M. Sc Chemistry Examination, SEM-I
November – 201_7_
Physical Chemistry Paper – III (Code: 2763)
(Chemical Thermodynamics)

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

Instructions: All questions carry equal marks

1 (A) Define terms: $\overline{H_2}, \overline{H^0{}_1}, \overline{L_2}, L$ 02

   (B) Derive following relationship   08

$$Log \frac{\gamma_{\pm}}{\gamma'_{\pm}} = \frac{\overline{L_2}}{4.576 \times v} \left[\frac{1}{T} - \frac{1}{T^l}\right]$$

   (C) Calculate the heat change when one mole of H_2SO_4 is added to a solution of one mole
       of H_2SO_4 in 400 moles H_2O at 25°C.   04

Given: moles H_2O	$\overline{L_1}$	$\overline{L_2}$
moles H_2SO_4	cal. Mol^{-1}	cal. Mol^{-1}
0	—	23540
200	-2.16	5842
400	-1.54	5638

OR

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

   (B) Deduce the apparent molar heat capacity.   06

   (C) Assuming $\overline{L_2}$ to remain constant, calculate the relative change in the mean ionic activity
       coefficient of 1 molar sulphuric acid solution from 0° to 27°C $\overline{L_2}$ for 1 molar sulphuric acid
       solution is 6000 cal.   04

2 (A) Explain homogeneous and heterogeneous equilibrium reactions.   06

   (B) Define equilibrium constant. Explain effect of concentration and pressure on it.   06

   (C) Does a catalyst affect the equilibrium position? Explain.   02

OR

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

   (B) Distinguish between homogeneous and heterogeneous equilibrium.   04

   (C) Explain Kc in homogeneous and heterogeneous system with suitable examples.   06

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

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

OR

3 (A) Discuss "Raoults law" and Henry's law in detail.   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.   02
    (B) Define: Osmotic cell and Rational activity coefficient.   04
    (C) Explain osmotic pressure method used for determining activity of solvent.   08

                                            OR

4   (A) Explain in detail Isopiestic method.   04
    (B) Discuss the E.M.F. method for determining activity of solvent in solution   08
    (C) What is activity coefficient?   02

5   (A) Discuss Lewis-Randall rule.   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})

                                            OR

5   (A) Discuss the determination of fugacity by equation of state 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: $\bar{V}_2 = 1/\rho [M_2 - V d\rho/dm]$, determine the partial molar volume of sodium nitrate
        in 1.0 molar (M.W. of sodium nitrate = 85 gm/mole)