

- (b) Discuss the Mc-Connell equation and its application by taking suitable example.
- (c) Discuss the hyperfine structure in ESR spectra of an electron interacting with two non-equivalent protons. [Hint : Use 'stick diagram' and take $a_1 > a_2$]
- (d) List the factors which determine the suitability of a nucleus for investigation by NMR spectroscopy.

3,2,2,2

Section C

6. (a) Draw stereogram corresponding to the following combination of symmetry elements :
- (i) $\bar{3}m$
- (ii) $\bar{4}+i$
- (iii) $\frac{3}{m}$
- (iv) $3m$.
- Also state for each case, which point group is generated ?
- (b) Draw space group diagram for Pm. Specify the coordinates of general positions.
- (c) Why is 2_1 called a neutral axis ?

5,2,2

Roll No.

Total Pages : 05

LMDQ/D-23

6532

PHYSICAL CHEMISTRY GENERAL CHEM-302

Time : Three Hours]

[Maximum Marks : 45

Note : Attempt *Five* questions in all, selecting *one* question from each Section. Q. No. 1 is compulsory. All questions carry equal marks.

1. This question is compulsory :
- (i) What is the basic criteria for a molecule to be IR active ?
- (ii) Why is there no translational spectroscopy ?
- (iii) Express in eV, the thermal energy of a gaseous molecule at 298 K.
- (iv) Why is NQR observed in solid state ?
- (v) A NMR frequency is approximately equal to 60 MHz. Calculate the corresponding energy in kJ/mol.
- (vi) Why are ESR signals plotted in first-derivative mode ?

(vii) In tetragonal crystal system, A-centred lattice does not exist. Why ?

(viii) Prove $\vec{a}^* \cdot \vec{a} = 1$ and $\vec{b}^* \cdot \vec{b} = 0$

(ix) What is the index used to determine the accuracy of a structure after refinement ? Give corresponding expression. 1×9=9

Section A

2. (a) Show that for a diatomic rigid rotor, the moment of inertia is given by $I = \mu r^2$, where symbols have their usual meaning. Discuss how are molecules classified based on their principal moments of inertia ? Give one example for each group.

(b) The rotational spectra of $^{79}\text{Br}^{19}\text{F}$ shows a series of equidistant lines 0.71433 cm^{-1} . Determine the energy of $J = 9 \rightarrow J = 10$ transition.

(c) What are the degeneracies of the following diatomic rotational energy levels : 5,2,2

(i) 0

(ii) $\frac{6h^2}{I}$

3. (a) The fundamental vibrational frequency of H^{35}Cl is 2890 cm^{-1} . Calculate the force constant of a molecule in Nm^{-1} .

(b) Discuss the quantum theory of Raman scattering.

(c) Elaborate with an example, the concept of 'zero-point energy'. 4,3,2

Section B

4. (a) Explain with energy level diagram, the operating principle of NMR spectroscopy. Based on this diagram, justify why do nuclei such as ^{12}C , ^{16}O do not show NMR spectra.

(b) Explain the following terms :

(i) Chemical shift

(ii) Spin-spin coupling constant

(iii) Spin-Lattice relaxation. 4,5

5. (a) Calculate number of ESR lines in the following free radicals :

(i) Pyrazine

(ii) n-propyl

(iii) $^{13}\text{CF}_2\text{D}$.

7. (a) Using reciprocal lattice concept, derive expression for interplanar spacing in case of cubic crystal system and determine the ratio $\frac{d_{112}}{d_{321}}$?
- (b) Write down expression of structure factor for body-centered lattice and derive the corresponding condition for systematic absences. Justify here which hkl reflection will be observed at smallest value of θ ?
- (c) Powder XRD pattern of cubic crystal gives the following three peaks :
 2θ : 43.16; 50.30; 73.99
Index these reflections. **3,3,3**

7. (a) Using reciprocal lattice concept, derive expression for interplanar spacing in case of cubic crystal system and determine the ratio $\frac{d_{112}}{d_{321}}$?
- (b) Write down expression of structure factor for body-centered lattice and derive the corresponding condition for systematic absences. Justify here which hkl reflection will be observed at smallest value of θ ?
- (c) Powder XRD pattern of cubic crystal gives the following three peaks :
 2θ : 43.16; 50.30; 73.99
Index these reflections. **3,3,3**