Roll No. ……..

CHE–503

Physical Chemistry

M. Sc. CHEMISTRY (MSCCH–12/13/16)

First Year, Examination, 2017

Time : 3 Hours **Max. Marks : 80**

Note : This paper is of **eighty (80)** marks containing **three (03)** Sections A, B and C. Attempt the questions contained in these Sections according to the detailed instructions given therein.

Section–A

(Long Answer Type Questions)

Note : Section 'A' contains four (04) long answer type questions of nineteen (19) marks each. Learners are required to answer *two* (02) questions only.

1. (a) Define Joule-Thomson coefficient. Show that it is zero for an ideal gas and has a positive value for a real gas. 9

   (b) Derive an expression for Joule-Thomson coefficient of a van der Waals' gas. 10

2. (a) Solve the Schrödinger wave equation for particle in an infinite one-dimensional box with potential energy zero inside the box and also normalize the wave function. 12

   (b) Why can the zero point energy of a particle in a box not be zero ? 7

3. (a) Derive the second order reactions when initial concentrations of all reactants are same. Derive an expression for the half-life period of such a reaction. 10

   (b) Discuss critically the effect of temperature on the reaction rates, with particular mention of the significance of activation energy. 9

4. (a) What do you mean by the e. m. f. of a cell ? Discuss, in brief how you will proceed to determine the e. m. f. of a cell. 12

   (b) What is L. J. P. ? Derive an expression for it. 7

Section–B

(Short Answer Type Questions)

Note : Section 'B' contains eight (08) short answer type questions of eight (08) marks each. Learners are required to answer *four* (04) questions only.

1. Explain Huckel theory of π-conjugated systems.
2. (a) Derive a relation between $C_P - C_V$ for ideal gases.

   (b) Derive the relation between ΔU and ΔH for an ideal gas.

3. Deduce ΔS (change in entropy) and ΔG (change in Gibbs' free energy) of mixing of two different ideal gases at T°K and P atm.
4. What are the basic assumptions of Debye-Huckel theory ? How does it explain the variation of equivalent conductance of a strong electrolyte with concentration ?

5. Explain *two* approximation methods generally used for elucidating the mechanism of complex reaction.
6. With suitable example explain eigen value and eigen function.
7. Explain *two* basic laws of photochemistry.
8. Explain the terms fluorescence and phosphorescence.

Section–C

(Objective Type Questions)

Note : Section 'C' contains ten (10) objective type questions of one (01) mark each. All the questions of this Section are compulsory.

1. The entropy of a perfect crystalline solid at an absolute zero is :
   (a) Positive (b) Negative
   (c) Abnormal (d) Zero
2. In an isolated system entropy change is ..... for a reversible change.
3. The unit of ionic mobility in C. G. S. is .....
4. Phosphorescence is represented as :
   (a) $T_1 \rightarrow S_0 + h\nu$
   (b) $T_1 \rightarrow S_0 + \Delta$
   (c) $S_1 \rightarrow S_0 + h\nu$
   (d) $S_1 \rightarrow T_1 + \Delta$
5. In the electrochemical reaction

$$2Fe^{3+} + Zn \rightarrow Zn^{2+} + 2\,Fe^{2+}$$

   increasing the concentration of Fe^{2+} :
   (a) Increase the cell e. m. f.
   (b) Increase the current flow
   (c) Decrease the cell e. m. f.
   (d) Alter the pH of the solution

6. What is the unit of the rate constant of *n*th order reaction ?

7. The Daniel cell is :

   (a) $Pt\,(s)|Zn\,(s)|\,Zn^{2+}\,(aq)||\,Cu^{2+}\,(aq)|Cu(s)|\,Pt^{2+}\,(s)$

   (b) $Pt\,(s)|Zn\,(s)|\,Zn^{2+}\,(aq)||\,Ag^{+1}\,(aq)|Ag(s)|\,Pt^{2+}\,(s)$

   (c) $Pt\,(s)|Fe\,(s)|\,Fe^{2+}\,(aq)||\,Cu^{2+}\,(aq)|Cu(s)|\,Pt^{2+}\,(s)$

   (d) $Pt\,(s)|\,H_2\,(s)|\,H_2SO_4\,(aq)||\,Cu^{2+}\,(aq)|Cu(s)|\,Pt^{2+}\,(s)$

8. Quantum yields of photochemical reactions are due to :
   (a) Lowering the activation energy
   (b) High frequency of collision
   (c) Accompanying side reactions
   (d) Formation of free radicals

9. The MOT :
   (a) Puts equal importance on both ionic and covalent structures
   (b) Overestimates the importance of ionic structures
   (c) Underestimates the importance of covalent structures
   (d) None of the above

10. If *n* denotes the number of eigen states of a hydrogen atom, then its discrete energy levels are proportional to :

   (a) n (b) n^2

   (c) $\frac{1}{n^2}$ (d) $\frac{1}{n}$