लक्ष्यं विश्वगानम्

WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 4th Semester Examination, 2023

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) Why is the vapour pressure of a solvent lowered when a non-volatile non-electrolyte solute is dissolved in it? Why is it necessary that the solute should be non-volatile? 3+1

(b) Find the osmotic pressure of a 0.001 (M) solution of K_2SO_4 at 27°C. 3

(c) Derive thermodynamically using chemical potential a relation between the depression of freezing point of a dilute solution with its molal concentration. Is elevation of freezing point possible? 4+2

(d) What do you mean by an eutectic mixture? 1

2. (a) In the phase diagram of water, the slope of the solid/liquid curve is negative, while for carbon dioxide it is positive. Explain with suitable equation. 2+1

(b) Account for the following fact: 3

An azeotrope has a fixed boiling point at a fixed pressure although it is not a chemical compound.

(c) What is meant by upper critical solution temperature (UCST)? Draw a temperature-composition diagram for a system showing UCST and find the number of degree of freedom in its different regions. 1+2+3

(d) State the principle of fractional distillation. 2

Unit-II

3. (a) State the Debye-Hückel limiting law. Graphically show the variation of $\log_{10}\gamma_{\pm}$ versus square root of ionic strength of 1-1, 2-1 and 2-2 electrolytes in aqueous solution, where, $\gamma_{\pm}$ is the mean ionic activity coefficient. In which case is the limiting law applicable better? 1+3+2

(b) Equal volumes of 0.01 (M) K_2SO_4 and 0.02 (M) $BaSO_4$ solutions are mixed. What will be the ionic strength of the resultant solution? 2

(c) Specific conductance of pure water is 38.4×10^{-9} ohm^{-1}cm^{-1} at 18°C. The equivalent conductance at infinite dilution of H^+ and OH^- are 315.2 ohm^{-1}cm^{2}gm eqv^{-1} and 173.8 ohm^{-1}cm^{-1}gm eqv^{-1} respectively. Calculate the ionic product of water at 18°C. 3

(d) Indicate with an example the essential characteristics to be considered in selecting the electrodes for a potentiometric titration. 3

4. (a) For the concentration cell Ag | AgCl(s) | HCl (a_1) | HCl (a_2) | AgCl (s) | Ag 3+2

(i) Write the various processes at the two electrodes and at the liquid junction

(ii) Derive expression for ΔG of the cell.

(b) The molar orientation polarization of chloroform decreases sharply with increasing temperature but that of carbon tetrachloride remains almost invariant with temperature. Explain with the help of an appropriate equation. 3

(c) Why Debye equation for the dipole moment should be applicable to gases and vapours only? Find the C.G.S. unit of μ^2/kT, where μ is the permanent dipole moment of a molecule. 2+1

(d) The cell corresponding to the reaction: 3

$$Hg_2Cl_2\,(s) + H_2\,(1\text{ atm}) \longrightarrow 2Hg\,(l) + 2H^+\,(a=1) + 2Cl^-\,(a=1)$$

has the emf, $E^0_{298\text{K}} = +0.27$ (V) and $\left(\dfrac{\delta E^0}{\delta T}\right)_P = -3.2\times10^{-4}$ (V K^{-1}).

Find the values of ΔH^0 and ΔS^0 of the reaction.

Unit-III

5. (a) Hydrogen like wave function for 1s orbital is given by $\psi = b_0 e^{-r/a_0}$ (where r_0 is the Bohr radius). 4

(i) Find out the normalization constant, b_0.

(ii) Specify the values of n, l and m for 1s electron.

(iii) Determine the most probable value of r in this state and comment on the result.

(b) For a rigid rotor $\psi_{J,M}(\theta,\phi) = \dfrac{1}{\sqrt{2\pi}}\Theta(\theta)e^{iM\phi}$ and the operator for z-component of angular momentum in spherical coordinate is $\hat{L}_z = -i\hbar\dfrac{\partial}{\partial\phi}$. Show that the wave function is an eigenfunction of the operator and find the corresponding eigen value. 2+1

(c) Write down the expression of $\hat{H}$ for the H_2^+ molecular ion. 2

(d) Write a short note on Born-Oppenheimer approximation. 3

6. (a) How is the concept of angular momentum relevant in quantum mechanics for our system of Interest? 3

(b) Find the value of the commutator, $[\hat{L}^2, \hat{L}_z]$ and interpret the result. 3

(c) Draw the radial function $R_{nl}(r)$ and the radial probability distribution function $r^2[R_{nl}]^2$ for the 2s orbital. Calculate the number of radial nodes. 2+1

(d) Using the results $\hat{L}^2 Y_{l,m} = \lambda\hbar^2 Y_{l,m}$ and $\hat{L}_z Y_{l,m} = m\hbar Y_{l,m}$; find the maximum allowed limit for the value of m. (m and λ are pure integers). 3

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