

## FACULTY OF SCIENCE

M.Sc. I – Semester (CBCS) Examination, December 2016

Subject: Chemistry

Paper – III

Physical Chemistry

Time: 3 Hours

Max.Marks: 80

Note: Answer all questions from Part-A and Part-B.

Each question carries 8 marks in Part-A and 12 marks in Part-B.

## PART – A (4x8 = 32 Marks)

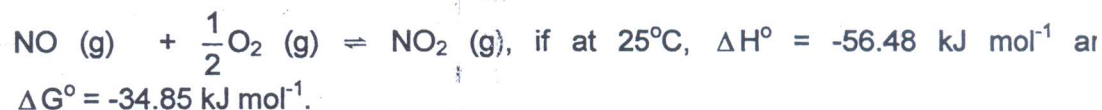
[Short Answer Type]

- 1 a) Calculate the change in entropy accompanying the heating of one mole of Helium gas, assumed ideal, from a temperature of 298 K to a temperature of 1000 K at constant pressure. Given that  $C_V = \frac{3}{2}R$ .
- b) Derive Gibbs – Durham equation.
- 2 a) Calculate the e.m.f. of the electrode concentration cell.  
Pt | H<sub>2</sub>, HCl, H<sub>2</sub> | Pt. at 25°C if P<sub>1</sub> = 600 torr and P<sub>2</sub> = 400 torr.  
(P=1) ... (P<sub>2</sub>)
- b) How do you determine pH of a solution by using glass electrode? Explain.
- 3 a) Derive Schrödinger wave equation from wave mechanics.
- b) Calculate the no. of degenerate energy levels for the first three states of a particle moving in a three dimensional box of length equal to L.
- 4 a) Explain the primary salt effect on the rate of a reaction in solution.
- b) Define the terms.
  - i) Isokinetic temperature and
  - ii) Hammond's postulate

## PART – B (4x12 = 48 Marks)

[Essay Answer Type]

- 5 a) Calculate K<sub>p</sub> at 25°C and 325°C for the reaction.



- b) Show that  $\left(\frac{\partial \mu_i}{\partial P}\right)_{T, P, n_1, n_2, \dots, n_i} = -\bar{V}_i$ .

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OR

- c) Derive Clausius – Clapeyron equation.
- d) Define partial molar volume and obtain the relation between solution volume and partial molar volume.
- 6 a) Explain the concept of activity and activity coefficients in electrolytic solutions.
- b) Calculate the value of the liquid junction potential at 25°C between two solutions of HCl having activities 0.05 and 0.005 respectively. The transference number of H<sup>+</sup> in HCl is 0.83.

OR

- c) Explain Bjerrum theory of ion association.
- d) Calculate the mean activity coefficient ( $\gamma_{\pm}$ ) of Na<sub>2</sub>SO<sub>4</sub> at a molality of 0.001 in aqueous solution at 25°C. (For water at 25°C, A = 0.509).
- 7 a) Derive the normalized wave function of the particle moving in a one dimensional box of length 'L'.
- b) A cricket ball weighing 100 g is to be located within 0.1 Å. What is the uncertainty in its velocity? Comment on your result.

OR

- c) Show that eigen functions with different eigen values of Hermitian operator are orthogonal to each other.
- d) Discuss the postulates of quantum mechanics.
- 8 a) Explain the transition state theory and derive the Eyring's equation.
- b) Discuss the Hammett's equation and write its significance.

OR

- c) i) What is Taft's equation? Explain its significance.
- ii) In a base catalysed aliphatic ester hydrolysis reaction, if the reaction constant is found to be -3.7, what would be the rate constant of ethyl substituted ester hydrolysis. The polar substituent constant of ethyl is -0.1 and the rate constant of the aliphatic ester hydrolysis is  $2.5 \times 10^{-4} \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  (consider the steric effect to be insignificant).
- d) What are opposing reactions? Derive the first order rate constant expression for the forward reaction.

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