

NS-122

December-2015

M.Sc., Sem.-I

**403 : Chemistry
(Physical Chemistry)****Time : 3 Hours]****[Max. Marks : 70****Instructions :** (1) Attempt all questions.

(2) Necessary constants :

$$N_A = 6.02213 \times 10^{23} \text{ mol}^{-1}$$

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

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

$$c = 2.998 \times 10^{10} \text{ cm s}^{-1} = 2.998 \times 10^8 \text{ m s}^{-1}$$

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

1. (a) Explain the term chemical potential and show that

7

$$(\delta G/\delta n_i)_{P,T,n} = (\delta A/\delta n_i)_{V,T,n} = (\delta H/\delta n_i)_{P,S,n} = (\delta U/\delta n_i)_{V,S,n}$$

OR

Discuss the Nernst's heat theorem and derive an equation giving the relation between free energy, enthalpy and heat capacity.

(b) (i) What are partial molar properties ? Show how partial molar volume can be determined by density measurements. 4

(ii) A solution of ethyl alcohol in water has a density of 0.8494, the mole fraction of water being 0.6. If the partial molar volume of alcohol in the solution is 57.5 CC. Calculate that of water. (C_2H_5OH 46 g/mol) 3**OR**

(b) (i) How fugacity of real gases can be evaluated graphically? 4

(ii) Explain the effect of temperature and pressure on partial molar free energy. 3

2. (a) Discuss activated complex theory of bimolecular reactions. 7

OR

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

- (b) Discuss Lindemann theory of unimolecular reactions. 7

OR

- (b) (i) Write a note on branched chain reaction. 4
(ii) If the activation energy of a reaction is 80.9 kJ mol^{-1} , calculate the fraction of molecules at 400°C which have enough energy to form products. 3

3. (a) On which basis the solids are classified as metals, semi-conductors and insulator? Discuss the mechanism of electrical conductivity in each of the cases. 7

OR

What are Frenkel defects? Derive an expression for number of Frenkel defects in a crystal.

- (b) Explain bond theory of metals. 7

OR

- (b) (i) Write note on : Non stoichiometric defects. 4
(ii) Estimate the mole fractions of Schottky in NaCl crystal at 1000 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 is micelles? Explain critical micellar concentration. 7

OR

Discuss the BET and the Harkins and Jura method of determining the surface area of adsorbents.

- (b) Derive Gibb's adsorption isotherm equation and explain surface activity from this equation. 7

OR

- (i) Write a note on surface tension and detergents. 4
(ii) For a $1.0 \times 10^{-10} \text{ M}$ aqueous solution of n-butanoic acid $d\gamma/dc = -0.080 \text{ N m}^2 \text{ mol}^{-1}$, at 25°C . Using the Gibbs adsorption equation, determine the surface excess of the acid and also calculate the average surface area available to each molecule. 3

5. Answer the following : (one mark each)

- (i) Why solids with F centre are paramagnetic ?
- (ii) Why the rate constant vary with temperature ?
- (iii) Name the properties of solids.
- (iv) Name different types of atomic imperfection in solids.
- (v) For real gases activity is proportional to it's _____.
- (vi) The ratio f/p approaches _____ when p (the actual pressure) approaches _____.
- (vii) When E_a of a reaction is zero, the reaction rate becomes independent of _____.
- (viii) Why rate of reaction always increases with temperature whether the reaction is exothermic or endothermic ?
- (ix) What is chain length ?
- (x) What is adsorption isostere ?
- (xi) Adsorption of gases on solid surface is generally exothermic because _____ decreases.
- (xii) What is enthalpy of adsorption ?
- (xiii) What types of attraction forces are present between adsorbent and adsorbate in physisorption ?
- (xiv) Why is the value of ΔG at m pt. of ice zero ?
