

D-562

December-2011

Sem-I

Time : 3 Hours]

[Max. Marks : 70

Instructions : (1) All questions carry equal marks.

(2) Necessary constants :

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

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

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

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

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

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

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

$$F = 96500 \text{ C}$$

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

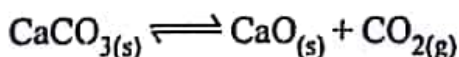
OR

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



- (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 3.0×10^{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, $k = 1.38 \times 10^{-23}$ 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 Å². 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 $\frac{dr}{dc} = -0.135$ Nm² mol⁻¹ at 298 °K. Calculate surface excess (Gibbs adsorption) of the acid. 3

5. Answer in brief (one mark each) :

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- ✓(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.
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