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DEPARTMENT OF SCIENCES, MANIPAL UNIVERSITY, MANIPAL

I SEMESTER M.Sc. END SEMESTER EXAMINATIONS, NOV/DEC 2015 SUBJECT: PHYSICAL CHEMISTRY I [CHM 605]

REVISED CREDIT SYSTEM

Time: 3 Hours

MAX. MARKS: 50

Instructions to Candidates:

- Answer ANY FIVE FULL questions.
- Draw diagrams and write equations wherever necessary.
- **1. a)** Justify the statement: Increase in frequency of AC current will always increase the conductance of strong electrolytes.

b) The time required for 10% completion of a first order reaction at 298 K is equal to that required for its 25% completion at 308 K. If the pre exponential factor for the reaction is $3.56 \times 10^9 \text{ sec}^{-1}$, calculate the rate constant at 318 K and the energy of activation.

c) Define chemical potential. Derive the Gibbs- Duhem equation. How does chemical potential vary with temperature and pressure.

[2+2+6]

2. a) Justify the statement: Collision theory seriously fails when applied to polyatomic gas phase reactions.

b) The vapour pressure of ice \leftrightarrow water system at 273.0075 K is 4.58 mm and at 273 K is 759.80 mm of mercury. Calculate the molar heat of fusion of ice, given that the specific volumes of ice and water at 273 K are 1.0907cm³ and 1.0001cm³ respectively. Density of mercury at 273 K is 13.6 gcm⁻³.

c) Explain transition state theory for reactions in solution. Derive an expression for the variation of rate constant with ionic strength of solution.

[2+2+6]

3. a) Give reason: At low pressure fugacity is numerically equal to pressure.

b) Derive rate expression for the variation of substrate concentration in enzyme catalysis.

c) Derive Debye-Huckel limiting law equation applicable to dilute solutions. What

corrections are suggested to make it applicable also to solutions which are not so dilute.

[2+2+6]

- **4 a**) Justify the statement: Langmuir adsorption isotherm explains chemical adsorption whereas, B.E.T adsorption isotherm explains chemical adsorption.
 - b) Calculate the mean activity coefficient of 0.01 molal solution of Na₂SO₄ in water.

c) Explain Boderstien-Lind mechanism for the formation of hydrogen bromide and derive mathematical expression for the rate constant.

- [2+2+6]
- 5 a) Write note on the asymmetry effect and electrophoretic effect.
 b) Discuss the application of the condensed phase rule to the study of succinic nitrile-water-alcohol between 18.5 °C and 31 °C.
 c) Derive vant-Hoff equation. Mention its limitations. State and explain the Nernst heat

theorem.

[2+2+6]

6 **a**) Justify the statement: Equilibrium treatment and steady state treatment are applied under different conditions while explaining homogeneous catalysis.

b) Calculate the surface area per gram of silica gel at S.T.P, if the volume of nitrogen gas required forming a monolayer on it is 130 cm³ g⁻¹. (The area occupied by a nitrogen molecule is 0.162 nm^2)

c) Derive Gibbs adsorption isotherm for adsorption from solutions.

[2+2+6]
