

(110)

No. of Printed Pages : 4

SARDAR PATEL UNIVERSITY

M. Sc. SEMESTER-II Examination

Friday 26th October, 2018

10.00 A.M. To 01.00 P.M.

Topics in Physical Chemistry-II: PS02CCHE23 [Total Marks: 70]

N.B. Figures to the right of each of the question indicate marks

1. Choose appropriate answer of the following [08]

(i) According to the collision theory, all collisions do not lead to reaction. Which choice gives both reasons why not all collisions between reactant molecules lead to reaction?

(1) The total energy of two colliding molecules is less than some minimum amount of energy

(2) Molecules cannot react with each other unless a catalyst is present

(3) Molecules that are improperly oriented during collision will not react

(4) Solids cannot react with gases

(a) 1 & 3 (b) 1 & 2 (c) 1 & 4 (d) 2 & 3

(ii) The rate of reaction of spontaneous reaction is generally very slow. This is due to the fact that..

(a) the equilibrium constant of the reaction is < 1

(b) the activation energy of the reaction is large

(c) the reaction is exothermic

(d) the reaction is endothermic

(iii) The symmetry point group of the most stable geometry of the following molecule Cl(H)C=C=C(H)Cl is.....

(a) C_1 (b) C_{2v} (c) C_2 (d) C_{2h}

(iv) A first-order reaction has a rate constant of $3.0 \times 10^{-3} \text{ sec}^{-1}$. The time required for the reaction to be 75 % complete is

(a) 95.8 s (b) 201 s (c) 231 s (d) 462 s

(1)

(PTO)

- (v) Which pairing of molecule and point group is correct?
 (a) CHCl_3 , C_{3v} (b) CH_2Cl_2 , T_d (c) CCl_4 , D_{4d} (d) CCl_2Br_2 , C_{2h}
- (vi) Which one of the following statements regarding V_{max} and K_M is false?
 (a) V_{max} is the maximum rate at which a particular enzyme-catalyzed reaction can proceed
 (b) K_M is the concentration of substrate at which the rate of the reaction reaches V_{max}
 (c) A small value of K_M tells us that an enzyme binds strongly to its substrate
 (d) A large value of K_M tells us that an enzyme shows little specificity for a given substrate
- (vii) CO_2 has
 (a) stretching modes only
 (b) 3 vibrational modes
 (c) 4 vibrational modes, 2 of which are degenerate
 (d) an IR active symmetric stretch
- (viii) The number of degrees of vibrational freedom possessed by CH_4 is:
 (a) 10 (b) 6 (c) 4 (d) 9

2. Attempt any SEVEN of the following

[14]

- For a linear molecule with C_{∞} axis show that it belongs to $C_{\infty v}$
- Give the procedure for determining the irreducible representations of the vibrational modes in non-linear molecules.
- How many modes of vibration of planar trans-1,2-dichloroethylene have? Sketch all the modes with a neat diagram.
- Enlist the conditions for Orthogonality of a matrix and prove that $AA^T = E$ meets such condition.
- Obtain the relation: $\ln\left(\frac{m}{m-x}\right) = (k_1 + k_{-1})t$
- State the effect of temperature on enzyme catalysis.

(2)

7. Identify the point groups of the following: BF_4^+ , SF_4 , XeF_4 , NO_2

8. Write about the objections to Hinshelwood theory.

9. State the applications of stirred flow reactor.

3. [A] What is relaxation time? Obtain the relation $\tau = (k_1 + 2k_2 x_c)^{-1}$ [6]

[B] What are Parallel reactions? Derive mathematical relations for the concentrations of A, B and C, considering first order reactions. [6]

OR

[B] Explain how does an ionic strength of a solution affect the rates of reactions? [6]

4. [A] Discuss in detail about the collision theory of bimolecular reactions. [6]

[B] Discuss in detail the kinetic mechanism involved in the photochemical reaction of Hydrogen-Bromine. [6]

OR

[B] (i) Explain the conditions for the kinetic and thermodynamic control of opposing reactions. [3]

(ii) The rate constant for second-order reaction is $5.70 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 25°C and $1.64 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 40°C . Calculate the activation energy and the pre-exponential factor. (Given: $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$) [3]

5. [A] The character table for D_5 point group is: [6]

D_5	E	$2C_5(z)$	$2(C_5)^2$	$5\sigma_v$
τ_1	1	1	1	1
τ_2	1	1	1	-1
τ_3	2	a	b	c
τ_4	2	d	e	f

Deduce unknown values of a to f.

[B] Obtain the transformation matrix corresponding to σ_v , σ'_v and σ''_v [6]

OR

[B] (i) For an orthogonal matrix show that C_2^+ and C_2^- are the same symmetry operations while C_3^+ & C_3^- are different symmetry operation. [3]

(ii) For NH_3 molecule prove that: [3]

(a) $C_3^1 \times \sigma_{v1} = \sigma_{v2}$ (b) $C_3^1 \times \sigma_{v2} = \sigma_{v3}$ (c) $C_3^1 \times \sigma_{v3} = \sigma_{v1}$

(3)

(P.T.O)

6. [A] Give the symmetry enabled selection rules for Infrared spectra. [6]

[B] Explain about the symmetries of normal modes of ethylene using group theory formulations. [6]

OR

[B] NH_3 belongs to C_{3v} point group, considering the character table for the same prove that: (i) $\Gamma_{\text{vib}} = 2A_1 + 2E$ and (ii) $\Gamma_{\text{int}} = 2A_1 + 2E$ [6]

C_{3v}	E	$2C_3(z)$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	-1	R_z	
E	2	-1	0	(x,y) (R_x, R_y)	($x^2 - y^2, xy$) (xz, yz)

— X —

(4)