Q.P. Code – 42536

Fifth Semester B.Sc. Degree Examination, October/November 2019

(CBCS Scheme)

Chemistry

Paper VI (5.2) — PHYSICAL CHEMISTRY

Time : 3 Hours] *[Max. Marks : 90*

Instructions to the Candidates :

1) *The question paper has Two Parts, Part A and Part B*

2) *Answer Both the Parts.*

PART – A

Answer any **TEN** of the following questions. Each question carries **2** marks : **(10 × 2 = 20)**

($h = 6.626 \times 10^{-34}$ JS, $c = 3 \times 10^{8}$ ms^{-1}, $m_e = 9.11 \times 10^{-31}$ kg)

1. How can you justify the quantisation of energy for a particle in one dimensional box? **(2)**

2. What is the commutator of the two operators $\hat{A}$ and $\hat{B}$? What is its value when the operators commute? **(2)**

3. An electron is confined to an infinite one dimensional box of length 4×10^{-10} m. Calculate its energy in the fourth energy level. **(2)**

4. Write the expression for the angular and radial wave functions for hydrogen like particles. **(2)**

5. Write expression for ψ_{MO} and ψ_{+MO} for H_2^+ ion according to LCAO method. **(2)**

6. Write any two postulates of Molecular orbital theory. **(2)**

7. How many signals are observed in the PMR spectrum of ethyl alcohol? Indicate their multiplicity. **(2)**

8. Calculate the ESR frequency in a magnetic field of 3.5 T. Given g = 2 and $\mu_B = 9.273 \times 10^{-24}$ JT^{-1}. **(2)**

9. Why N_2 molecule does not exhibit rotational spectrum but NO exhibit? **(2)**

10. What are

    (a) fundamental bands and

    (b) hot bands. **(2)**

11. What happens to the quantum yield of photosynthesis of HCl, if the vessel contains traces of oxygen. Explain with reason. **(2)**

12. Calculate the value of Einstein corresponding to a radiation of wavelength 300 nm. **(2)**

PART – B

Answer any **SEVEN** of the following questions. Each question carries **10** marks : **(7 × 10 = 70)**

13. (a) Derive Schrodinger wave equation based on the postulates of quantum mechanics.

    (b) Let $\hat{A} = 4x^2$ and $\hat{B} = \frac{d}{dx}$ and $f(x) = \alpha x^3$. Find $\hat{A}\,\hat{B}\,f(x)$ and $\hat{B}\,\hat{A}\,f(x)$.

    (c) Give the expression for a wave function of a particle is one dimensional box. Convert it into a normalized wave function. **(4 + 3 + 3)**

14. (a) Derive Heisenberg's uncertainity principle from the expectation values of x, x^2, p_x and p_x^2.

    (b) If $\hat{A}$ and $\hat{B}$ are two operators such that $[\hat{A}\,\hat{B}] = 1$, show that $[\hat{A}\,\hat{B}^2] = 2\,\hat{B}$.

    (c) Show that the square of the angular momentum (L^2) and its z-component (L_z) commute with each other. (Given –

    $[\hat{L}_x^2, \hat{L}_z]$ = its $(L_x L_y + L_y L_x)$ and

    $[\hat{L}_y^2, \hat{L}_z]$ = its $(L_x L_y + L_y L_x)$ and

    $[L_z^2, L_z] = 0$) **(4 + 3 + 3)**

15. (a) Solve the Schrodinger wave equation of a simple harmonic oscillator for θ (Theta) equation.

(b) What is degeneracy? Calculate the degeneracy of the energy level with energy equal to $14h^2/8ma^2$.

(c) Show that the function $\cos ax$ is an eigen function of $\frac{d^2}{dx^2}$. Find the corresponding eigen value. **(4 + 3 + 3)**

16. (a) Sketch the molecular orbital diagram of LiH molecule. Calculate it s bond order.

(b) Using LCA_0 approximation, write down the complete wave function for a heteronuclear diatomic molecule AB assuming that it has 85% covalent character and 15% conic character.

(c) Compare the main features of the valence bond theory with that of the molecular orbital theory. **(4 + 3 + 3)**

17. (a) Explain the mechanism of photochemical dissociation of HI.

(b) Derive the expression for the operator $\left(\frac{d}{dx}x\right)^2$.

(c) What is Zero point energy? What does it signify? **(4 + 3 + 3)**

18. (a) State the following with reference to rotational spectra

(i) energy expression

(ii) region of appearance

(iii) criterion

(iv) selection rule.

(b) The separation of rotational spectral lines occurred at 332 m^{-1} for NO molecule. Calculate internuclear distance. (Given, $\mu_{NO} = 1.24 \times 10^{-26}$ kg ; $h = 6.626 \times 10^{-34}$ JS).

(c) Mention any three applications of rotational spectra. **(4 + 3 + 3)**

19. (a) Show that pure vibrational spectra consists of a single line of same frequency.

(b) Vibrational rotational spectrum of HBr shows an absorption band centred at $2.652 \times 10^5\ m^{-1}$. Calculate the force constant and Zero point energy. (Given – $\mu = 1.653 \times 10^{-27}$ kg, $h = 6.627 \times 10^{-34}$ JS, $c = 3 \times 10^8\ ms^{-1}$.

(c) Calculate the total number of modes of vibrations for

(i) CO_2 and

(ii) H_2O molecules.

Indicate how many of them are IR active. **(4 + 3 + 3)**

20. (a) Discuss the origin of Raman spectra. Explain the terms

(i) Rayliegh lines

(ii) Stokes lines.

(b) State mutual exclusion rule. What are antistokes lines?

(c) State Franck-condon principle. What are singlet and triplet states? **(4 + 3 + 3)**

21. (a) Explain fine splitting of proton NMR spectra in

(i) $ClCH_2CH_2I$ and

(ii) CH_3CHO.

(b) Give the hyperfine splitting of ESR spectrum of methyl radical ($\bullet CH_3$).

(c) What is chemical shift? What are the scales used to measure it? How are they related? **(4 + 3 + 3)**

22. (a) Derive Beer–Lambert's law. What are its limitations?

(b) A substance absorbs 2.6×10^6 quanta of radiation per second. 0.002 mol of substance undergoes chemical reaction in 1200 S. Calculate quantum efficiency.

(c) What is photosensitization? Explain with an example. **(4 + 3 + 3)**
