Physical

Seat No. : 198

KJ-604

December-2012

403 : Chemistry, Paper - III

(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.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) State the third law of thermodynamics. Show how the absolute entropy of a substance can be determined with the help of this law. **07**

OR

Derive Gibbs-Duham equation. **07**

(B) (i) Determine fugacity using Van der Waal's equation. **04**

(ii) For the water-gas reaction **03**

$$CO_{2(g)} + H_{2(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)}$$

$\Delta H = 10{,}000$ Cal, whereas the conventional chemical constants are $H_2 = 1.6$, $CO_2 = 3.2$, $CO = 3.5$ and $H_2O = 3.6$.

Calculate K_p at 800 °C.

OR

(i) Discuss density measurement method for the determination of partial molar volume. 04

(ii) The vapour pressure of liquid chlorine is 3.88 atmosphere at 298 °K and molar volume of vapour under these conditions is 6.10 litre.mole^{-1}. Calculate the fugacity of liquid chlorine at 298 °K. (R = 0.82 litre.atm.mole^{-1}.deg^{-1}) 03

2. (A) Derive the Michaelis Menten equation of enzyme catalyzed reaction. 07

OR

Define chain reaction and discuss kinetics of chain reaction. 07

(B) (i) Write a note on branched chain reaction. 04

(ii) At 290 °C the frequency factor of the unimolecular decomposition of $(CH_3CO)_2$ is found to be 8.5×10^{15} sec^{-1}. Calculate entropy of activation (ΔS^*) for reaction. 03

OR

(i) Derive theory of absolute reaction rates. 04

(ii) Calculate the frequency factor (A) for the decomposition of organic substance at 300 °K. The value of entropy of activation (ΔS^*) is 6.48 Cal.mole^{-1}.deg^{-1}. (e.u.) 03

3. (A) Define Frenkel defects and derive an equation to calculate number of Frenkel defects in solid. 07

OR

Classify materials into conductors, semiconductors and insulators. Explain on what basis this classification is made. 07

(B) Discuss defects in solid. 07

OR

Discuss superconductivity. 07

4. (A) Derive BET equation. 07

OR

Derive Gibbs' absorption isotherm equation and explain positive and negative surface activity from it. 07

(B) (i) Explain critical miceller concentration. 04

(ii) For 1×10^{-4} m solution of n-butanoic acid $\frac{d\gamma}{dc}$ is –0.08 N.m^2.mole^{-1} at 25 °C. Calculate surface excess (Gibbs adsorption) of the acid. 03

OR

$\Gamma = -\frac{C}{RT}\frac{d\gamma}{dC}$

(i) Give difference between physical adsorption and chemical adsorption. 04

(ii) According to BET isotherm the value of V_m for adsorption of nitrogas on silica gel at – 183 °C is 116.2 $ml.gm^{-1}$, the area occupied by a one molecule of nitrogen gas is 16.2×10^{-20} $metre^2$. Calculate surface area of silica gel. ($N = 6.023 \times 10^{23}$) 03

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

(1) What is fugacity ?

(2) State Raoult's law.

(3) Define chemical potential.

(4) What is unimolecular reaction ?

(5) Define Enzyme.

(6) Define order of reaction.

(7) What is unit cell ?

(8) Define super conductor.

(9) Define crystal.

(10) Define energy of activation.

(11) What is sorption ?

(12) What is mercerization ?

(13) Define Adsorption isotherm.

(14) What is adsorbate and adsorbant ?