

Seat No. : \_\_\_\_\_

**MT-128**  
**December-2016**  
**M.Sc., Sem.-I**  
**403 : Chemistry**  
**(Physical Chemistry)**

Time : 3 Hours]

[Max. Marks : 70

Instructions : (1) Attempt all questions.

(2) Necessary constants :

$$k_B = 1.3806 \times 10^{-16} \text{ erg K}^{-1} = 1.3806 \times 10^{-23} \text{ J K}^{-1}$$

$$h = 6.6260 \times 10^{-27} \text{ erg s} = 6.6260 \times 10^{-34} \text{ J s}$$

$$R = 8.3145 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1} = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$$

1. (a) What are the limitations of thermodynamics ? Discuss the Nernst's heat theorem and derive an equation giving the relation between free energy, enthalpy and heat capacity. 7

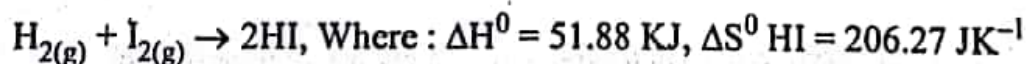
**OR**

State the third law of thermodynamics. Show how the absolute entropy of a substance can be determined with the help of this law.

- (b) What is meant by chemical potential ? Derive the Gibb's-Duhem equation. 7

**OR**

- (i) Explain how are fugacity and activity related to chemical potential. 4
- (ii) Calculate the value of equilibrium constant of the following reaction



$$\Delta S^0_{\text{H}_2} = 130.6 \text{ JK}^{-1} \text{ and } \Delta S^0_{\text{I}_2} = 116.73 \text{ JK}^{-1}. \quad \text{3}$$

2. (a) Discuss the theory of absolute reaction rate. Give the limitations of this theory. 7

OR

Explain the mechanism and kinetics of chain reaction between hydrogen and bromine.

- (b) Derive the Michaelis-Menten equation of enzyme catalyzed reaction. 7

OR

(i) Write a note on explosion limits. 4

(ii) Calculate the activation energy of a reaction whose rate constant is tripled by 10 °C rise in temperature at 27 °C. 3

3. (a) Name the different types of imperfections in solids. Derive an equation to calculate number of Schottky defects in solids. 7

OR

Discuss stoichiometry defects in solids.

- (b) Discuss bond theory of solids. 7

OR

(i) Write note on perovskites. 4

(ii) Calculate the mole fraction of Schottky in NaCl crystal at 800 K. The energy for formation of this defects is 2 eV. ( $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J K}^{-1}$ ) 3

4. (a) What are surface active agents? Explain critical micellar concentration. 7

OR

What is surface tension? Derive Gibbs' adsorption isotherm equation.

- (b) Discuss the BET and the Harkins and Jura method of determining the surface area of adsorbents. 7

OR

(i) Give difference between physical and chemical adsorption. 4

(ii) Write note on surface tension and detergents. 3

5. Answer the following : (one mark each)

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- (i) Define activity of a substance in term of fugacity.
  - (ii) What is physical significance of fugacity ?
  - (iii) Define standard chemical potential.
  - (iv) Give the relation which defines the variation of chemical potential with temperature.
  - (v) On which two theories of reaction rates is the Arrhenius equation based' ?
  - (vi) Why rate of reaction always increases with temperature whether the reaction is exothermic or endothermic ?
  - (vii) What is transition state ?
  - (viii) What do you mean by threshold energy and activation energy ?
  - (ix) Which factor is mainly responsible for imperfections in solids' ?
  - (x) What is stoichiometric defects ?
  - (xi) Name the defects which arise due to the irregularity in the arrangement of atoms or ions.
  - (xii) Pure silicon is an insulator but becomes a semi conductor on heating. Why' ?
  - (xiii) What is chemisorptions.
  - (xiv) Name the factors which are responsible for adsorption of gases on solids.
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