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SEAT No._____ No. of Printed Pages: 04

[21]

SARDAR PATEL UNIVERSITY

M. Sc. (CHEMISTRY) SECOND SEMESTER Examination 2018

Monday, 16th April 2018

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
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 types of planes in C_4H_4 molecule are:

(a) one σ_h, two σ_v (b) two σ_h, two σ_v
(c) two σ_h, two σ_d (d) one σ_h, two σ_v and two σ_d

ii) Which one of the following statements are wrong ?

(a) Two IRs of a group of different dimensions can be equivalent representations
(b) Two IRs of a group of different dimensions cannot be equivalent representations
(c) Two IRs of a group of the same dimensions are entirely nonequivalent or if these are related by similarity transformation then these are equivalent
(d) Two IRs of a group of the same dimensions are always nonequivalent

Chose the correct choice out of the following:
(1) (b), (c) (2) (a), (d) (3) (b), (d) (4) (c), (d)

iii) The point group formed as a result of the direct product of the C_3 with C_i is:

(a) S_6 (b) C_{3h} (c) C_{3v} (d) D_{3h}

iv) In CH_4, the number of operations which send the carbon atom into itself are:

(a) 12 (b) 6 (c) 24 (d) 3

v) When the velocity of enzyme activity is plotted against substrate concentration, which of the following is obtained?

(a) Hyperbolic curve (b) Parabola
(c) Straight line with positive slope (d) Straight line with negative slope

[P.T.O.]

vi) Which of the following statements about K_m, the Michaelis constant in Michaelis-Menten kinetics is correct?

(a) It is defined as the concentration of substrate required for the reaction to reach maximum velocity.
(b) It is defined as the dissociation constant of the enzyme-substrate complex.
(c) It is expressed in terms of the reaction velocity.
(d) It is a measure of the affinity the enzyme has for its substrate.

vii) Given that a reaction absorbs energy and has an activation energy of 50 kJ/mol, which of the following statements are correct?

(1) The reverse reaction has an activation energy equal to 50 kJ/mol.
(2) The reverse reaction has an activation energy less than 50 kJ/mol.
(3) The reverse reaction has an activation energy greater than 50 kJ/mol.
(4) The change in internal energy is less than zero.
(5) The change in internal energy is greater than zero.
Chose the correct one
(a) (1) and (4) (b) (2) and (4) (c) (3) and (4) (d) (2) and (5)

viii) What is the final amount of fluid in the vessel if the system is in steady state?

(a) Same as the initial amount (b) Twice the initial amount
(c) Zero (d) None of the mentioned

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

i) Derive the matrix representation for $\mathbf{C}_{n(z)}$ (clock wise rotation by θ)

ii) State the symmetry based selection rules for electronic transitions

iii) Derive the matrix for **E** for the hybrid orbitals of methane molecule.

iv) Using SALC approach: show that $\Gamma_{s1,s2} = \mathbf{A}_1 + \mathbf{B}_2$ for water molecule.

v) Prove that: $\mathbf{C}_{2(z)} \cdot \sigma_{xy} = \sigma_{yz}$

vi) Define: Supermolecules and zero point energy in relation to the Activated Complex Theory (ACT).

vii) Why trial and error method is not precise for determining rate laws?

viii) Justify the statement for the gas:

There is no distinction between a collision and an encounter.

ix) Define: turn over number ? and discuss its significance.

3 a) Derive the character table for C_{4v} point group. [06]

b) (i) Explain various symmetry elements present in a molecule with a C_3 principal axis. [03]

(ii) What does the symbol **D** stand for ? and how one gets D_{3h} ? – explain with an example of PCl_5. [03]

OR

b (i) Prove that $(ABC)^{-1} = C^{-1}B^{-1}A^{-1}$ [03]

(ii) Show through matrix that the inverse of $C_{2(z)}$ is $C_{2(z)}$ only. [03]

4 a) Based on symmetry considerations, show that $\Gamma_{vib} = 2\ A_1 + 1\ B_2$ for water molecule [06]

b) (i) Work out the reproducible representations, Γ_{int} for water using internal coordinate method. [03]

(ii) Show that the character $\chi_{\sigma h} = 3$ for hybridization in BF_3. [03]

OR

b) (i) π --- π^* transition in formaldehyde is fully allowed and while **0---0** band is forbidden - Explain [03]

(ii) Work out that the character for $\chi_{C2(x)}$ in naphthalene is **0** using group theory. [03]

5 a) Discuss that enzymically catalyzed reactions exhibit saturation kinetics and derive equation for Lineweaver-Burk plot. [06]

$$\frac{1}{V_0} = \frac{1}{V_{max}} + \frac{k_m}{V_{max}}\left(\frac{1}{[S]}\right)$$

b) (i) Give a brief account on: primary kinetic salt effect. [03]

(ii) Discuss how relaxation time method is useful for studying fast reactions. [03]

OR

b) What is a chain reaction? Derive kinetic expression for the gas phase reaction of hydrogen with bromine to give HBr. [06]

6 a) What is oscillatory reaction ? and discuss any one oscillatory reaction with its mechanism. [06]

b) Explain Isolation method for determining rate laws. [06]

OR

b) (i) Distinguish: threshold energy and activation energy and establish the relationship: $E_a = E_{thr} + \frac{1}{2}RT$. [03]

(ii) Prove the statement: ***Transition Sate Theory (TST) reduces to the Hard Sphere Collision Theory (HSCT) when the structure of the molecules is ignored.*** [03]

—X—

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Character Table for C_{2v}

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