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CH/AC/OC/CA 403

First Semester M.Sc. Degree Examination, December 2018 (Chemistry/Applied Chemistry/Organic Chemistry/Analytical Chemistry) (2015 Batch)

PHYSICAL CHEMISTRY (CBCS-Repeaters)

Time: 3 Hours Max. Marks: 70

Note: i) Answer **10** sub-divisions from Part **A** and **any five** questions from Part **B**.

ii) Figures to the **right** indicate marks.

PART - A

Answer any 10 sub-divisions:

 $(10 \times 2 = 20)$

- 1. a) State and explain the third law of thermodynamics.
 - b) Define the terms, (i) fugacity, (ii) activity.
 - c) Write the Van't Hoff equation and mention its limitations.
 - d) What are complex reactions? Illustrate with an example.
 - e) List the general features of chain reactions.
 - f) In the triangular phase diagram of a 3-component system a double salt (2 salt and water) indicate the formation of composition: 30% A, 50% B and 20% C.
 - g) Evaluate the ionic strength of a solution formed by mixing 100 mL of 0.1 M NaCl and 200 mL of 0.5 M NaOH in 1 L volume.
 - h) Distinguish between electrophoretic and asymmetric effects.
 - i) Sketch a polarogram and explain the importance of various regions.
 - j) Explain the effect of inhibitors on enzyme catalysis.
 - k) Differentiate between physical adsorption and chemisorption.
 - I) Mention any 4 industrial applications of catalysis.



PART – B

Ar	ารพ	ver any five questions : (5×10=5	0)
2.	·	Discuss the method of determination of absolute entropy of a solid based on third law of thermodynamics. Explain the determination of partial molar volume by intercept method.	6
3.	•	Deduce Gibbs -Duhem equation and explain its significance. Derive an expression for the elevation of boiling point based on thermodynamic considerations.	5
4.	•	Deduce the expressions for the rate constants of consecutive reactions. Discuss the effect of ionic strength of the medium on the rates of reactions.	4
5.	ŕ	Give the Hammett Equation. Show that it is equivalent to a linear free energy relationship. Discuss the phase diagram of a 3 component system with two pairs of partially miscible liquids.	4
6.	·	Discuss the kinetics of enzyme reactions and obtain the Michaelis-Menten equation. Derive the Bronsted relationships of catalytic activity and acid-base strength.	5
7.	,	Discuss the prototropic mechanism of acid base catalysis. Explain the method of in determination of surface area based on BET theory.	5
8.	·	Deduce an expression for the Debye-Huckel limiting law and write various forms of it. Explain the significance of ionic atmosphere. Calculate the thickness of the ionic atmosphere of 0.02 M solution of a uni-univalent electrolyte in 70% ethanol solution in water at 25°C. $ (D = 38.5, e = 1.602 \times 10^{-19} \text{ C}; k = 1.38 \times 10^{-23} \text{J.K}^{-1}; N = 6.023 \times 10^{23} \text{ mol}^{-1}) $	5
9.		Give the principle and any two applications of coulometry. Discuss the application of polarography in pharmacy and agriculture.	4