

**2018**

**M.Sc. 2nd Semester Examination**

**CHEMISTRY**

**PAPER—CEM-201**

**Subject Code—24**

*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 )**

**Group—A**

**Group—A(a)**

Answer any *two* questions of the following.

2×2

1. A hydrogen atom is placed in an electric field along the x-axis. Find the orbital that mixes most with the ground state, 1s orbital.

*(Turn Over)*

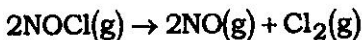
2. Find the average value of radius  $\langle r \rangle$  in the 2S state of hydrogen atom in terms of Bohr radius,  $a_0$ .
3. State and explain the parity selection rules for electric dipole transition during two photon absorption process.
4. Define turn over number of an enzyme catalyzed reaction.

**Group—A(b)**

Answer any *two* questions of the following.

2×2

5. Write down the principle of relaxation method.
6. The Arrhenius parameters for the thermal decomposition of NOCl



are  $A = 10^{13} \text{ M}^{-1} \text{ s}^{-1}$ ,  $E_a = 105 \text{ kJ mol}^{-1}$  at 300K.

Find out the value of enthalpy of activation.

7. Which of the following statements are true ?

- (a) A vibration is infrared active if it belongs to the same symmetry species as a component of dipole moment, i.e. to the same species as either  $x$ ,  $y$  or  $z$ .
- (b) A vibration is Raman active if it belongs to the same symmetry species as a component of polarizability, i.e. to one of the binary products  $x^2$ ,  $y^2$ ,  $z^2$ ,  $xy$ ,  $xz$ ,  $yz$  or to a combination of products such as  $x^2 - y^2$ .
- (c) All of the above.
- (d) None of the above.

8. How can you differentiate fluorescence from Raman signals ?

**Group—B**

**Group—B(a)**

Answer any *two* questions of the following.

4×2

9. Show that in the  $n^{\text{th}}$  eigen state of Harmonic oscillator, the average kinetic energy  $\langle T \rangle$  is equal to the average potential energy  $\langle V \rangle$ .

10. The Hamiltonian operator of a particle executing simple Harmonic motion is

$$H = A a^+ a + B(a^+ + a)$$

where 'A' and 'B' are constant. Find the energy expectation value of the particle.

11. An electron in hydrogen atom is in superposition of states described by the wavefunction,

$$\psi(r, \theta, \phi) = \frac{1}{6} [4\psi_{1,0,0} - 2\psi_{2,1,1} + \sqrt{6}\psi_{2,1,0} - \sqrt{10}\psi_{2,1,-1}]$$

Find the expectation values of  $L^2$  and  $L_z$ .

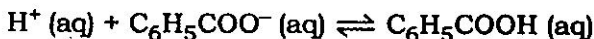
12. Find out the expression for relaxation time of a kinetic reaction whose forward reaction path is bimolecular and backward reaction path is unimolecular. Given, initial concentrations of both the reactants' are same.

### Group—B(b)

Answer any *two* questions of the following.

4×2

13. Calculate the relaxation time for the reaction



for a temperature jump experiment to a final temperature of 298 K. The solution was initially prepared by adding 0.015 moles of benzoic acid to water such that a liter of total solution was made. Assume that both the forward and backward reactions are first order in each reactants and the forward and backward rate constants are

$$k_1 = 3.5 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ and}$$

$$k_{-1} = 2.2 \times 10^6 \text{ s}^{-1} \text{ respectively.}$$

14. (a) What are the parameters that control the intensity of Rayleigh Scattered lines ?
- (b) What are the disadvantages of Raman spectroscopy ? 2+2
15. (a) Explain, in brief, the rule of mutual exclusion.
- (b) What are the advantages of studying biological samples of Raman spectroscopy ? 2+2
16. (a) What are the parameters that control the widths of Raman spectral lines.
- (b) Why LASER is required as a light source in Raman spectroscopic studies ? 2+2

**Group—C****Group—C(a)**

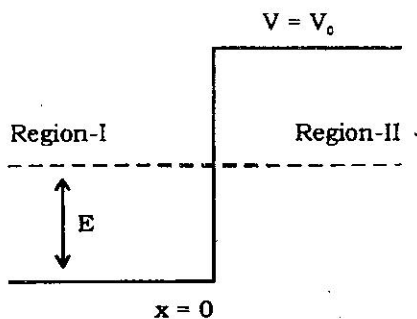
Answer any *one* question of the following.

8×1

17. Consider a particle of mass  $m_e$  moving in 1-dim in the +ve x-direction in a potential defined by

$$V = 0 \quad \text{for } x < 0$$

$$V = V_0 \quad \text{for } x > 0$$



Write down the time independent Schrödinger equation and their possible solution for eigen functions in the Region-I & II. Show that the transmission co-efficient is not zero unless the potential energy of the barrier is infinite.

18. Wave function for Harmonic Oscillator is given by,

$$\psi_v = N_v H_v \left( \alpha^{1/2} x \right) e^{-\alpha x^2 / 2}$$

where symbols have their usual significances.

Show that there must be some fluctuation in dipole moment of the oscillator to show any transition between the vibrational level and deduce the selection rule for the same. Identify relation for the Hermite polynomials is given below,

$$\xi H_v(\xi) = v H_{v-1}(\xi) + \frac{1}{2} H_{v+1}(\xi).$$

**Group—C(b)**

Answer any *one* question of the following.

8×1

19. (a) What is an enzyme inhibition reaction? Derive the expression of rate equation of a mixed enzyme inhibition reaction.

(b) How does an oscillatory reaction occur?

(c)  $\gamma_{\max}$  and  $\kappa_m$  for an enzyme catalyzed reaction are  $2.0 \times 10^{-3} \text{ Ms}^{-1}$  and  $1.0 \times 10^{-6} \text{ M}$  respectively. Find out the rate of the reaction when the substrate concentration is  $1.0 \times 10^{-6} \text{ M}$ .

4+2+2

20. (a) Show the different modes of vibrations of a  $AB_2$  type non-linear molecule and assign the modes of vibrations which are IR active and which are Raman active ?
- (b) What is resonance Raman spectroscopy ?
- (c) What is CARS ?

3+3+2