



**WEST BENGAL STATE UNIVERSITY**  
B.Sc. Honours 4th Semester Examination, 2022



**CEMACOR08T-CHEMISTRY (CC8)**

**PHYSICAL CHEMISTRY-III**

Time Allotted: 2 Hours

Full Marks: 40

*The figures in the margin indicate full marks.  
Candidates should answer in their own words and adhere to the word limit as practicable.  
All symbols are of usual significance.*

**Answer any three questions taking one from each unit**

**Unit-I**

1. (a) Consider a one component system. Explain the variation of the slope of  $\mu$  vs.  $T$  plot at constant pressure as we go from **solid**  $\rightarrow$  **liquid**  $\rightarrow$  **gas**. 4
- (b) The melting point of pure phenol is **40.5°C**. A solution containing 0.18 gm acetanilide in 13.0 gm phenol freezes at **39.5°C**. Calculate the cryoscopic constant of phenol. Why the concentration is expressed in molality instead of molarity? 3+1
- (c) What do you mean by the abnormal colligative properties? What is Van't Hoff factor? Consider a **0.6%** aqueous solution of NaCl. It is experimentally observed that the solution freezes at **-0.3°C**. Calculate the Van't Hoff factor and degree of dissociation of NaCl in the aforesaid solution. 2+1+3
2. (a) State Gibbs phase rule of a thermodynamic system at equilibrium. Find out the number of Phase(s), Component(s) and Degree(s) of Freedom of the following systems at equilibrium. 2+3
  - (i)  $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$  ; (ii)  $\text{NH}_4\text{Cl}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{HCl}(\text{g})$
- (b) State Raoult's law and Henry's law. Show that Henry's law follows from Raoult's law for dilute solutions. 2+2
- (c) Consider the Maxwell's equation for a single phase given by  $\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$ . 2+3

Derive Clapeyron equation from this relation. Show that

$$\left(\frac{\partial P}{\partial T}\right)_{\text{solid} \rightarrow \text{gas}} > \left(\frac{\partial P}{\partial T}\right)_{\text{liquid} \rightarrow \text{gas}}$$

**Unit-II**

3. (a) What do you mean by activity and activity coefficient of an ionic solution? Discuss how the electrophoretic and relaxation effects play the role to reduce the ionic mobility in Debye-Hückel theory. 2+4

- (b) Calculate the equilibrium constant for the reaction given by 2+3
- $$\text{Cu}^{2+} + \text{Zn} \rightleftharpoons \text{Cu} + \text{Zn}^{2+}$$
- [Given:  $E_{\text{Cu}^{2+}/\text{Cu}}^0 = 0.337 \text{ V}$  ;  $E_{\text{Zn}^{2+}/\text{Zn}}^0 = -0.763 \text{ V}$  at  $25^\circ\text{C}$ ].
- (c) Discuss the principle of determination of pH of a solution by using quinhydrone electrode. 3
4. (a) What do you mean by reversible and irreversible electrochemical cells? Explain with an example. 2+2
- (b) Determine the standard equilibrium constant of the following reaction at 298 K. 4
- $$2\text{Fe}^{3+} + \text{Sn}^{2+} \rightarrow 2\text{Fe}^{2+} + \text{Sn}^{4+}$$
- [  $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 = 0.771 \text{ V}$  ;  $E_{\text{Sn}^{4+}/\text{Sn}^{2+}}^0 = 0.150 \text{ V}$  ]
- (c) What is the principle underlying potentiometric titrations? Explain how can we determine the pH of a solution using Quinhydrone electrode. 1+3
- (d) State whether the statement is true or false: 2
- “In order to minimize Liquid Junction Potentials, one must use a salt bridge containing a salt such that  $t_+ = t_-$ .”

### Unit-III

5. (a) Find the value of the commutator,  $[L_x, L_y]$ . 4
- (b) Show that  $Y_1^{-1}(\theta, \phi)$  is normalized and orthogonal to  $Y_0^0(\theta, \phi)$ . 4
- Given:  $Y_1^{-1}(\theta, \phi) = (3/8)^{1/2} \sin \theta e^{-i\phi}$  and  $Y_0^0(\theta, \phi) = (1/4\pi)^{1/2}$
- (c) Write down the electronic Hamiltonian of  $\text{H}_2^+$ . 2
- (d) Draw the radial probability density with respect to distance from the nucleus for 2s orbital of hydrogen atom. 2
6. (a) Write down the time-independent Schrödinger equation for H-atom in polar coordinates with the meaning of the symbols. 2
- (b) Find out the average distance of the electron of a hydrogen atom in 1s orbitals. 3
- [Given:  $\psi_{1s} = \left( \frac{1}{\pi a_0^3} \right)^{1/2} \cdot e^{-r/a_0}$  ]
- (c) Write the Hamiltonian operator for the hydrogen molecule stating the meaning of the symbols. 2
- (d) Explain the concepts of molecular orbital theory and valence bond theory. State the strengths and limitations of valence bond approach to molecular bonding. 3+2

**N.B. :** Students have to complete submission of their Answer Scripts through E-mail / Whatsapp to their own respective colleges on the same day / date of examination within 1 hour after end of exam. University / College authorities will not be held responsible for wrong submission (at in proper address). Students are strongly advised not to submit multiple copies of the same answer script.

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