Seat No. : 320

N27-103

December-2014

M.Sc., Sem.-I

403 : Chemistry

(Physical Chemistry)

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 $\cdot$ K^{-1} $= 1.38 \times 10^{-23}$ J K^{-1}

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

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

$R = 8.314 \times 10^{7}$ ergs K^{-1} M^{-1}

$= 8.314$ J K^{-1} M^{-1}

$= 1.987$ Cal $\cdot$ K^{-1} M^{-1}

$F = 96500$ C

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

OR

Discuss method of intercept for the determination of partial molar volume.

(b) Determine fugacity using Vander Waal's equation. 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.

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

(ii) What is fugacity of gas when it's activity coefficient is 0.836 at 12 atmosphere pressure ?

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

OR

Define chain reaction and discuss kinetics of chain reaction.

(b) (i) Write a note on explosion limits. 4

(ii) Calculate frequency factor (A) for the decomposition of N_2O_5 at 25 °C. The value of entropy of activation (ΔS^*) is 4.354 cal.mol^{-1}.deg^{-1}.(e.u.). 3

OR

(i) Derive theory of absolute reaction rates. 4

(ii) At 558 °K the frequency factor (A) for a reaction is found to be 8.7×10^{15} second^{-1}. Calculate the entropy of activation (ΔS^*) for reaction. 3

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

OR

Classify materials into conductors, semiconductors and insulators. Explain on what basis this classification is made.

(b) Discuss defects in Solid. 7

OR

Discuss Super Conductivity.

4. (a) Derive Gibbs adsorption isotherm equation and explain positive and negative surface activity from it. 7

OR

What are miceller ? Explain critical miceller concentration.

(b) Derive BET equation. 7

OR

(i) Write a note on detergents. 4

(ii) According to BET isotherm, the value of V_m for adsorption of nitrogen gas on silica gel at –183 °C is 116.2 $ml \cdot gm^{-1}$. The surface area of silica gel is 506.3 meter$^2 \cdot gm^{-1}$. Calculate the area covered by one molecule of nitrogen. 3

5. Answer in brief (one mark each) : 14

(1) What is fugacity ?

(2) Define chemical potential.

(3) Define ideal solution.

(4) What is unimolecular reaction ?

(5) Define Chain Length.

(6) Define order of reaction.

(7) What is unit cell ?

(8) Define semi-conductor and give two examples.

(9) Define Schottky defects.

(10) What is Sorption ?

(11) What is adsorption isotherm ?

(12) What is unit of surface tension (γ) in C.G.S. ?

(13) What is enzyme ?

(14) What is adsorbate ?