

2021
B.A./B.Sc.
Fifth Semester
CORE – 12
CHEMISTRY
Course Code: CHC 5.21
 (Physical Chemistry - V)

Total Mark: 70

Pass Mark: 28

Time: 3 hours

Answer five questions, taking one from each unit.

UNIT-I

1. (a) Define the following terms: 1×3=3
 - (i) Activity coefficients
 - (ii) Mean activity coefficients
 - (iii) Ionic strength
- (b) Write a note on liquid junction potential. 3
- (c) Explain with the help of a neat diagram the electrophoretic effect. 5
- (d) The resistance of a 0.02 mol dm³ solution of acetic acid (cell constant = 0.2063 cm⁻¹) was found to be 888 ohm. What is the degree of ionization of the acid at this concentration? 3
 (Given Λ° for acetic acid = 387.9×10^{-4} ohm mol⁻¹m²)
2. (a) Discuss the concentration cells with transference. 6
- (b) Calculate the ionic strength of 2
 - (i) 0.02 molal KCl
 - (ii) 0.05 molal BaCl₂
- (c) Write notes on: 2×2=4
 - (i) Walden's rule
 - (ii) Debye-Falkenhagen effect
- (d) The specific conductance of saturated solution of AgCl at 25°C after subtracting. 2

UNIT-II

3. (a) State the criterions of a reversible electrode. 2
(b) Explain the Gouy-Chapmann model of diffuse double layer. 5
(c) Define EMF of a cell. Show how EMF measurements can be used in determining (i) free energy (ii) enthalpy (iii) entropy of a cell reaction. 1+6=7
4. (a) Determine the EMF and equilibrium constant of a cell reaction. 4
(b) Explain the working of calomel electrode and prove that it is a reversible electrode. 5
(c) Show how to determine the pH/H⁺ concentration of a solution by EMF measurement using hydrogen electrode. 5

UNIT-III

5. (a) Explain the molecular orbital treatment of H₂⁺. 7
(b) Write short notes on 2×2=4
(i) anharmonicity
(ii) bonding and antibonding orbitals
(c) Give the comparison of LCAO-MO and VB treatments of H₂. 3
6. (a) Derive the expression for valence bond energy of H₂ in terms of various integrals. 6
(b) Explain the importance of approximation methods. 4
(c) Write a short note on need for modification of Schrodinger equation for many electrons atoms. 4

UNIT-IV

7. (a) Show that the electronic transition possesses both vibrational and rotational fine structures. 5
(b) What do you understand by electronic transition? Explain in detail. 5
(c) Write short notes on: 2×2=4
(i) Fluorescence
(ii) Phosphorescence
8. (a) Discuss the high resolution NMR spectrum of acidified ethanol. 6

- (b) What is chemical shift? Explain how tetramethyl silane is used for measuring chemical shift. 5
- (c) A compound shows a proton NMR peak at 240 Hz downfield from the TMS peak in a spectrometer operating at 60 MHz. What are the values of the chemical shift δ and τ in ppm relative to TMS? 3

UNIT-V

9. (a) State and explain Lambert-Beer's law. Also give its limitations. 1+3+1=5
- (b) Write short notes on: 3×2=6
- (i) Chemiluminescence
- (ii) Photostationary state
- (c) Define quantum yield. Give example of high and low quantum yield. 1+2=3
10. (a) State the physical significance of adsorption coefficients. 4
- (b) Give a detail account on the role of photochemical reactions in biochemical processes. 5
- (c) State and explain Stark-Einstein law of photochemical equivalence. 5
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