Seat No. : _____

D-562

December-2011

Sem-I

Time : 3 Hours] [Max. Marks : 70

Instructions : (1) All questions carry equal marks.

(2) Necessary constants :

$N = 6.022 \times 10^{23}$ mole^{-1}

$k = 1.38 \times 10^{-16}$ ergs $k^{-1} = 1.38 \times 10^{-23}$ jk^{-1}

$h = 6.626 \times 10^{-27}$ ergs. sec. $= 6.626 \times 10^{-34}$ J. sec.

$C = 2.998 \times 10^{10}$ cm. sec^{-1}. $= 2.998 \times 10^{8}$ m.sec^{-1}

$R = 8.314 \times 10^{7}$ ergs. k^{-1} m^{-1}

$= 8.314$ $jk^{-1}m^{-1}$

$= 1.987$ Cal. $k^{-1}m^{-1}$

$F = 96500$ C

1. (a) Discuss method of intercept for the determination of partial molar volume. 7

OR

Derive an equation for the approximate calculation of the fugacity of a gas.

(b) State the third law of thermodynamics. Show how the absolute entropy of a substance can be determined with the help of this law. 7

OR

(i) Heat of dissociation of calcium carbonate is 42500 cal. Find the dissociation pressure of calcium carbonate at 1000 °K, given that the chemical constant for carbon dioxide is 3.4. 4

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

(ii) The vapour pressure of liquid chlorine is 3.66 atm. at 273 °K and the molar volume of the vapour under these conditions is 6.01 litre.mole^{-1}. Calculate the fugacity of liquid chlorine at 273 °K. ($R = 0.082$ litre.atm. mole^{-1}.deg^{-1}.) 3

2. (a) Discuss the Lindemann theory of unimolecular reactions. 7

OR

Define chain reaction and discuss kinetics of chain reaction.

(b) (i) Derive theory of absolute reaction rate. 4

(ii) Calculate frequency factor (A) for a reaction $\frac{1}{2} Cl_2 + H_2 \rightleftharpoons HCl + \frac{1}{2} H_2$ at 450 °K. The value of entropy of activation (ΔS^*) is 12.74 cal. mol^{-1} deg^{-1}. (e.u.) 3

OR

(i) Write a note on enzyme catalyzed reaction. 4

(ii) Calculate the entropy of activation (ΔS^*) for a reaction $H_2 + I_2 \rightleftharpoons 2HI$ at 473 °K. The value of frequency factor (A) is 8.0×10^{10} $second^{-1}$. 3

3. (a) Derive equation to calculate Schottky defects in solids. 7

OR

Discuss defects in solids.

(b) Discuss super conductivity. 7

OR

The energy of formation of a Schottky defect in NaCl crystal is 2.4 eV and that for a Frenkel defect is 3.6 eV estimate the mole fraction of these defects in a crystal of NaCl at 1300 °K. (1 eV = 1.602×10^{-19} J, k = 1.38×10^{-23} JK^{-1})

4. (a) Discuss BET and the Harkins and Jura methods of determining the surface area of adsorbents. 7

OR

Derive Gibbs adsorption isotherm equation and explain positive surface activity from it.

(b) (i) Write a note on surface active agents. 4

(ii) According to BET isotherm the value of v_m for adsorption of nitrogen gas on silica gel at – 163 °C is 160.2 ml. gm^{-1}. One molecule of nitrogen covers area 16.2 $Å^2$. Calculate the surface area of silica gel. 3

OR

(i) Explain critical miceller concentration. 4

(ii) For a 5×10^{-5} M aq. solution of n-butanoic acid $\frac{dr}{dc} = -0.135$ Nm^2 mol^{-1} at 298 °K. Calculate surface excess (Gibbs adsorption) of the acid. 3

5. Answer in brief (**one** mark each) :

(1) Define fugacity.

(2) Define ideal solution.

(3) Define chemical potential.

(4) Define order of reaction.

(5) Define chain length.

(6) Define energy of activation.

(7) Define conductors.

(8) Define semiconductors.

(9) Define Unit Cell.

(10) What is adsorption isotherm ?

(11) What is sorption ?

(12) Define chemisorption.

(13) Define insulators.

(14) If the Miller indices are 100, then to which axis the given plane is parallel.
