2024
B.A./B.Sc.
Fourth Semester
CORE – 10
CHEMISTRY
Course Code: CHC 4.31
(Physical Chemistry - IV)

Total Mark: 70 *Pass Mark: 28*
Time: 3 hours

Answer five questions, taking one from each unit.

UNIT–I

1. (a) Discuss in detail the Debye-Hückel theory of strong electrolytes. 6
   (b) Explain the Ostwald's law. Write its uses and limitation. 5
   (c) Calculate the molar conductance at infinite dilution of an aqueous solution of NaCl at room temperature, given that mobilities of Na^+ and Cl^- ions at this temperature are 4.26×10^{-8} and 6.80×10^{-8} $m^2 V^{-1} s^{-1}$, respectively. 3

2. (a) How does the equivalent conductivity of electrolytes vary upon dilution? 4
   (b) Explain with a neat diagram the moving boundary method for determination of transport number of ions. 5
   (c) Molar ionic conductance at infinite dilution of K^+ and Br^- ions are 73.5 and 78.4 $Scm^2 mol^{-1}$ respectively. Calculate their transport number. 3
   (d) State and illustrate Kohlrausch's law. 2

UNIT–II

3. (a) What is the amount of Cl_2 liberated if 0.1 Faraday of electricity is passed through fused NaCl? 2
   (b) Construct a working cell comprising of Ni and Cu electrodes and
      (i) Give symbolic representation of the cell 2×3=6
      (ii) Calculate E^0_{cell}
      (iii) Write corresponding cell reaction.

(c) Can a solution of 1M $CuSO_4$ be stored in a vessel made of Ni metal? Given that $E^0_{Ni/Ni^{2+}} = +0.25$ V and $E^0_{Cu/Cu^{2+}} = -0.34$ V. 3

(d) What are reversible and irreversible cells? Give examples. 3

4. (a) Write the cell reaction and calculate E^0 for the cell $Zn \mid Zn^{2+}(1M) \mid\mid Fe^{2+}(1M), Fe^{3+}(1M) \mid Pt$.
Given that $E^0_{Fe^{3+}/Fe^{2+}} = +0.77$ V and $E^0_{Zn^{2+}/Zn} = -0.76$ V. 3

(b) Give a comparison between galvanic cells and electrolytic cells. 4

(c) Write notes on the following: 3½×2=7

(i) Corrosion (ii) Overvoltage

UNIT–III

5. (a) Show that: 2×3=6

(i) $\left[\hat{A}, \widehat{BC}\right] = \left[\hat{A}, \hat{B}\right]\hat{C} + \hat{B}\left[\hat{A}, \hat{C}\right]$

(ii) $\left[\hat{A}, \hat{B} + \hat{C}\right] = \left[\hat{A}, \hat{B}\right] + \left[\hat{A}, \hat{C}\right]$

(iii) $\left[\hat{A}^2, \hat{B}\right] = \hat{A}\left[\hat{A}, \hat{B}\right] + \left[\hat{A}, \hat{B}\right]\hat{A}$

(b) Derive an expression for a particle in 1-D box. Calculate the quantization of energy and zero-point energy using the expression. 6

(c) Write a note on the most probable distances of electron from the nucleus. 2

6. (a) Write a note on setting up of Schrödinger equation in spherical polar coordinates. 7

(b) Derive an expression for free particle using Schrödinger equation. 3

(c) Discuss the properties of wave functions. 4

UNIT–IV

7. (a) Show how to determine the bond length of a linear triatomic molecule using rotational spectra. 6

(b) Mention and explain all types of molecular spectra state and express Born-Oppenheimer approximation. 5

(c) Explain absorption and emission spectroscopy with the help of a neat diagram. 3

8. (a) Explain the selection rule for rotational spectra. 3

(b) What is the moment of inertia of a diatomic molecule with bond distance equal to 150 pm and reduced mass equal to 1.5×10^{-27} kg. 3

(c) Define the following terms: 1×3=3

(i) Overtones

(ii) Hot bands

(iii) Modes of vibration

(d) How will you determine the bond distances of polyatomic molecules using rotational spectroscopy. 5

UNIT–V

9. (a) Describe the temperature method for measurement of dipole moment of a molecule. 5

(b) Derive the expression for Clausius-Mossotti equation. 5

(c) Which has larger dipole moment? Explain. 4

(i) HF or HCl (ii) $CHBr_3$ or CBr_4

(iii) CO_2 or SO_2 (iv) Phenol or Chlorobenzene

10. (a) Explain polarization of a molecule in a magnetic field. 4

(b) How will you obtain Debye equation using induced polarization and orientation polarizability? 4

(c) Which of the following substances would be expected to behave paramagnetic or diamagnetic and why? 4

(i) N_2O_5 (ii) N_2O_4

(iii) NO_2 (iv) NO

(d) The dipole moment of H_2S is 0.95 D. If the bond angle is 97°, calculate the S-H bond moment. 2