

2022
M.Sc.
First Semester
 CORE – 03
CHEMISTRY
Course Code: MCHC 1.31
 (Physical Chemistry – I)

Total Mark: 70

Pass Mark: 28

Time: 3 hours

Answer five questions, taking one from each unit.

UNIT-I

- | | | |
|----|---|---|
| 1. | (a) Explain the algebra of operators. | 2 |
| | (b) Prove that if the eigenfunctions of a Hermitian operator have different eigenvalues, they are orthogonal. | 3 |
| | (c) Discuss the Lagrange's equation of motion. | 3 |
| | (d) Derive an expression for the energy of a rigid rotator using the Schrödinger equation. | 6 |
| 2. | (a) Write a note on energy eigenvalue equation. | 2 |
| | (b) Derive an expression for a particle in 1-dimensional box. | 5 |
| | (c) Discuss in detail the quantum mechanical tunnelling. | 7 |

UNIT-II

- | | | |
|----|---|---|
| 3. | (a) State and prove the Hellmann-Feynman theorem. | 5 |
| | (b) Considering the spin eigen functions discuss the singlet and triplet states of hydrogen molecule. | 3 |
| | (c) Show that $\psi_{sp} = \frac{1}{2}(2S \pm 2P_z)$ | 3 |
| | (d) Write the secular determinant for butadiene using Hückel molecular orbital theory. | 3 |
| 4. | (a) State and prove the variation theorem. | 6 |
| | (b) Write a note on non-crossing rule and correlation diagram. | 4 |

- (c) What are the approximations made in Hückel theory for conjugated π system? 4

UNIT-III

5. (a) What is CMC of surfactants? Explain the factors affecting the CMC of micellization of surfactants. 1+6=7
(b) Discuss the thermodynamics of micelle formation by mass action model. 4
(c) Define surface free energy. Calculate the height to which water will rise in a glass capillary if the radius of the tube is 0.02 cm. The surface tension of water is 0.0728 Nm^{-1} . 1+2=3
6. (a) Derive an expression for Laplace equation for pressure across an interface. 4
(b) If the area occupied by a nitrogen molecule is 0.805 nm^2 , calculate the surface area per gram of silica gel. 2
(c) Write the assumption of Langmuir adsorption isotherm and derive the expression pertaining to it. 6
(d) Give the classification of surfactants. 2

UNIT-IV

7. (a) Describe the substitutional and interstitial solid solutions and explain the distortions that are caused by them. 6
(b) What is an element of symmetry? Show that a cube has 23 elements of symmetry. 2+4=6
(c) What are intrinsic semiconductors? Give examples. 2
8. (a) Discuss the thermodynamics of formation of Schottky and Frenkel defects. 6
(b) A certain solid crystallizes in a body centred cubic lattice. First order X-ray ($\lambda = 0.154 \text{ nm}$) reflection maximum for a set of (200) planes was observed at 30° . Calculate the edge length of the unit cell. 3
(c) Explain with a neat diagram the band theory of solids. 5

UNIT-V

9. (a) Explain the following giving reasons: 3
- (i) Molecules for which dipole moment varies during vibration exhibit vibrational spectra.
 - (ii) Homonuclear molecules like N_2 and O_2 are microwave inactive but HCl and CO are microwave active.
 - (iii) Vibrational frequency ν for an excited state of a molecule is smaller than the ground state.
- (b) Calculate ΔE for radiation of wavelength $\bar{\nu} = 2.5 \text{ cm}^{-1}$. 2
- (c) Discuss the rotational spectra of polyatomic molecules. 4
- (d) Calculate the reduced mass and the moment of inertia of $D^{35}Cl$ molecule using internuclear distance of 0.1275 nm. 4
(Given $^{35}Cl = 34.97 \mu$ and $D = 2.014 \mu$)
- (e) What is selection rule? 1
10. (a) The fundamental and first overtone of NO are centred at 1876.06 cm^{-1} and 3720 cm^{-1} respectively. Evaluate the equilibrium vibrational frequency, the anharmonicity constant and the zero point energy of the molecule. 3
- (b) Explain the P, Q, R branches. 3
- (c) Discuss the quantum theory of Raman spectroscopy and show how stokes and anti-stokes lines appear in the Raman spectrum of a molecule. 5
- (d) Explain the effect of isotopic substitution in rotational spectroscopy. 3
-