Seat No. : 410

DC-121

December-2018

M.Sc., Sem.-I

403 : Physical Chemistry

Time : 2:30 Hours] **[Max. Marks : 70**

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}

$h = 6.626 \times 10^{-27}$ erg.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}.

$F = 96500$ C

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

$= 8.314$ $JK^{-1}M^{-1}$

$= 1.987$ cal. $K^{-1}M^{-1}$

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 and calculate given below example. **14**

Calculate the entropy change accompanying the conversion of 1 mole of ice at 273 °K and 1 atmospheric pressure into steam at 373 °K and 1 atmospheric pressure, given that at 273 °K, the molar heat of fusion of ice, ΔH_f is 6.002 kJ mole^{-1} and at 373 °K, the molar heat of vapourisation of water, ΔH_v is 40.602 kJ mole^{-1}. It is also assumed that the molar heat capacity in the temperature range 373 – 273 °K remains constant at 75.22 JK^{-1} mol^{-1}.

OR

(i) Derive Gibbs-Duham equation. **7**

(ii) For a reaction $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ **7**

$\Delta H = 43200$ cal., whereas the conventional chemical constants are $N_2 = 2.6$, $O_2 = 2.8$ and $NO = 3.5$. Calculate K_p at 2200 °K.

(B) Answer in brief any **four** of the following : 4

(i) Define : Chemical potential

(ii) Define : Raoult's law

(iii) Define : Activity co-efficient

(iv) Define : Fugacity

(v) Define : Non-ideal solution

(vi) Write only equation of density measurement method for determination of partial molar volume.

2. (A) Define chain reaction. Discuss kinetics of chain reaction and calculate given below example. 14

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}.

OR

(i) Discuss Lindemann theory of unimolecular reactions. 7

(ii) Calculate frequency factor(A) for the unimolecular decomposition of $(CH_3CO)_2$ at 285 °C. The value of the entropy of activation (ΔS^*) is 13.15 cal.mol^{-1}.deg^{-1} (e.u.). 7

(B) Answer in brief any **four** of the followings : 4

(i) Define : Chain length

(ii) Define : Unimolecular reaction

(iii) Define : Order of reaction

(iv) Define : Energy of activation

(v) Define : Enzyme

(vi) What is molecularity of reaction ?

3. (A) Derive an equation to calculate number of Schottky defects in solid and calculate given below example. 14

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

OR

(i) Discuss Perovskites. 7

(ii) Classify materials into conductors, semi-conductors and insulators. Explain on what basis this classification is made. 7

(B) Answer in brief any **three** of the following : 3

(i) What is unit cell ?

(ii) Define : Schottky defects.

(iii) Define insulator and give one example.

(iv) Pure silicon is an insulator but becomes a semi-conductor on heating. Why ?

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

4. (A) Derive Gibbs adsorption isotherm equation and calculate given below example : 14

For a 1.01×10^{-4}M aqueous solution of n-butanoic acid at 27 °C $\frac{d\gamma}{dc} = -0.081\ Nm^2\ mole^{-1}$.

If we use the Gibbs adsorption equation, determine the surface excess of butanoic acid and also calculate the average surface area available to each molecule.

OR

(i) What are miceller ? Explain critical miceller concentration. 7

(ii) In the study of adsorption of nitrogen gas on Fe-Al_2O_3 at 77 °K, the area occupied by a molecule of nitrogen is 16.2×10^{-20} metre^2. If the specific area of Al_2O_3 is 12.46 metre^{-2}gm^{-1}, calculate the value of V_m is BET isotherm. 7

(B) Answer in brief any **three** of the following : 3

(i) What is adsorption isotherm ?

(ii) What is sorption ?

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

(iv) What is adsorbate and adsorbant ?

(v) What is specific surface area ?
