2022

M.Sc.

2nd Semester Examination (CCAE)

CHEMISTRY

PAPER—CEM-201

PHYSICAL CHEMISTRY-II

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.

Group—A

Answer any *four* questions. 4×2

1. A quantum mechanical rigid rotator is described by the following wave function,

$$\psi(\theta,\varphi) = \frac{1}{\sqrt{30}}\left[Y_4^0(\theta,\varphi) + 5Y_6^0(\theta,\varphi) - 2Y_6^3(\theta,\varphi)\right]$$

where $Y_l^m(\theta,\varphi)$ are the spherical Harmonics. Find the probability of the system to be found with $l = 6$.

2. Probability density of IS electron near the nucleus of H-atom is maximum. – Explain.

3. State differences between order and molecularity.

4. Cite one example of i) Fractional order reaction and ii) negative order reaction.

5. What is relaxation time?

6. Coherent Anti-Stokes Raman Spectroscopy can be considered as an alternative technique to give a stronger signal than normal Raman spectroscopy – criticize or justify.

Group—B

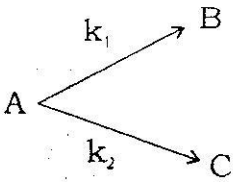
Answer any *four* questions. 4×4

7. State and prove Eckart's theorem.

8. For a quantum Harmonic Oscillator, show that;

$$\left|n\rangle = \frac{(a\dagger)^n}{\sqrt{n!}}\right|0\rangle$$; where symbols have their usual significances.

9. Calculate concentrations of B and C at any time t of the above parallel reaction $k_1 k_2$.



10. For a consecutive reaction $A \rightarrow B \rightarrow C$ calculate the time when [B] will be maximum.

11. State limitations of Collision theory. How are these limitations overcome by Ledermann's hypothesis?

12. Carbon dioxide is IR inactive, but it is Raman active. Explain with the shape of polarization ellipsoid.

Group—C

Answer any *two* questions. 2×8

13. (a) Deduce the expression of Hamiltonian operator of a linear Harmonic Oscillator in terms of raising and lowering operators.

(b) Consider a linear Harmonic Oscillator as a superposition of state,

$$\varphi(x,0) = \frac{1}{\sqrt{2}}\left[\varphi_0(x) + \varphi_1(x)\right]$$

Show that at any time t; $\langle x \rangle = \sqrt{\frac{h}{2m\omega}} Cos(\omega t)$.

14. Deduce the selection rule for a diatomic molecule undergoing transition from the vibrational quantum level v to v'.

Given below the recursion relation of Hermite polynomial,

$$\xi H_V(\xi) = \upsilon H_{\upsilon-1}(\xi) + (1/2) H_{\upsilon+1}(\xi)$$

15. Derive an expression for relaxation time of the reaction

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} P$$

16. (a) Give an example of *Auto Catalytic Reaction.*

(b) Derive an expression for Michaels Constant for homogeneous enzyme catalysed reaction. 2+6

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