

2017**M.Sc.****2nd Semester Examination****CHEMISTRY****PAPER—CEM-201***Full Marks : 40**Time : 2 Hours**The figures in the margin indicate full marks.**Candidates are required to give their answers in their own words as far as practicable.**Illustrate the answers wherever necessary.***(Physical Chemistry)**

Answer four questions,
taking one question from each group.

Group—A

Answer any one of the following.

1. (a) Hamiltonian operator of a simple Harmonic Oscillator is given by

$$H = \left(a^{\dagger}a + \frac{1}{2} \right) \hbar\omega$$

(Turn Over)

Evaluate : (i) $a |n\rangle = ?$

(ii) $a^+ |n\rangle = ?$

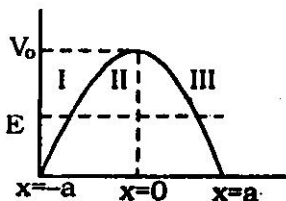
Show that, $|n\rangle = \frac{(a^+)^n}{\sqrt{n!}} |0\rangle$.

(b) Give a schematic plot for radial probability density $(|R_{ne}(r)|^2)$ of the following hydrogenic orbitals

(i) $|R_{ne}(r)|^2$ vs. $\frac{r}{a_0}$ for $n=2, l=0$

(ii) $|R_{ne}(r)|^2$ vs. $\frac{r}{a_0}$ for $n=3, l=1$. 3+3+2+2

2. (a) Consider a particle of mass 'm' moving in 1-dim and its potential is schematically shown below,



Transmission co-efficient of the particle to the region-III is given by

$$T = \exp \left[-2 \left\{ \frac{8\pi^2 m}{h^2} (V(x) - E) \right\}^{1/2} \cdot d \right]$$

where 'd' is the thickness of the barrier. Use the appropriate form of the potential to show,

$$T = \exp \left[-\frac{\pi^2 d}{h} \{2m(V_0 - E)\}^{1/2} \right]$$

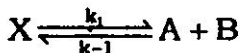
Comment on your result.

- (b) Use operator method to obtain the zero point energy of a simple Harmonic Oscillator. 6+4

Group—B

Answer any one of the following.

3. (a) The kinetic reaction



is completed within a time 1 μ sec. Describe a suitable method to study such a kinetic reaction and hence give an idea to determine the forward and backward rate constant.

- (b) "A 'Lineweaver-Burk' plot is not suitable to determine the individual rate constant of a enzyme catalysis reaction". - Justify the statement. (6+2)+2

4. (a) Define 'turnover number' of a kinetic reaction.
- (b) Define autocatalytic reaction with a suitable example.
- (c) What are the main criteria of a redox reaction occurring through outer sphere mechanism ?
- (d) The gas phase reaction $\text{CO} + \text{Cl}_2 \xrightarrow{k} \text{COCl}_2$, is second order (first order in each reactant). If $P_{\text{CO}}^0 = P_{\text{Cl}_2}^0 = 0.1 \text{ atm}$ and $t_{\frac{1}{2}}$ is 1 hour at 25°C but 30 min at 35°C , then
- (i) Calculate k at 25°C .
- (ii) Calculate E and A of Arrhenius equation and ΔS^\ddagger and ΔH^\ddagger of the transition state theory. 2+2+2+4

Group—C

Answer any one of the following.

5. (a) An electron in hydrogen atom is in superposition state described by the wave function,

$$\psi(r) = A \left[4\psi_{100}(r) - 2\psi_{211}(r) + \sqrt{6}\psi_{210}(r) - \sqrt{10}\psi_{211}(r) \right]$$

- (i) Find the normalization constant 'A'.
- (ii) What is the expectation value of energy, E of electron ?
- (iii) What is the expectation value of \hat{L}^2 ?
- (b) The wave function of a simple Harmonic Oscillator is in the superposition state.

$$\psi(x, 0) = \frac{1}{\sqrt{2}} [\psi_0(x) + \psi_1(x)]$$

Find $\psi(x, t)$?

2+3+3+2

6. (a) Write down the salient features of transition state theory.
- (b) Define heterogeneous catalysis with a suitable example.
- (c) Antibiotic resistant bacteria have an enzyme penicillinase that catalyzes the decomposition of the antibiotic. The molecular mass of penicillinase is 30,000 g/mole the turnover number of the enzyme at 28°C is 2000 sec⁻¹. If 6.4 μg of penicillinase catalyzes the destruction of 3.11 mg of amoxicillin, an antibiotic with a molecular mass of 364 g/mole in 20 secs at 28°C, how many active sites does the enzyme have ?

4+3+3

Group—D

Answer any *one* of the following.

7. (a) Show different types of modes of vibration of AB_3 type molecule. Assign the IR and Raman active modes of vibrations.
- (b) How can you differentiate fluorescence from Raman signals ?
- (c) Mention some disadvantages of Raman spectroscopy.
- (d) Why is it easier to study the biological samples by Raman spectroscopy ?
- (e) What is the full form of SERS ? What are the metals that usually respond in SERS ?

2+2+2+2+2

8. (a) What would be the selection rule under harmonic approximation for a molecule to exhibit vibrational Raman spectrum of homonuclear diatomic molecule ?
- (b) Raman shift of a given Raman spectral line does not change if the frequency (ν_0) of the incident radiation is changed - Criticize or justify the statement.

- (c) How many normal modes of vibration are possible for HBr, OCS (linear) and SO₂ and C₆H₆ ? Identify the modes which are IR active and Raman active separately.
- (d) Write down the equation describing the dependence of the intensity of Rayleigh scattering on the wavelength, intensity of the light source.
- (e) What is coherent anti Stokes Raman Spectroscopy ? What are its advantages ? 2+2+2+2
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