[35] SEAT No._____ No. of Printed Pages: 04

SARDAR PATEL UNIVERSITY

M. Sc. (CHEMISTRY) SECOND SEMESTER Examination 2019

Saturday, 23rd March 2019

10.00 a.m. to 1.00 p.m.

PS02CCHE23, Topics in Physical Chemistry – II

N.B.: i. Figures to the right of each of the question indicate marks
ii. Unless otherwise mentioned, symbols and notations have their usual standard meanings, please see the required character tables at the end
iii. Neat sketches are to be drawn to illustrate answers, wherever required
iv. Assume suitable standard data, if necessary and indicate the same clearly

1 **Choose an appropriate answer:** **[08]**

i) The symbols for different types of mirror planes are:

(a) $\sigma_{v'}$, $\sigma_{v''}$ (b) σ_h, σ_v, σ_d
(c) σ_d, $\sigma_{v'}$, $\sigma_{v''}$ (d) σ_h, σ_{d1}, σ_{d2}

ii) Constitution of the group A, combination of elements B and combination of two elements gives a unique result C: The A B C are:

(a) Collection, elements and binary operation
(b) Elements, binary operation and single valued
(c) Binary operation, single valued and closed
(d) Closed, collection and binary operation

iii) The number of operations generated by C_α rotation axis and a general example for such a molecule are:
(a) infinite, A---X (b) infinite, A---A (c) infinite, A ---X---B (d) all the three

iv) Chose the correct statements out of the following:

(I) The character is + 1 for identity IR which is totally symmetric
(II) It is not necessary for the identity IR to be present in all IRs
(III) The character of identity operation in IR equals the order of the group
(IV) In a given representation (reducible or IRs) the sum of squares of IRs equals the order of the group.
(a) I,IV (b) II,III (c) I,III (d) III,IV

v) Most reactions are more rapid at high temperatures than at low temperatures. This is **consistent** with:
(I) an increase in the activation energy with increasing temperature
(II) an increase in the rate constant with increasing temperature
(III) an increase in the percentage of "high energy" collisions with increasing temperature
(a) only I (b) only II (c) I and II only (d) II and III only

(P.T.O.)

vi) In Oscillatory reaction, the essential initial reactants _____ and the final products _____
(a) monotonically increase, monotonically increase
(b) monotonically decrease, monotonically decreases
(c) monotonically decrease, monotonically increase
(d) monotonically increase, monotonically decreases

vii) The rate of conversion (J) is an _____ property whereas rate of reaction (r) is an _____ property.
(a) Extensive, Extensive (b) Intensive, Extensive
(c) Extensive, Intensive (d) Intensive, Intensive

viii) Decomposition of ethylene oxide is:
(a) parallel reaction (b) competing reaction
(c) both parallel as well as competing reaction (d) sequential reaction

2 Answer the following questions as directed **(ANY SEVEN)** **[14]**

i) Show through the matrix that C_3^2 is inverse of C_3^1.

ii) Give two examples of point groups formed by combination of $C_n + nC_2$ and $C_n + nC_2 + \sigma_h$

iii) Draw the neat structural sketches for H_2O,  and SO_2 and give their symmetrical equivalence.

iv) Give the three fundamental stretches of H_2O and label them.

v) Considering the three hybrid orbitals of h_1, h_2 *and* h_3 for BF_3 molecule and show that $\chi_E = 3$ and $\chi_{C3} = 0$

vi) Explain: Equilibrium structure and Saddle Point in relation to activated complex theory.

vii) Define Oscillatory reaction and give two examples of it.

viii) Give schematic diagram for continuous flow methods for studying reaction kinetics in open systems.

ix) Explain briefly Chain reactions.

3 a) Draw the coordinate systems for NH_3 which belongs to C_{3v} point group and hence derive the matrices for σ_v , $\sigma_{v'}$, $\sigma_{v''}$. **[06]**

b) (i) σ_{yz}. σ_{xz} results into $C_{2(z)}$ - prove through matrix multiplication. **[03]**

(ii) What are IRs ? Enlist three rules which gives their utility in constructing a character table. **[03]**

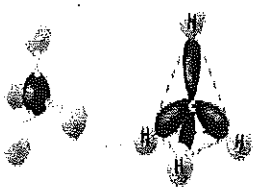
OR

b (i) Take a general example of MX_4 compound , depict its symmetry elements and assign a point group. [03]

(ii) Derive the matrix representation of σ_{yz} plane in H_2O molecule. [03]

4 a) [06]

Considering the character table for Tetrahedral geometry of methane molecule (as shown), establish the reducible representations for various symmetry elements and show that $\Gamma_h = 1\ A_1 + 1\ T_2$



Tetrahedral geometry of methane

b) The reducible representations for bond vectors r_1 and r_2 and bond angle α for H_2O molecule are given as: [06]

C_{2v}	E	$C_{2\,(z)}$	σ_{xz}	σ_{yz}	IR streches
$\Gamma_{r1,r2}$	2	0	0	2	?
Γ_α	1	1	1	1	?

Using character table find out the number of A_i and B_i for $\Gamma_{r1,r2}$ and Γ_α respectively.

OR

b) (i) Given the following: [03]

	E	C_2	σ_v	$\sigma_{v'}$
χ_Γ	3	1	1	3
χ_{A2}	1	1	-1	-1

Prove that the Γ_{IC} has no A_2 coeffcient

(ii) Explain vibronic bands and what is meant by $0 \rightarrow 0$ band ? [03]

5 a) Discuss with suitable examples of chemical reactions: Competing reactions. [06]

OR

a) Deduce kinetic expression for photochemical reaction: $H_2+Cl_2 \rightarrow 2HCl$, combination of hydrogen and chlorine in the *presence* of oxygen. [06]

b) (i) Why a large amount of inert salt is frequently added to ionic reaction mixtures? Justify your answer with kinetics reasoning. [03]

(ii) In relation to enzyme inhibition, explain competitive inhibition and noncompetitive inhibition using Lineweaver-Burk plot. [03]

6 a) Explain Initial rate method for determining rate laws. Give limitations of this method. [06]

b) Define: Steady State Approximation. Discuss the kinetics expression for the reaction; $A \rightarrow B$, with an intermediate *I*, steady state reaction in the case of (I) $k_1 >> k_2$ and (II) $k_1 << k_2$ [06]

OR

b) (i) Discuss temperature dependence of rate constant. [03]

(ii) Write in detail assumptions of hard-sphere collision theory of gas-phase reactions. [03]

(P.T.O.)

Character table for C_{2v} point group

	E	C_2 (z)	σ_v (xz)	σ_v (yz)	Linear, rotations	Quadratic
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

Character table for point group T_d

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	Linear functions, rotations
A_1	+1	+1	+1	+1	+1	-
A_2	+1	+1	+1	-1	-1	-
E	+2	-1	+2	0	0	-
T_1	+3	0	-1	+1	-1	(R_x, R_y, R_z)
T_2	+3	0	-1	-1	+1	(x, y, z)