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14 (CHM-1) CH 106

2019

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 :

(a) Mention the conditions for the formation of a mathematical group by a set of elements. 3

(b) Prove that in an Abelian group, each element is a class by itself. 3

Contd.

- (c) Consider elements 1, 2, and 3. The following multiplication table is provided for these elements :

	1	2	3
1	1	2	3
2	2	3	1
3	3	1	2

Whether these elements 1, 2, and 3 form a mathematical group or not? Justify your answer. 3

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

(a) Define symmetry operations. What is the point group of a perfect cube? Mention the symmetry elements present in a cube. $2+1+2=5$

(b) Write out all the operations generated by S_5 and S_6 axes. Express each one in conventional notation. Why do we not have S_n point groups with n being odd? $3+2=5$

(c) (i) Identify the point groups of N_2O , diborane, and cyclohexane (chair).

(ii) Why do we not have S_n point groups with n being odd?

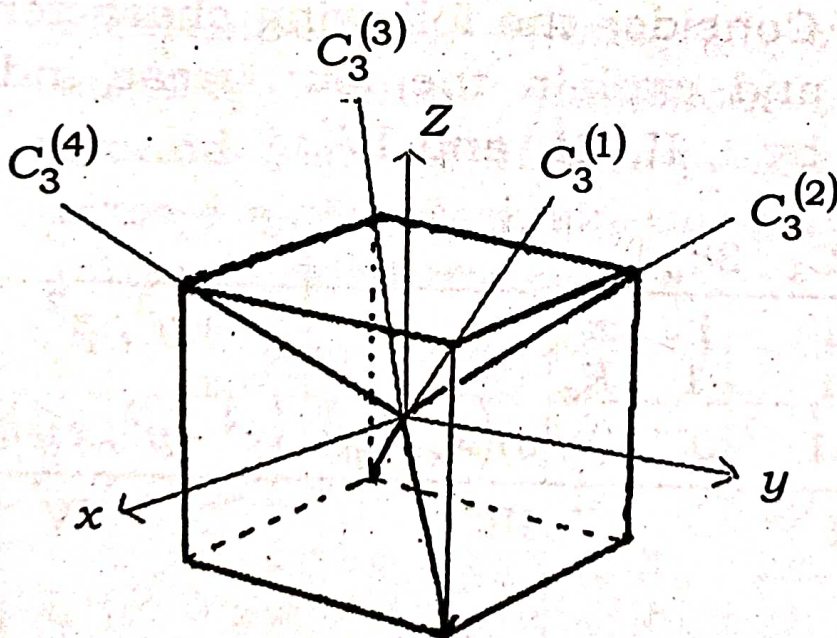
$$3+2=5$$

3. Answer **any two** of the following questions:

$$4 \times 2 = 8$$

(a) Write the matrices for the symmetry operations E , C_n , i , s , and S_n considering a point (x, y, z) .

(b) Write the matrices describing the effect of the C_3 and C_3 operations corresponding to the four C_3 axes of a tetrahedron on a point (x, y, z) .



- (c) Complete the following character table for the D_{3h} point group and find the combination of irreducible representation for the reducible representation Γ :

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		$x^2 + y^2, z^2$
	1	1	-1	1	1	-1	R_z	
E'							(x, y)	$(x^2 - y^2, xy)$
A_1''	1	1	1	-1	-1	-1		
A_2''							z	
E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)
Γ	4	1	0	0	3	0		

- (d) Consider the following character table and explain the four areas indicated by I, II, III, and IV :

C_3	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	$(x, y)(R_x, R_y)$	$(x^2 - y^2, xy)(xz, yz)$
II	I		III		IV

4. Answer **any two** of the following questions :
5×2=10

(a) 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_{3v} point group. [Character table for C_{3v} is provided in question no 3.(d)] 5

(b) Considering the integral, $\int \psi_i \mu \psi_j d\tau$ for electronic transitions, identify the allowed electronic transitions from the ground state of H_2O molecule to the excited states. Mention the polarization of the allowed transitions. 5

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) Identify the IR and Raman active vibrational modes of cisplatin. (One of the character tables given in this question paper may be used.) Whether mutual exclusion principle of IR and Raman spectroscopy is applicable here? 5

(d) Construct the symmetry adapted linear combinations (SALCs) for sigma bonding in XeF_4 (square planer) molecule. The following character tables may be used : 5

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

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

- (e) Give an overview of various ways in which group theory finds application in quantum mechanics. 5

5. Answer **any three** of the following questions : $2 \times 3 = 6$

(a) State the selection rule for an electronic transition to be allowed from the direct product of irreducible representations.

(b) For the $Mo_2X_8^{4-}$ ion, find the symmetry (irreducible representation) of the 5 bonding orbital shown below. (Character table for D_{4h} may be used.)



δ

(c) 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		$x^2 - y^2$
B_1	1	-1	1	1	-1	z	xy
B_2	1	-1	1	-1	1		(xz, yz)
E	2	0	-2	0	0	$(x, y); (R_x, R_y)$	

(d) Assign the symmetry types for the normal modes vibration of water molecule.

(e) Show the splitting pattern of ^1G and ^3F terms in a tetrahedral field.

6. Answer **any four** of the following questions :

1×4=4

- Why cannot perfect crystals have a C_5 axis of symmetry?
- What is the notation scheme commonly used to represent symmetry elements in crystallography called?
- How many point and space groups one can find in crystallography?

(d) Name a crystal system having four threefold rotational axis.

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

(f) Define space group of crystals.

7. Explain symmetry elements rotoinversion and rotoreflection with suitable examples.

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OR

Discuss the similarities and differences between molecular and crystallographic symmetry.
