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 :

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

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

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

$H_{2(g)} + I_{2(g)} \rightarrow 2HI$, Where : $\Delta H^0 = 51.88$ KJ, ΔS^0 HI $= 206.27$ JK^{-1}

$\Delta S^0 H_2 = 130.6$ JK^{-1} and ΔS^0 $I_2 = 116.73$ JK^{-1}. 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 Mechaelis-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 stoichiometriy 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. ($1\ eV = 1.602 \times 10^{-19}\ J\ K^{-1}$) 3

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

OR

What is surface tension ? Derive Gibb's 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)

(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.
