(7 Pages) **Reg. No. :** .....

Code No. : 6354 **Sub. Code : PCHM 33**

M.Sc. (CBCS) DEGREE EXAMINATION,
NOVEMBER 2021

Third Semester

Chemistry — Core

PHYSICAL CHEMISTRY — III

(For those who joined in July 2017 onwards)

Time : Three hours Maximum : 75 marks

PART A — (10 × 1 = 10 marks)

Answer ALL questions.

Choose the correct answers :

1. Which of the following principal axis correspond to benzene?

   (a) C_2 (b) C_3

   (c) C_6 (d) C_5

2. How many reflection planes do $[PtCl_4]^{2-}$ ions have?

   (a) 1 (b) 4

   (c) 3 (d) 5

3. Normal modes of vibration of CH_4 molecule is

(a) 15 (b) 9

(c) 6 (d) 3

4. Which of the following molecule have both IR and Raman active modes?

(a) CO_2 (b) C_2H_2

(c) trans-N_2F_2 (d) HCN

5. $^3J_{HH}$ coupling constants are dependent on

(a) Magnetic field strength

(b) Relative orientation of the coupled protons

(c) Sample concentration

(d) 90° pulse width

6. How many signals does the aldehyde $(CH_3)_3CCH_2CHO$ have in ^1H NMR and ^{13}C NMR spectra?

(a) Five ^1H signals and six ^{13}C signals

(b) Three ^1H signals and four ^{13}C signals

(c) Five ^1H signals and four ^{13}C signals

(d) Three ^1H signals and six ^{13}C signals

7. ESR spectrum of anthracene radial anion consists of

(a) 25 lines (b) 50 lines

(c) 75 lines (d) 100 lines

8. NQR spectra is observed in ———— region.

(a) Microwave (b) Radiofrequency

(c) X-ray (d) UV/Visible

9. What is the main factor on which chemical shift depends in Mössbauer spectra?

(a) Electron density (b) Transition energy

(c) Intensity of light (d) All of these

10. In mass spectrometer, the sample that has to be analysed is bombarded with which of the following?

(a) protons (b) electrons

(c) neutrons (d) alpha particles

PART B — ($5 \times 5 = 25$ marks)

Answer ALL questions, choosing either (a) or (b).
Each answer should not exceed 250 words.

11. (a) Construct the multiplication table for water molecule.

Or

(b) Differentiate between reducible and irreducible representations.

12. (a) Group theory is useful in constructing the hybrid orbit. Discuss it by taking CH_4 molecule.

Or

(b) Discuss the electronic spectra of ethylene.

13. (a) What magnetic field strength must be applied to a free proton for spin transition to occur at 60 MHz? ($Y = 26.7522 \times 10^7 rad\ T^{-1}S^{-1}$).

Or

(b) Discuss the nuclear spin-spin interaction taking the sample of ethyl alcohol.

14. (a) Explain the significance of 'g' value in ESR spectroscopy. Explain the factors which influence the 'g' value.

Or

(b) Give a detailed note on the double resonance technique in ESR spectroscopy.

15. (a) State and explain the Franck – Condon principle.

Or

(b) Draw and explain Fortrat diagram.

PART C — (5 × 8 = 40 marks)

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

16. (a) State and explain the great orthogonality theorem. By using the GOT construct C_{3v} character table.

Or

(b) Find the symmetry elements and symmertry operations and determine the point groups of the following molecules.

(i) Benzene

(ii) Trans-N_2F_2

(iii) Diborane

(iv) BF_3

(v) FeF_6^{3-}

(vi) $CHClBr(CH_3)$

(vii) IF_5

(viii) Thiophene.

17. (a) Obtain the hybrid orbitals for the sigma bonds in BF_3 molecule.

Or

(b) Discuss the salient features of HMO. Apply the HMO, arrive at the delocalization energy for 1, 3 – butadiene system.

18. (a) (i) Discuss the principle and application of INDOR.

(ii) Discuss the theory and principle of ^{19}F NMR.

Or

(b) How many kinds of protons are in the following molecules?

(i) CH_3CH_3

(ii) $CH_3CH_2CH_3$

(iii) $(CH_3)_2CHCH_2CH_3$

(iv) $C_6H_5CH_3$

(v) $C_6H_5NO_2$

(vi) $CH_2 = CH_2$

(vii) $CH_3CH = CH_2$

(viii) $CH \equiv CH$.

19. (a) Explain the theory, principle and applications of NQR spectroscopy.

Or

(b) (i) In an ESR spectrometer operating at 9.233 GHz, the center of the spectrum of CH_3 radical occurred at 329.4 mT. Calculate the 'g'-value of the free radical.

(ii) Illustrate Kramers' degeneracy using energy level diagram.

20. (a) Discuss the theory, principle application of photoelectron spectroscopy.

Or

(b) Discuss the theory, principle and applications of Mössbauer spectroscopy.

———————