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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: 28/11/2016

MAX. MARKS: 50

Instructions to Candidates:

- Answer **ANY FIVE FULL** questions.
- Draw diagrams and write equations wherever necessary.
- a) Justify the statement: In aqueous media ion association in pairs rarely occurs for 1: 1 electrolytes but in non- aqueous solutions ion association is extremely important.

b) A substance decomposes at 600 K with a rate constant of 3.72×10^5 s⁻¹.Calculate the half-life of the reaction. What fraction will remain undecomposed if the substance is heated for 3 h at 600 K?

c) Define the term fugacity. How is it determined and calculated at low pressures? Mention its physical significance.

[2+2+6]

2. a) Justify the statement: Free energy change for adsorption is negative both for physisorption and chemisorption.

b) Ether boils at 306.5 K at 760mm of Hg. At what temperature will it boil at a pressure of 750 mm of Hg? (Latent heat of vaporization of ether is 369.86 J g^{-1} .)

c) Derive a mathematical expression to relate rate constant of reactions in gas phase and solution phase. With an example explain the effect of solvation on reaction in solutions.

[2+2+6]

3. a) Justify the statement with appropriate equation: Chemical potential decreases with increase in temperature.

b) Compare the assumptions of Lindemann theory and RRK theory for unimolecular gas phase reaction.

c) Derive Lippman equation. Write the principle involved in the determination of interfacial tension of mercury.

[2+2+6]

4. a) Justify the statement: Application of BET adsorption isotherm is a useful tool to calculate surface area of the catalyst

b) Calculate the thickness of the ionic atmosphere in 0.01 N solutions of 1:2 electrolyte in ethyl alcohol and in nitrobenzene Comment on your results. Given: Dielectric constant of ethyl alcohol and nitrobenzene are 24.3 and 34.8 respectively.

c) Write the mechanism for thermal decomposition of ethane and prove that reaction follows first order kinetics.

[2+2+6]

5. a) Justify: Activity coefficients vary only with ionic strength of the uni-univalent electrolyte solution.

b) Draw and explain with a suitable example the phase diagram for a system of two salts and water of type crystallization of pure components only.

c) State and explain the third law of thermodynamics. Show that the application of Nernst theorem provides a method of calculation of free energy change with the knowledge enthalpy change.

[2+2+6]

6. a) Justify the statement with appropriate equation: Reason for the first and second explosion limits of gas phase combustion of hydrogen is not same.

b) Write appropriate equation and distinguish between protolytic and prototropic catalysis.

c) Explain the following:

(i) Potential energy surface and PME

(ii) General mechanism of surface reaction.

[2+2+6]
