Birla Institute of Technology & Science, Pilani, Rajasthan - 333 031
2nd Semester, 2021-22

CHEM F244: Physical Chemistry-III

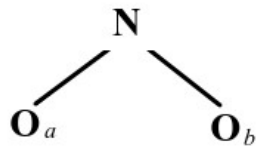
Date: March 10, 2022 **Time: 90 minutes**
Mid-semester Test **Max. Total Marks 60**

Q. 1. (a) Identify and write all possible symmetry elements for the point group, S_5, and write the conventional name of the group if any. **[6]**
(b) State whether the group is (i) Cyclic (ii) Abelian **[2]**
(c) Find the order of the group. How many symmetry classes are present for this group? **[2]**
(d) For the given point group, write the characters of each class corresponding to the non-degenerate irreducible representations that are symmetric with respect to the *proper* rotation operations and write the Mulliken symbols for these representations. **[10]**

Q. 2. (a) Identify the point groups of all possible position isomers of **(i)** dichlorobenzene **(ii)** trichlorobenzene. **[6]**
(b) Write the mathematical statement of the great orthogonality theorem and explain each term/quantity involved in the expression. **[4]**
(c) Write 3D matrix representations for **(i)** a 3-fold counter-clockwise improper rotation about X-axis (as seen from the positive side of the axis). **(ii)** a 4-fold clockwise proper rotation about Y-axis (as seen from the positive side of the axis). **[3+3]**
(d) State the Euler's theorem on homogeneous state functions and and the hypervirial theorem. **[2+2]**

Q. 3. Consider nitrogen dioxide molecule as shown schematically in the figure below:

$\boldsymbol{C_{2v}}$	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_v$	$\hat{\sigma}_v'$	$h=4$	
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



The molecule belongs to $\boldsymbol{C_{2v}}$ point group and is oriented in xz-plane (the σ_v plane) as shown in the figure. The character table for $\boldsymbol{C_{2v}}$ group is also given herewith. Given: $s_a, p_{x,a}, p_{y,a}, p_{z,a}$ are the atomic orbitals on O_a and $s_b, p_{x,b}, p_{y,b}, p_{z,b}$ are the corresponding quantitites on O_b.
(a) Evaluate the following: **(i)** $P^{A_1} p_{z,a}$; **(ii)** $P^{B_1} p_{x,b}$; **(iii)** $P^{B_2} p_{y,b}$; and **(iv)** $P^{A_2} s_a$ **[8]**
(b) If $s, p_x, p_y, p_z, d_{xy}, d_{x^2-y^2}$ are some orbitals on the nitrogen atom, and $\hat{\mu}_x, \hat{\mu}_y, \hat{\mu}_z$ are components of dipole moment operator, then, without explicitly solving but only through the symmetry considerations, find whether the following integrals vanish or survive: $I_1 = \int s \hat{\mu}_z p_z d\tau$; $I_2 = \int s \hat{\mu}_z d_{xy} d\tau$; $I_3 = \int p_x \hat{\mu}_z p_y d\tau$; $I_4 = \int p_z \hat{\mu}_x d_{xz} d\tau$. (Hint: Note the mathematical form of the dipole moment operator). **[4]**
(c) If the atom O_a were replaced by its isotope, then which symmetry operations would be dropped? What would be the point group of the resulting molecule? To which irreducible representations of the (new) point group, the linear and the quadratic bases given in the $\boldsymbol{C_{2v}}$ character table above would belong? (Consider only the the non-zero SALC's). **[8]**

END