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DEPARTMENT OF SCIENCE I SEMESTER M.Sc. (CHEMISTRY) END SEMESTER EXAMINATIONS, NOV/DEC 2016

SUBJECT: PHYSICAL CHEMISTRY I [CHM 605]

REVISED CREDIT SYSTEM

Time: 3 Hours

Date: 31/12/2016

MAX. MARKS: 50

Instructions to Candidates:

- Answer ANY FIVE FULL questions.
- Draw diagrams and write equations wherever necessary.
- **1. a)** Justify the statement with relevant mathematical equation: Enzyme catalysis follows first order at low substrate concentration and zero order at higher concentration of substrate.

b) Calculate the ionic strength of HCl solution with molality 0.010 and mean activity coefficient $v\pm$ of Na₂SO₄ at a molality of 0.001 M in aqueous solution.

c) Write Bodestain –Linde mechanism for the formation of hydrogen bromide. Derive mathematical expression to prove that overall order of the reaction is 3/2

[2+2+6]

2. a) Justify: Activity coefficients after reaching a minimum start rising again with ionic strength.

b) Show that in case of first order reaction, the time required for 99.9 % of the reaction to take place is about ten times that required for half the reaction

c) What are the limitations of Helmholtz –Perrin model for electrical interface? Explain Gouy-Chapman diffuse charge model. Mention the reasons for its failure.

[2+2+6]

3. a) Justify the statement: Gibbs adsorption isotherm is used for predicting the positive and negative adsorption for adsorption from solution.

b) Deduce the integrated form of Clausius – Clapeyron equation as applied to liquid \rightleftharpoons vapour equilibrium.

c) Discuss in detail, equilibrium treatment and steady state treatment as applied to homogeneous catalysis.

[2+2+6]

4. a) Justify the statement: Phase diagram of a three component mixtures are represented by triangular diagrams.

b) Derive a mathematical expression to show the linear relationship between rate constant and dielectric constant of the medium for reactions in solutions.

c) Deduce Maxwell's relationships from fundamental property relationships.

[2+2+6]

5. a) Justify the following statement: CTST overcomes all the limitations of collision theory. b) The first order decomposition of NLO into NLO has not a state of 4.5 ± 10^3 s⁻¹

b) The first order decomposition of N_2O_4 into NO_2 has rate constant value of $4.5 \times 10^3 \text{ s}^{-1}$ at 274 K and an energy of activation of 58 kJ mol⁻¹. At what temperature its half-life would be 6.93×10^{-5} seconds?

- c) Explain the following:
- (i) Thermal decomposition of acetaldehyde
- (ii) Theory for chemical adsorption

[2+2+6]

6. a) Calculate the entropy change accompanying the conversion of 1 mole of ice at 273.1K and 1 atm.pressure into steam at 373.1 K and 1atm pressure. $\Delta H_f = 6.00 \text{ kJ mol}^{-1}$, $\Delta H_v = 40.5 \text{ kJmol}^{-1}$ and molar heat capacity in this range of temperature is 76 JK⁻¹mol⁻¹.

b) Derive Gibb's phase rule and write the significance of it.

c) Discuss Debye Huckel model of ion - ion interaction. Write the Debye Huckel and Onsager equation and explain the significance of asymmetry and electrophoretic effects in it.

[2+2+6]
