

**FACULTY OF SCIENCE**  
**M. Sc I Semester Examination, January 2018**

**Subject: Physical 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.**

**Section-A (4x8=32 Marks)**  
 (Short Answer Type)

- 1 (a) What is Clausius inequality? Discuss its significance.  
 (b) Give the expression for entropy of mixing  $\Delta S_{\text{mix}}$  when two ideal gases are mixed.
- 2 (a) Define an electrochemical cell? Based on the usage of electrodes classify them giving an example for each.  
 (b) If the emf of the cell  $\text{Cu} | \text{Cu}^{2+} (0.1\text{M}) | \text{Ag}^+ (M=? | \text{Ag}$  at  $25^\circ\text{C}$  is  $0.422\text{V}$  and  $E^0$  is  $0.46\text{V}$ , calculate the molarity of  $\text{Ag}^+$  ions.
- 3 (a) Define an operator. Write about i) Hermitian operator ii) complex functions.  
 (b) A microscope using suitable photons is employed to locate an atom within a distance of  $0.1\text{\AA}$ . What is uncertainty involved in the measurement of its velocity?
- 4 (a) State and explain Lindemann's theory of reaction rates.  
 (b) Explain how the structure affects the reactivity with two examples.

**Section-B (4x12=48 Marks)**  
 (Essay Answer Type)

- 5 (a) State third law of thermodynamics. Explain how absolute entropy of a liquid at  $25^\circ\text{C}$  be evaluated?  
 (b) In a reversible process, the molar entropy of an ideal gas at  $300\text{K}$  is  $150\text{JK}^{-1}\text{mol}^{-1}$ . Find its value at  $600\text{K}$ . ( $C_{p,m}=21\text{JK}^{-1}\text{mol}^{-1}$ )  

**OR**

 (c) Derive Gibbs-Helmholtz equation and explain its usefulness.  
 (d) Calculate  $\Delta G$  when two moles of an ideal gas are compressed isothermally and reversibly at  $100^\circ\text{C}$  from a pressure of  $10\text{atm}$  to  $20\text{atm}$
- 6 (a) Define single electrode potential. Classify various types of electrodes with examples?  
 (b) Derive an expression for the liquid junction potential of the cell  
 $\text{Ag} | \text{AgCl(s)} | \text{HCl} (a_1) : \text{HCl} (a_2) | \text{AgCl(s)} | \text{Ag}$   

**OR**

 (c) Define and differentiate between activity, activity coefficient and mean ion activity coefficient in electrolytic solutions?  
 (d) Derive Debye-Huckel Onsager equation. Discuss its validity and limitations.

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7 (a) Write the Schrodinger wave equation for a particle in a box of dimensions  $x=0$  to  $x=a$ . Calculate the energy of the particle in the box for  $n=1$  when  $x=a/2$ .

(b) If  $y=e^{-kx}$ , what is the eigen value when the operator  $\left(\frac{d^2}{dx^2} - x^2\right)$  operates on  $y$ .

**OR**

(c) Write about postulates of quantum mechanics.

(d) What are commuting operators? What is their significance in quantum mechanics?

8 (a) Draw a potential energy surface diagram and explain the significance of reaction coordinate, activated complex and activation parameters.

(b) The rate constant of a reaction are  $1.6 \times 10^{-3} \text{ s}^{-1}$  and  $1.6 \times 10^{-2} \text{ s}^{-1}$  at  $10^\circ\text{C}$  and  $20^\circ\text{C}$  calculate the activation energy

**OR**

(c) What are chain reactions? Write the mechanism of  $\text{H}_2\text{-Br}_2$  reaction and derive the rate law.

(d) Write a note on influence of ionic strength on reaction rates.

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