

RANI RASHMONI GREEN UNIVERSITY

DEPARTMENT OF CHEMISTRY

Semester – IV, Final Examination – 2025

M.Sc. Course in Chemistry

Course ID: CHEM-CB-42I

Full Marks: 40

Time: 2 h

Answer **any one** question from **each unit** in your own words with proper scientific justification.

**Unit-1: Chemical Application of Group Theory-2**

1. (a) In determining the type of splitting of the state of a *d*-electron in an octahedral field, illustrate how the characters,  $\chi(\alpha)$ 's, of the matrices of reducible representation, corresponding to O-point group, is given by:

$$\chi(\alpha) = [ \text{Sin} ( l + \frac{1}{2} ) \alpha ] / \text{Sin} \alpha / 2 ,$$

where the symbols have their usual significance.

- (b) Show that on splitting of such one-electron d-level in octahedral symmetry, the irreducible representation spanned,  $E_g + T_{2g}$

Character table

<i>O</i>	<i>E</i>	$6C_4$	$3C_2$ ( $=C_4^2$ )	$8C_3$	$6C_2$	
$A_1$	1	1	1	1	1	$x_2 + y_2 + z_2$
$A_2$	1	-1	1	1	-1	
<i>E</i>	2	0	2	-1	0	$(2z^2 - x^2 - y^2,$ $x^2 - y^2)$
$T_1$	3	1	-1	0	-1	$(R_x,$ $R_y, R_z); (x, y, z)$
$T_2$	3	-1	-1	0	1	$(xy, xz, yz)$

[4+4]

2. (a) Define projection operator ( $P^j_{s't'}$ ) in terms of the following:

$$P^j_{s't'} \varphi^i_t = \varphi^i_{s't'} \delta_{ij} \delta_{tt'}$$

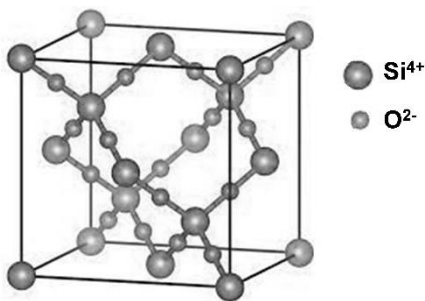
- (b) Show how to construct Symmetry Adapted Linear Combinations (SALCs) of internal coordinates ( $\Delta r, \Delta \theta$ ) of a pyramidal  $AB_3$  molecule, which span E representation (The relevant character table is given below).

$C_3$	E	$C_3$	$C_3^2$		$\epsilon = \exp(2\pi/3)$
A	1	1	1	$z, R_z$	$x^2 + y^2, z^2$
E	$\left[ \begin{array}{c} 1 \\ 1 \end{array} \right]$	$\left[ \begin{array}{c} \epsilon \\ \epsilon^* \end{array} \right]$	$\left[ \begin{array}{c} \epsilon^* \\ \epsilon \end{array} \right]$	$(x, y) (R_x, R_y)$	$(x^2 - y^2, xy)(yz, xz)$

- (c) Explain why the component of the transition dipole moment integral gives a non-zero value if the integrand forms the basis of a totally symmetric representation of the point group of the molecule. [2+4+2]

## Unit-2: Solid State Chemistry-2

3. (a) Write the general chemical formula of Zeolite.
- (b) Mention common applications of Clay-minerals.
- (c) Following Zachariasen rules, explain the glass formation properties of  $SiO_2$  (given: the coordination number ratio of cation:anion = 4:2). The structure of  $SiO_2$  is given below.



[2+2+4]

4. (a) What are the characteristics of solid electrolyte?  
 (b) Give one example of solid electrolyte.  
 (c) What is dielectric material?  
 (d) What is the function of dielectric materials in capacitor?  
 (e) Write the applications of piezoelectric materials. [3+1+1+1+2]

### Unit-3: Bioinorganic Chemistry-3

5. (a) Explain, why on binding of oxygen, Fe moves into the plane of porphyrin ring in myoglobin?  
 (b) What is the cooperative phenomena observed in hemoglobin during reversible oxygen binding?  
 (c) Write the colour of Deoxymyoglobin (Mb) & Oxymyoglobin? [3+3+2]
6. (a) Name different types of electron transfer proteins.  
 (b) What makes Zn-metal more suitable for use them in biological acid-base catalysis?  
 (c) Describe the mechanism of action of carbonic anhydrase. [2+2+4]

### Unit-4: Crystallography

7. (a) A  $C_5$  axis produces result incompatible with the defining properties of a lattice. – Justify or criticize.  
 (b) Why a nickel filter is used in X-ray diffraction (XRD) using a copper source?  
 (c) Draw diagram for roto-inversion,  $\bar{3}$  and roto-reflection,  $S_6$ - Comment on their equivalency.  
 (d) What are essential symmetry elements for Isometric (Cubic) system. [2.5+1.5+2.5+1.5]
8. (a) Predict the possible space group with proper explanation for following systematic absences:  $00l, l \neq 2n$  and  $hk0, h \neq 2n$ .  
 (b) Define structure factor. how the intensity of scattered radiation depends on structure factor?  
 (c) Define Screw rotation. Draw the diagram for  $4_3$ .

(d) Write Crystallographic symbols for the following Schönflies symbols:



[2+2+2+2]

### Unit-5: Highlighting Chemistry of d-Block Elements

9. (a) Why electron exchange reaction of  $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$  system is faster than  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}/[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ?

(b) Deduce the rate expression for  $\text{S}_{\text{N}}^1_{\text{CB}}$  mechanism of base catalysed hydrolysis of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]$  complex?

(c) How sonochemistry works for d-block elements? [3+3+2]

10. (a) The following Co (III) complexes show first order rate constants at 25°C for aquation which differ by a factor  $10^4$ . Suggest an explanation.



(b) The following rate data have been reported for aquation at 298 K of complex  $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$ , where 'X' is different leaving groups.

Leaving Group (X)	$k \times 10^6 \text{ (sec}^{-1}\text{)}$
$\text{NO}_3^-$	27
I <sup>-</sup>	8.3
Br <sup>-</sup>	6.3
Cl <sup>-</sup>	1.7
$\text{NO}_2^-$	Very Slow

What do these suggest about the intimate mechanism for aquation.

(c) Write a short note on mechano-chemical method of synthesis.

[3+3+2]