October 2025
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 <u>five</u> questions, taking <u>one</u> from each unit.

UNIT–I

1. (a) Calculate the ionic strength of: 2
        (i) 0.25 molal KCI
        (ii) 0.3 molal $BaCl_2$
    (b) The resistance of a 0.02 mol dm^3 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 $\Lambda°$ for acetic acid = 387.9×10^{-4} ohm $mol^{-1}m^2$)
    (c) Explain in detail the principle of conductometric titration for
        determination of solubility and solubility products of sparingly
        soluble salts.   5
    (d) Explain with the help of a neat diagram the electrophoretic
        effect.   4

2. (a) Derive an expression for concentration cells with transference. 6
    (b) Write a note on each of the following: 2×2=4
        (i) Debye-Falkenhagen effect
        (ii) Wien effect
    (c) How does the liquid junction potential relate to the transport
        number of ions t_+ and t_-? Explain with relevant mathematical
        expressions.   4

UNIT–II

3. (a) What are redox electrodes? Explain with suitable examples.   4

(b) State the principle of potentiometric titration and discuss its application for acid-base titration. 4

(c) Illustrate the working of metal-metal ion electrodes. 4

(d) State the criterions of a reversible electrode. 2

4. (a) Discuss the application of EMF measurement for determination of free energy, enthalpy, and entropy of a cell reaction. 6

(b) Write a note on electrocatalysis. 3

(c) Write a note on each of the following: 2½×2=5
   (i) Quinone-hydroquinone electrodes
   (ii) Calomel electrode

UNIT–III

5. (a) Write a note on setting up of Schrödinger equation for many-electron atoms. 6

(b) Write a note on each of the following: 3×2=6
   (i) Perturbation theorem
   (ii) Approximate methods in quantum mechanics.

(c) What are bonding and antibonding orbitals? 2

6. (a) State and prove the variation theorem. 6

(b) Explain the molecular orbital treatment of hydrogen H_2^+. 5

(c) Discuss the basic principles of MOT. 3

UNIT–IV

7. (a) An electronic transition possesses both vibrational and rotational fine structures. Justify the statement. 3

(b) Write a note on each of the following: 2×2=4
   (i) Stokes and anti-stokes lines
   (ii) Rule of mutual exclusion

(c) State and explain with potential energy curves of Franck-Condon principle. 5

(d) What is Larmor precession? 2

8. (a) 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 values in ppm relative to TMS? 3

(b) Discuss the high-resolution NMR spectrum of ethanol
   (acidified). 6
(c) What is chemical shift? Explain how tetramethylsilane is used
   for measuring chemical shifts. 5

UNIT–V

9. (a) State and explain Stark-Einstein law of photochemical
    equivalence. 5
   (b) What is actinometry? Discuss. 4
   (c) Explain the photochemical equilibrium and the differential rate
    of photochemical reactions. 5

10. (a) State and explain Lambert-Beer's law. Also, give its limitations.
    5
    (b) Write short notes on the following with supporting formulae:
     (i)   Molar extension coefficient   3×3=9
     (ii) Photochemical rate law
     (iii) Integrated absorption coefficient

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