

SARDAR PATEL UNIVERSITY

M. Sc. (Chemistry) Semester-II Examination, 2019 (NC) (CBCS)

Thursday, 21st November, 2019

10.00 A.M. To 01.00 P.M.

Subject: **Topics in Physical Chemistry-II** Paper: **(PS02CCHE23)**

N.B. Figures to the right of each of the question indicate marks [Total Marks: 70]

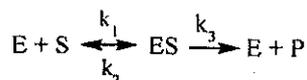
Q.1 Choose an appropriate answer of the following [08]

- i) The enzyme catalyzed reaction is faster than a metal catalyzed reaction because as compared to the latter, the activation energy of the former is
(a) same (b) greater (c) lesser (d) all of these
- ii) The rate of reaction increases with increase of temperature because ...
(a) an increase in the number of activated molecules
(b) an increase in the number of collisions
(c) lowering of threshold energy
(d) activation energy is lowered
- iii) Which of the following molecules belong to C_s point group?
(a) Dinitrogen trioxide (b) Nitrogen dioxide
(c) Dinitrogen pentoxide (d) Nitrous oxide
- iv) The point group _____ is obtained when C_n and nC_{2s} is perpendicular to C_n axis and no other symmetry elements.
(a) D_{nh} (b) C_s (c) D_n (d) S_n
- v) Doubly degenerate vibrations normally occur when the molecule has a rotational axis is _____ then _____ fold.
(a) lower, two (b) higher, two
(c) lower, three (d) higher, three
- vi) For the rate law $\text{Rate} = k[A]^{1/2}[B]$, the partial order with respect to A is _____, the partial order with respect to B is _____, and the total order is _____.
(a) 1/2; 0; 2 (b) 1/2; 1; 1
(c) 1/2; 1; 3/2 (d) 1; 0; 1/2
- vii) Water molecule has _____ vibrational modes.
(a) 3 (b) 2 (c) 4 (d) 1
- viii) Increase in the concentration of the reactants leads to the change in
(a) heat of reaction (b) threshold energy
(c) collision energy (d) activation energy

Q.2 Answer the following (any seven) [14]

1. State the conditions for a molecule to be infrared active.
2. What is activation energy? What are the effects of collisions on activation energy?
3. Explain how the photochemical reactions of hydrogen-chlorine differ from that of hydrogen-bromine.
4. For ammonia molecule prove that:
(a) $C_3^2 \cdot \sigma_v \cdot C_3^1 = \sigma_v''$ and (b) $C_3^2 \cdot \sigma_v' \cdot C_3^1 = \sigma_v$
5. Obtain the relation: $[A] = [A]_0 e^{-(k_1+k_2)t}$ considering the reaction to be of first order.
6. Derive a matrix for the symmetry element E.
7. Explain the role of a carrier gas in a chain reaction.
8. Write about the infrared activity of water molecule.
9. Prove that $C_n^n = E$ giving suitable example.

Q.3 [A] For the enzyme catalyzed reaction of type: [06]



Derive an equation for maximum rate of reaction and explain how it varies under the low and high substrate concentration.

[B] What are consecutive reactions? Derive the mathematical relation for the concentrations of reactants and products. [06]

OR

[B] Discuss the plug flow method for determining the rate of fast reactions and derive the relation $C_f = C_i e^{-kt}$ [06]

Q.4 [A] Discuss in detail the Rice-Ramsperger-Kassel-Marcus (RRKM) theory. [06]

[B] Explain the kinetic mechanism involved in the photochemical decomposition of ethane. [06]

OR

[B] For a first order parallel reaction, the Arrhenius factor for formation of two products is 10^{10} and 10^8 sec^{-1} and their energy of activation are 150 kJ mol^{-1} and 75 kJ mol^{-1} , respectively. At what temperature the two products will be formed at the same rate? (Given: $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) [06]

(2)

Q.5 [A] Construct the character table for C_{3v} point group. [06]

[B] Answer the following:

i) Show that under orthogonal transformation the length of the vector remains unchanged. [03]

ii) What is a matrix? What are the conditions for the matrix to be orthogonal? [03]

OR

[B] Derive the transformation matrix for clock-wise and anticlock-wise rotations. [06]

Q.6 [A] For a C_{2v} point group, generate the matrix taking Sulphur dioxide (SO_2) as an example. Show that $\Gamma_v = 2A_1 + B_2$ [06]

C_{2v}	E	$C_{2(z)}$	σ_{xz}	σ_{yz}		
A_1	1	1	1	1	T_z	$x^2; y^2; z^2$
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	T_x, R_y	xz
B_2	1	-1	-1	1	T_y, R_x	yz

[B] Explain the electronic spectra of Carbonyl chromophore taking a suitable example. [06]

OR

[B] Discuss the binding in water molecule. [06]

