WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 4th Semester Examination, 2021

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) Using the concept of chemical potential, derive thermodynamically the relation between the elevation of boiling point of a solvent and molality of the solution. Clearly mention the assumptions and approximations used in the derivation. 3+1

   (b) Liquid carbon dioxide cannot exist at normal atmospheric pressure, whatever be the temperature. — Justify. 2

   (c) The heat of fusion of ice is 6.0 $kJmol^{-1}$. Calculate the freezing point of water in a solution containing a non-volatile nonelectrolyte solute where the mole fraction of water is 0.8. 3

   (d) State the degrees of freedom for an azeotrope in two component liquid-vapour equilibrium. Explain why an azeotropic mixture is not considered to be a compound. 1+1

   (e) Consider the phase transition $H_2O(l) \rightleftharpoons H_2O(v)$ and depict with a graphical representation, the variation of chemical potential of H_2O against temperature at constant pressure in the vicinity of its boiling point. 3

2. (a) Derive Duhem-Margules equation for binary solution stating clearly the assumptions. 3

   (b) Show that the expression of osmotic pressure of a dilute solution is similar to that of an ideal gas. State the assumptions and approximations involved. 3+1

   (c) What do you understand by phase (P), component (C) and degrees of freedom (F) of a thermodynamic system? 3

   (d) A mixture of 100 g water and 80 g of Phenol separates into two layers at 60° C. One layer, $\mathbf{L_1}$, consists of 44.9% water by mass, the other layer $\mathbf{L_2}$, consists of 83.2% water by mass. Calculate the total number of moles in $\mathbf{L_1}$ and $\mathbf{L_2}$. 4

   [Given: molar mass of Phenol is 94.4 g mol^{-1}]

Unit-II

3. (a) What are the factors on which the Debye-Hückel constant (A) depends? 2

   (b) Discuss the principle of standardization of a given Mohr's salt solution by standard potassium dichromate solution. Show the plot of E_{cell} (volt) vs. $N_{oxidant}$, where $N_{oxidant}$ is the number of drops of oxidant. Also calculate $E^0_{Fe^{3+}/Fe^{2+}}$. 3+2+1

(c) For AgI $K_{sp} = 1\times10^{-16}$ at 298 K. What will be the potential of $Ag^+ | Ag(s)$ electrode in a saturated solution of AgI? Also calculate the standard reduction potential of $Ag(s) | AgI(s) | I^-$ electrode at 298 K. Given: E^0 of $Ag^+ | Ag(s) = 0.80$ V at 298 K. 2+2

(d) How does molar polarisation vary with temperature for polar molecules? 2

4. (a) Show schematically the plots of $\log f_\pm$ versus $\sqrt{C}$ (where C is the molar concentration) for the dilute aqueous solutions of two strong electrolytes $AlCl_3$ and Na_2SO_4 in the same graph at 298 K and hence show that their slopes are in the ratio $3:\sqrt{2}$. 3

(b) Given that standard potentials of the Cu^{2+}/Cu and Cu^+/Cu couples are + 0.340 V and + 0.552 V, respectively. Evaluate standard potential (E^0) of (Cu^{2+}/Cu^+) system. 3

(c) Set up a reversible cell without transference for the process: 1+1+1

$$CuSO_4\,(a_1) \longrightarrow CuSO_4\,(a_2) \;;\quad (a_2 < a_1)$$

What is liquid junction potential? How it can be eliminated?

(d) Explain how the pH of a solution can be determined by the use of a glass electrode. 3

(e) If the dipole moment for Chlorobenzene is 1.57 D then find that for *m*-dichlorobenzene. 2

Unit-III

5. (a) Evaluate the following commutators and comment on the results. 2+2

(i) $[L_x, L_z]$ (ii) $[L_z, L^2]$

(b) (i) Define an orbital. 1+2+1

(ii) Find the number of radial nodes in the wave functions of the following orbitals:

$2p$ and $3s$

(iii) What is the physical significance of a node?

(c) Calculate the probability of finding a1s electron of hydrogen within a distance $2a_0$ from the nucleus. What is the probability beyond $2a_0$? 3+1

6. (a) What is Born-Oppenheimer approximation? 2

(b) Suppose an atom has two electrons in two different orbitals. What will be the values for the total spin quantum number S and the multiplicity? 2

(c) Consider a trial function $\psi = x(a-x)$ for a particle in a one-dimensional box of length a. Show that this function satisfies the boundary conditions. Apply the variation method to get an upper bound to the ground state energy of the particle and compare the result with true value. 4

(d) Under what conditions the mixing between two atomic orbitals would result in a molecular orbital with better combination in LCAO-MO method? Explain qualitatively with suitable examples. 4

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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