Reg. No. $\square$

## 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 :

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

Answer any five questions :
( $5 \times 10=50$ )
2. a) Discuss the method of determination of absolute entropy of a solid based on third law of thermodynamics.

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b) Explain the determination of partial molar volume by intercept method.
3. a) Deduce Gibbs -Duhem equation and explain its significance.

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b) Derive an expression for the elevation of boiling point based on thermodynamic considerations.

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4. a) Deduce the expressions for the rate constants of consecutive reactions.
b) Discuss the effect of ionic strength of the medium on the rates of reactions .
5. a) Give the Hammett Equation. Show that it is equivalent to a linear free energy relationship.
b) Discuss the phase diagram of a 3 component system with two pairs of partially miscible liquids.
6. a) Discuss the kinetics of enzyme reactions and obtain the Michaelis-Menten equation.

b) Derive the Bronsted relationships of catalytic activity and acid-base
strength.
7. a) Discuss the prototropic mechanism of acid base catalysis.
b) Explain the method of in determination of surface area based on BET theory.
8. a) Deduce an expression for the Debye-Huckel limiting law and write various forms of it.
b) 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 $25^{\circ} \mathrm{C}$.

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\left(\mathrm{D}=38.5, \mathrm{e}=1.602 \times 10^{-19} \mathrm{C} ; \mathrm{k}=1.38 \times 10^{-23} \mathrm{~J} \cdot \mathrm{~K}^{-1} ; \mathrm{N}=6.023 \times 10^{23} \mathrm{~mol}^{-1}\right)
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9. a) Give the principle and any two applications of coulometry.
b) Discuss the application of polarography in pharmacy and agriculture.
