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 :

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

$k_B = 1.3806 \times 10^{-16}$ 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

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

$R = 8.3145 \times 10^{7}$ erg K^{-1} mol$^{-1} = 8.3145$ J K^{-1} 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 unimoleculer 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 stoichiomeiric 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 eV = 1.602×10^{-19} J K^{-1}) **3**

4. (a) What is micelles ? Explain critical miceller 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 1.0×10^{-10} M aqueous solution of n-butanoic acid $d\gamma/dc = -0.080$ N m^2 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) **14**

(i) Why solids with F centre are paramagnetic ?

(ii) Why the rate constant very 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 Ea 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 ?

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