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 μ vs. T plot at constant pressure as we go from **solid ⟶ liquid ⟶ 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) $\mathbf{CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)}$; (ii) $\mathbf{NH_4Cl\,(s) \rightleftharpoons NH_3\,(g) + HCl\,(g)}$

   (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

$$Cu^{2+} + Zn \rightleftharpoons Cu + Zn^{2+}$$

[Given: $E^0_{Cu^{2+}/Cu} = 0.337$ V ; $E^0_{Zn^{2+}/Zn} = -0.763$ V at 25°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

$$2Fe^{3+} + Sn^{2+} \rightarrow 2Fe^{2+} + Sn^{4+}$$

$[E^0_{Fe^{3+}/Fe^{2+}} = 0.771$ V ; $E^0_{Sn^{4+}/Sn^{2+}} = 0.150$ 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 H_2^+. 2

(d) Draw the radial probability density with respect to distance from the nucleus for 2*s* 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 1*s* 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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