WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 4th Semester Examination, 2020

CEMACOR08T-CHEMISTRY (CC8)

PHYSICAL CHEMISTRY

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 (μ) derive thermodynamically a relation between the osmotic pressure of a binary solution and its molar concentration. Clearly mention the assumptions and approximations used in your derivation. 4+2

   (b) Starting from a suitable form of Duhem-Margules equation, derive the condition that for an azeotrope the mole fraction of each component in the liquid phase is equal to that in the vapor phase. 3

   (c) The vapor pressure of benzaldehyde is 400 torr at 154 ºC and its normal boiling point is 179 ºC. Calculate the molar enthalpy of vaporization of benzaldehyde. Mention the assumption(s), if any, in your calculation. 2+1

   (d) The intermolecular attraction between the molecules of all components (solute and solvent) in an ideal solution must be identical in nature. Justify or criticize. 2

2. (a) Draw the chemical potential versus temperature diagram at constant pressure for a pure substance in the three states of matter with proper explanation. Comment on the relative magnitudes of ΔT_f and ΔT_b from the plot. Mention the assumptions in your answer (ΔT_f is the depression of freezing point, ΔT_b is the elevation of boiling point). 2+1+1

   (b) (i) For an ideal solution plot the variation of the quantity p_1/p_1^0 as a function of x_2. 1+2+2

   (ii) Sketch the plot of p_1/p_1^0 as a function of molality of the solute if water is the solvent.

   (iii) How is the plot of p_1/p_1^0 with molality affected when the solvent is changed to toluene?

   (x_2 = mole fraction of solute, p_1^0 = vapor pressure of pure solvent, p_1 = partial vapor pressure of solvent in solution).

   (c) Using the Clausius-Clapeyron equation show that the slope of the solid-gas coexistence curve is greater than the slope of the liquid-gas coexistence curve at the triple point. 3

(d) The vapor pressure of benzene is expressed by the following empirical relationship $\ln(p/\text{torr}) = 17.63 - \frac{3884\,\text{K}}{T}$. Find the boiling point of benzene when the atmospheric pressure is 500 torr. 2

Unit-II

3. (a) (i) Derive the expression $\left[\frac{\partial(E^0/T)}{\partial(1/T)}\right]_p = -\frac{\Delta H^0}{nF}$, where the terms have usual significance. 3+1

(ii) Justify whether the standard emf (E^0) of a cell is an intensive or extensive property.

(b) A cell is represented by Pb | PbI_2 (s) | KI (aq) | AgI (s) | Ag 4

Write down the cell reaction. If the cell has an e.m.f of 0.2078 V at 25 ºC and $\left(\frac{\partial E}{\partial T}\right)_P = -1.88\times10^{-4}$ V/K, calculate ΔG and ΔS for the cell reaction.

(c) Write down the Debye Huckel Limiting Law explaining all the terms. Calculate the mean ionic activity coefficient of a 2-1 electrolyte at a molality of 0.01 aqueous solution at 15 ºC [A = 0.50 at 15 ºC] 1+2

(d) Why does Clausius-Mossoti equation fail in case of polar molecules? How is it modified in the form of the Debye equation? 3

4. (a) For the concentration cell 2+2

Ag | AgCl (s) | HCl (a_1) | HCl (a_2) | AgCl (s) | Ag

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

(ii) Derive the expression for ΔG and e.m.f of the cell

(b) How does molar polarization vary with temperature? Explain using proper equation. Find the C.G.S unit of $\frac{\mu^2}{kT}$. 2+1

(c) The thermodynamic dissociation constant for acetic acid, HAc, is 1.75×10^{-5} at 25 ºC. 3

Calculate using the Debye-Huckel theory, the degree of dissociation of 0.001 M acid in 0.05 M $Ca(NO_3)_2$.

(d) 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. 2

(e) Calculate the equilibrium constant for the formation of I_3^- from $I_2(aq)$ and I^- at 25 ºC using the following data 2

$I_2(aq) + 2e^- \rightleftharpoons 2I^-$ $\quad E^0 = 0.619$ Volt

$I_3^- + 2e^- \rightleftharpoons 3I^-$ $\quad E^0 = 0.536$ Volt

Unit-III

5. (a) The operator for the z-component of angular momentum in spherical polar coordinates is given as $\hat{L}_z = -i\hbar\frac{\partial}{\partial\varphi}$ where $0 \le \varphi \le 2\pi$ and $Y_{l,m}(\theta,\varphi)$ is an eigen function of the operator. 1+3+2

   (i) Construct a suitable eigen value equation giving proper justification for your answer.

   (ii) Solve the eigen value equation applying the technique of separation of variables to find a suitable solution for the φ-part.

   (iii) Verify if the solution gives quantized values for L_z.

   (b) What are the relative merits and demerits of VB method as compared to the LCAO-MO method? 2

   (c) The radial wavefunctions for the 1s and 2s orbitals of H-atom are given below. Without using any explicit formula justify the number and location of nodes in the two wavefunctions and indicate the same graphically. 3+1

$$R_{1s} = 2a_0^{-3/2}e^{-r/a_0}$$
$$R_{2s} = (2a_0)^{-3/2}(2-\tfrac{r}{a_0})e^{-r/2a_0}$$

   (a_0 is Bohr radius).
   Find the SI units of the functions R_{1s} and R_{2s}.

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

   (b) (i) If we measure L_y of a particle whose state function is an eigen function of $\hat{L}^2$ with eigen value $12\hbar^2$, what possible outcomes for the measurement do you expect? Give proper justification for your answer. 3+1

   (ii) What possible outcome do you expect if L_z is also measured at the same time? Justify.

   (c) (i) Using the expression for ψ_{1s} find an expression for the average distance $(< r >)$ of a 1s electron from the nucleus for a hydrogen-like atom. 3+(1+1)

   (ii) Using your expression for $< r >$ calculate the average distance of a 1*s* electron from the nucleus for H-atom and He^+ ion and state the significance of your result.

   Given: $\psi_{1s} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}e^{-zr/a_0}$, $\int_0^\infty x^n e^{-ax}dx = \frac{n!}{a^{n+1}}$, Bohr radius, $a_0 = 0.529$ Å, Z = atomic number.

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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