**CH/AC/OC/CA H 403**

**I Semester M.Sc. Degree Examination, December 2018**
**CHEMISTRY/APPLIED CHEMISTRY/ORGANIC CHEMISTRY/**
**ANALYTICAL CHEMISTRY**
**(CBCS : 2016 – 17 Syllabus)**
**Physical Chemistry**

Time : 3 Hours

Max. Marks : 70

**Note :** i) Answer Part – **A** and **any four** questions from Part – **B**.
ii) Figures to the **right** indicate marks.

PART – A

1. Answer **all** subdivisions. **(2×9=18)**

   a) Differentiate between Arrhenius and van't Hoff intermediates in homogeneous catalysis.

   b) What are Bronsted relationships ? Explain their significance.

   c) Describe the effect of temperature and pressure on heterogeneous catalysis.

   d) State the steady state principle and mention its significance in the study of complex reactions.

   e) The reaction $H_2 + Br_2 \longrightarrow 2\,HBr$ is a composite reaction. Justify.

   f) Predict with reasoning the effect of ionic strength on the rates of the following reactions :
      i) Reaction between $I^-$ and $S_2O_8^{2-}$ and
      ii) Reaction between $CH_3COOH$ and NaOH.

   g) Comment on the physical significance of Walden product.

   h) Sketch a polarogram and explain the importance of various regions.

   i) 'Process of corrosion of any material is always spontaneous in nature'. Justify the statement.

**P.T.O.**

## PART – B

Answer **any four** of the following questions. **(4×13=52)**

2. a) Discuss the protolytic and prototropic mechanisms of acid catalysis. **7**

   b) Discuss the kinetics of enzyme catalysed reactions and derive the Michaelis-Menten equation. Mention the different cases. **6**

3. a) Derive the BET equation and explain its application for the determination of surface area. **6**

   b) The adsorption of nitrogen on $ZnSiO_4$ at liquid nitrogen temperature fits BET equation. The volume of nitrogen necessary to form a monolayer on the powdered sample weighing 17.52 g is found to be 11.05 $cm^3$ at STP. Calculate the surface area per gram of the power sample. One molecule of nitrogen occupies 16.2 $(Å)^2$. **4**

   c) Explain the p-type semiconductor catalysis with an example. **3**

4. a) Discuss the kinetics of parallel reactions considering them as of first order. **6**

   b) Write the Hammett Equation and explain its importance in the study of kinetics of reactions. Show that it is equivalent to a linear free energy relationship. **(4+3)**

5. a) Discuss the effect of solvent on the rates of ionic reactions in solution based on the double sphere model. **6**

   b) Explain the collision theory of bimolecular reactions. Mention the merits and limitations of the theory. **7**

6. a) Deduce an expression for the Debye-Huckel limiting law and write various forms of it. **6**

   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°C.

   (D = 38.5, e = 1.602 ×$10^{-19}$ C; K = 1.38×$10^{-23}$ J.$K^{-1}$; N = 6.023×$10^{23}$ $mol^{-1}$). **4**

   c) Explain the characteristics of Galvanic series and mention its limitations. **3**

7. a) List the types of corrosion and discuss any three of them with illustrative examples. **6**

   b) Explain the role of inhibitors in reducing the rate of corrosion. **4**

   c) Outline the principle of cyclic voltammetry technique. **3**

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