

1127

M.Sc. (Applied Chemistry/Pharmaceutical)
First Semester
Paper – 103: Physical Chemistry

Time allowed: 3 Hours

Max. Marks: 60

NOTE: Attempt five questions in all, including Question No. 1 which is compulsory and selecting one question from each Unit. Use of log tables and non-programmable calculator is permissible.

x-x-x

1. (a) Calculate the rate constant involved in the dissociation of NH_4OH , viz.,
$$\text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$$

from the following data: A 0.01 molar solution of NH_4OH is subjected to a sudden temperature jump terminating at 25°C , at which temperature, the equilibrium constant is $1.8 \times 10^{-5} \text{ mol dm}^{-3}$. The observed relaxation time is $0.109 \mu\text{s}$ and $x_e = 4.1 \times 10^{-4} \text{ mol dm}^{-3}$ (Equilibrium concentration).
- (b) Calculate the ionic strength of a solution obtained by mixing equal volumes 0.1 M NaCl, 0.1 M Na_2SO_4 and 0.1 M BaCl_2 solution.
- (c) Plot phase diagram for 3-component system when one of the component get hydrated.
- (d) (i) Explain the difference between monotropes and enantiotropes in polymorphism.
(ii) Write a short note on Temkin absorption isotherm. (3 x 4 = 12)

UNIT – I

2. (a) Write difference between Bose Einstein, Fermi Dirac and Maxwell Boltzmann Statistics. (6)
(b) Show that $Q_t Q_r Q_v Q_e = Q$ (3)
(c) What do you understand by thermodynamic probability? Derive relationship between entropy and thermodynamic probability. (3)
3. (a) What is meant by the term excess function? Write expressions for various excess functions like H^E , V^E , S^E , G^E . (5)
(b) Derive the limiting equation of Debye-Huckel theory for the activity coefficients of strong electrolyte. (5)
(c) What are partial molar quantities? Give their significance. (2)

UNIT – II

4. (a) Draw and discuss the phase diagram of a system consisting of two salts and water. Also explain its application in the crystallization of pure components. (6)
(b) Give a brief description of the triangular method for representation of phase diagram of a three component system. Describe phase diagram of a liquid system constituting three components with two pair of partially miscible liquids. (6)
5. (a) What are ternary phase diagrams? Discuss the application of phase rule to a ternary system composed of three liquid components with one partially miscible pair. (6)

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- (b) Show graphical representation of the phase diagram and describe phase behavior of a two component system in which two components are partially miscible in the liquid state and the solid phases of pure components. (6)

UNIT - III

6. (a) Describe various techniques for the detection and identification of polymorphs. (6)
(b) Discuss effect of solvent on the rate of reaction in solution phase. (6)
7. (a) What is relaxation technique in the study of fast reactions? Discuss briefly temperature jump method. (6)
(b) What do you understand by Primary Salt Effect? Derive the relation
$$\ln K = \ln K_0 + 2AZ_A Z_B \sqrt{\mu}$$
where the symbols have their usual meanings. (6)

UNIT - IV

8. (a) Derive Kelvin equation for V. P. of droplets. (4)
(b) Discuss the kinetics and mechanism of unimolecular surface reactions. (4)
(c) The density of liquid methane is $0.466 \times 10^{-3} \text{ kg m}^{-3}$. Calculate the approximate cross-sectional area of a methane molecule. (4)
9. (a) Discuss briefly BET theory of multilayer adsorption and explain how you will calculate surface area from it?. (6)
(b) Show that Langmuir adsorption Isotherm reduces to Freundlich adsorption Isotherm. (6)

x-x-x