Code No. 6027 / CBCS

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.

$Pt \mid H_2, HCl, H_2 \mid Pt$ at 25°C if P_1 = 600 torr and P_2 = 400 torr.
$(P=1) \quad (P_2)$

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_P at 25°C and 325°C for the reaction.

$NO\ (g) + \frac{1}{2}O_2\ (g) \rightleftharpoons NO_2\ (g)$, if at 25°C, ΔH° = -56.48 kJ mol^{-1} and ΔG° = -34.85 kJ mol^{-1}.

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

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^+ in HCl is 0.83.

OR

c) Explain Bjerrum theory of ion association.

d) Calculate the mean activity coefficient $(\gamma_\pm)$ of Na_2SO_4 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 2.5×10^{-4} $dm^3.mol^{-1}.s^{-1}$ (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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