Seat No. : 1187

DO-129

December-2017
M.Sc., Sem.-I
403 : Physical Chemistry

Time : 3 Hours] **[Max. Marks : 70**

Instructions : (1) Attempt all questions.
(2) Necessary constants :
$N_A = 6.02213 \times 10^{23}\ mol^{-17}$
$k_B = 1.3806 \times 10^{-16}\ erg\ K^{-1} = 1.3806 \times 10^{-23}\ J\ K^{-1}$
$h = 6.6260 \times 10^{-27}\ erg\ s = 6.6260 \times 10^{-34} J\ s$
$c = 2.998 \times 10^{10}\ cm\ s^{-1} = 2.998 \times 10^{8}\ m\ s^{-1}$
$R = 8.3145 \times 10^{7}\ erg\ K^{-1}\ mol^{-1} = 8.3145\ J\ K^{-1}\ mol^{-1}$

1. (A) Explain the term partial molar free energy. Show that
$(\delta G/\delta n_i)_{P,T,n} = (\delta A/\delta n_i)_{V,T,n} = (\delta H/\delta n_i)_{P,S,n} = (\delta U/\delta n_i)_{V,S,n}$ 7

OR

Explain the term fugacity and activity. What is the physical significance of Fugacity ? How are they related to chemical potential ? The activity of 2.0 moles of substance changes from 0.04 to 0.30. What would be the change in it's free energy at 25 °C ?

(B) What are partial molar properties ? Show how partial molar volume can be determined by density measurements. 7

OR

Explain how chemical potential varies with temperature and pressure. What is the physical significance of chemical potential ?

2. (A) Discuss activated complex theory of bimolecular reactions. 7

OR

Explain the mechanism and kinetics of chain reaction between hydrogen and bromine.

(B) Discuss the theory of absolute reaction rate. 7

OR

Write a note on branched chain reaction. If the activation energy of a reaction is 80.9 kJ mol^{-1}, calculate the fraction of molecules at 400 °C which have enough energy to form products.

3. (A) On which basis the solids are classified as metals, semi-conductors and insulators ? Discuss the mechanism of electrical conductivity in each of the cases. 7

OR

What are Frenkel defects ? Derive an expression for number of Frenkel defects in a crystal.

(B) Explain bond theory of metals. 7

OR

Write note on non-stoichiometric defects. Estimate the mole fractions of Frenkel defects in a NaCl crystal at 1000 K. The energy for formation of these defects is 3 eV. ($1\ eV = 1.602 \times 10^{-19}\ J\ K^{-1}$)

4. (A) What is micelles ? Explain critical micellar concentration. 7

OR

Discuss the BET and the Harkins and Jura method of determining the surface area of adsorbents.

(B) Derive Gibb's adsorption isotherm equation and explain surface activity from this equation. 7

OR

Write a note on surface tension and detergents. For a 1.0×10^{-10} M aqueous solution of n-butanoic acid $d\gamma/dc = -0.080\ N\ m^2\ mol^{-1}$, at 25 °C. Using the Gibbs adsorption equation, determine the surface excess of the acid and also calculate the average surface area available to each molecule.

5. Answer the following. (one mark each) 14

(i) Give any two applications of third law of thermodynamics.
(ii) Name any two point defects.
(iii) Explain the term defect in crystal.
(iv) Why is the value of ΔG at melting point of ice zero ?
(v) Define superconductivity.
(vi) Give any two applications of liquid crystals.
(vii) How does entropy change with pressure ?
(viii) Give any two assumptions of BET theory.
(ix) What is significance of $T\Delta S$ in $\Delta G = \Delta H - T\Delta S$?
(x) Explain why q + w is a state function.
(xi) Define Schottky defects.
(xii) What is unimolecular reaction ?
(xiii) Why a finely divided substance is more effective as an adsorbent ?
(xiv) Why a small rise in temperature increases the rate of reaction to a large extent ?