M. Sc Chemistry Examination, SEM-I
April - 2016
Physical Chemistry Paper – III (Code: 2763)
(Chemical Thermodynamics)

Time: 2.5 hours   **Total Marks: 70**

Instructions: All questions carry equal marks

1 (A) Define: $\overline{H}_1$, $\overline{H}^\circ_1$, $\overline{H}_2$, $\overline{H}^\circ_2$, $\overline{L}_1$, $\overline{L}_2$ 04

   (B) Deduce following relationship: $n_1\,\overline{L}_1 + n_2\,\overline{L}_2 = n_2\phi_L$ 05

   (C) How much heat is evolved when 1 mole of H_2SO_4 is added to 200 moles H_2O at 25°C.   05

Given: moles H_2O / moles H_2SO_4	$\overline{L_1}$, cal. Mol^{-1}	$\overline{L_2}$, cal. Mol^{-1}
200	-2.16	5842
100	-2.68	5888
0	--	23540

OR

1 (A) Deduce an expression $\Delta H_{c\rightarrow 0} = -n_2\phi_L$ for heats of dilution to infinite dilution.   04

   (B) Discuss the partial molar heat capacity.   06

   (C) The mean ionic activity coefficient of sodium chloride was found to be 0.641 at 80°C, 0.632 at 90°C and 0.622 at 100°C. Determine the value of $\overline{L}_2$ at about 90°C.   04

2 (A) Explain homogeneous and heterogeneous equilibrium reactions.   08

   (B) Does a catalyst affect the equilibrium position and equilibrium constant? Explain.   06

OR

2 (A) Does equilibrium constant has unit and depend on temperature? Explain.   04

   (B) Distinguish between homogeneous and heterogeneous equilibrium.   02

   (C) Explain Kc in homogeneous and heterogeneous system with suitable examples.   05

   (D) Define equilibrium constant. Explain effect of pressure on it.   03

3 (A) Discuss "Raoults law" and Henry's law in detail.   08

   (B) Explain ideal and non-ideal solutions giving suitable examples.   06

OR

3 (A) Discuss in brief: "Vapor pressure curves".   08

   (B) Explain deviation of the constituents of a mixture from ideal behaviour.   04

   (C) Write final equation suggested by Duhem-Margules.   02

4   (A) Give definition of activity coefficient.   02
     (B) Define: Osmosis, Osmotic cell and Rational activity coefficient.   06
     (C) Explain osmotic pressure method used for determining activity of solvent.   06
                                        OR

4   (A) Explain choice of standard state in detail.   06
     (B) Determine activity of solvent from vapour pressure method.   06
     (C) Define the tem activity.   02

5   (A) Discuss the determination of fugacity by graphical method   07

     (B) The variation of the density of aqueous sodium nitrate solution with molality at 25°C   07
         is given by: $\rho = 0.99708 + 3.263 \times 10^{-2} \, m - 9.63 \times 10^{-4} \, m^{3/2} - 4.73 \times 10^{-5} \, m^2$ gm/ml. Using the
         expression: $\overline{V}_2 = 1/\rho \, [M_2 - V \, d\rho/dm]$, determine the partial molar volume of sodium nitrate in
         1.0 molar (M.W. of sodium nitrate = 85 gm/mole)
                                        OR

5   (A) Discuss the variation of fugacity with temperature or pressure   07

     (B) The volume of NaCl solution per 1000 gm of water at 25°C is given by   07
         $V = 1002.9 + 16.40m + 2.5ml - 1.2m^3$ ml mol.$^{-1}$ Calculate partial molar volume and apparent
         molar volume of 1 molar NaCl solution. (Given: molar volume of pure water at 25°C is
         18.069 ml mol^{-1})