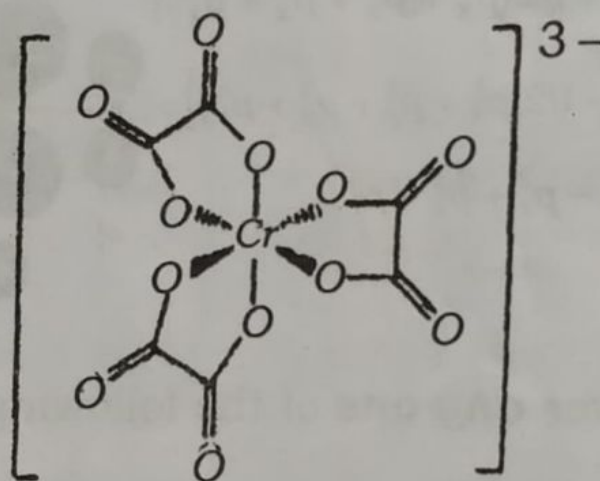
6. Answer **any one** of the following questions :
 $3 \times 1 = 3$

- (a) Discuss glide plane and screw axis in crystal symmetry with suitable diagrams.
- (b) The molecule show below belongs to the D_2 point group. Construct the group multiplication table for D_2 point group.



(c) State the meaning of the symbols P , 2_1 , and m in space group $P2_1/m$.

(d) The complex ion $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ has the D_3 point group symmetry. Comment on the polarization of the electronic transitions $A_2 \rightarrow A_1$ and $A_2 \rightarrow E$.



D_3	E	$2C_3$	$3C_2$		
A_1	1	1	1		$x^2 + y^2, z^2$
A_2	1	1	-1	z, R_z	
E	2	-1	0	$(x, y)(R_x, R_y)$	$(x^2 - y^2, xy)(xz, yz)$