(8 pages) **Reg. No. :** .....

Code No. : 8853 **Sub. Code : KCHM 33**

M.Sc. (CBCS) DEGREE EXAMINATION, NOVEMBER 2017.

Third Semester

Chemistry

PHYSICAL CHEMISTRY – III

(For those who joined in July 2016 – 2017)

Time : Three hours Maximum : 75 marks

PART A — (10 × 1 = 10 marks)

Answer ALL questions.

Choose the correct answer :

1. Find the point group if centre of symmetry is added to the symmetries of a molecule belonging to C_{4v} molecule.
   (a) D_{4h} (b) C_{6h}
   (c) D_{6h} (d) C_{2h}

2. An example of cyclic group is
   (a) C_2 (b) C_{2v}
   (c) C_{3v} (d) C_{2h}

3. Which of the following have both IR and Raman active modes?
   (a) CO_2 (b) C_2H_2
   (c) trans-N_2F_2 (d) NH_3

4. The number of vibrational modes for $POCl_3$ molecule is
   (a) 15 (b) 9
   (c) 6 (d) 2

5. Nuclei possessing electric quadrupole moment, if the spin quantum number is
   (a) $I = 0$ (b) $I = ½$
   (c) $I < 1$ (d) $I \leq 0$

6. As 's' electron density decreases, generally the isomer shift ————————.
   (a) increases
   (b) decreases
   (c) unchanged
   (d) increases and then deceases

7. Write the spin multiplicity of NMR signals of $CH_3CH_2OCH_2CH_3$
   (a) two triplets
   (b) a triplet and a quartet
   (c) two singlets
   (d) two singlets and two triplets

8. Which of the following systems will show electron spin resonance (ESR) spectrum?

(a) H_2 (b) Na^+

(c) Cl^- (d) NO_2

9. What happens to the λ_{max} wavelength of absorption as the number of conjugation increases?

(a) increases

(b) decreases

(c) unchanged

(d) increases and then deceases

10. Absorption of radiation in the UV range attributable to $n \rightarrow \pi^*$ electronic transition is characteristic of which type of compound?

(a) aromatic hydrocompound

(b) unsaturated carbonyl compounds

(c) non-conjugated polyenes

(d) conjugated polyenes

PART B — (5 × 5 = 25 marks)

Answer ALL questions, choosing either (a) or (b).

Each answer should not exceed 250 words.

11. (a) Construct C_{3v} point group multiplication table. Using multiplication table show that C_{3v} point group is non-abelian.

Or

(b) What is meant by similarity transformation? Using similarity transformation classify the symmetry operations of the point group of water molecule.

12. (a) Using group theory, determine whether $\pi \rightarrow \pi^*$ is allowed in the case of ethylene molecule.

Or

(b) Carryout normal mode analysis of NH_3 molecule using group theory.

13. (a) How does electric field gradient arise in NQR?

Or

(b) Write notes on :

(i) recoil energy

(ii) quadrupole splitting

14. (a) How many types of orientations take place when a proton is placed in a magnetic field? What are they? How do they arise?

Or

(b) In a given organic compound, two kinds of protons exhibit signals at 50 Hz and 200 Hz using a 60 MHz NMR instrument. What would be their equivalent positions using 90 MHz spectrometer. Also convert the signals at 50 Hz and 200 Hz into δ and t values.

15. (a) What type of transitions are observed in α, β–unsaturated carbonyl compounds? How absorption maximum and intensity are shifted when carbonyl group is not conjugated?

Or

(b) Discuss the principle and theory of different types of Lasers.

PART C — (5 × 8 = 40 marks)

Answer ALL questions, choosing either (a) or (b)
Each answer should not exceed 600 words.

16. (a) State "The Great Orthogonality Theorem". Discuss the Properties and significances of The Great Orthogonality Theorem.

Or

(b) What are reducible and irreducible and irreducible representations? Illustrate the Properties of reducible and irreducible representations. Give examples for reducible and irreducible representations.

17. (a) Discuss the salient features of HMO. Apply the HMO features on butadiene and determine the delocalization energy of butadiene.

Or

(b) How is group theory useful in explaining the possible electronic transition in ethylene and butadiene?

18. (a) (i) Write a note on interaction of nuclear quadrupole with electric field gradient.

(ii) How did you deduce the bonding nature of a molecule from NQR data?

Or

(b) Discuss the principle and experimental technique of mossbauer spectra.

19. (a) (i) How many different types of protons are present in allyl bromide molecule? Label the types of protons.

(ii) Aromatic protons are more deshielded than ethylene protons, although both the types of protons are attached to sp^2 hybridized carbon atom. Explain.

(iii) How will you distinguish between inter and intra molecular hydrogen bonding on the basis of PMR spectroscopy.

Or

(b) (i) Predict and explain the number of lines in the ESR spectra of the following systems?

(1) $CH_3\dot{C}H_2$

(2) $\dot{C}H_3$

(3) Mn^{2+}

(4) $C_6H_6^-$.

(ii) What will be the ESR frequency in a magnetic field of 25000 Gauss of g = 2 and $\beta = 9.273 \times 10^{24} JT^{-1}$?

Formula :

$$\upsilon = g\beta H / h = 2 \times 9.273 \times 10^{24} / 6.626 \times 10^{34} Js^{-1}$$

20. (a) (i) Acetaldehyde [CH_3CHO] is having absorption peaks at 160 nm, 180 nm and 292 nm. What type of transition is responsible for each of these absorptions?

(ii) Write notes on vibronic coupling.

Or

(b) (i) Two sets of photoelectrons are emitted from N_2 on excitation with He (I) radiation of wavelength 58.4 nm. These have kinetic energies of 5.60 eV and 4.23 eV respectively. Find the ionisation energies of these electrons.

(ii) Explain : Q-switching.

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