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
- (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.
  - (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.
  - (b) Discuss critically the effect of temperature on the reaction rates, with particular mention of the significance of activation energy.
- 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  $\pi$ -conjugated systems.
- 2. (a) Derive a relation between  $C_P C_V$  for ideal gases.
  - (b) Derive the relation between  $\Delta U$  and  $\Delta H$  for an ideal gas.
- 3. Deduce  $\Delta S$  (change in entropy) and  $\Delta G$  (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)  $T_1 \rightarrow S_0 + hv$
  - $(b) \quad T_1 \mathop{\longrightarrow} S_0 + \Delta$
  - (c)  $S_1 \rightarrow S_0 + hv$
  - (d)  $S_1 \rightarrow T_1 + \Delta$
- 5. In the electrochemical reaction

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

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

- [4]
- 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<sup>2+</sup>(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<sup>2+</sup>(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) 1 (d) 1

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

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