RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. FOURTH SEMESTER EXAMINATION, AUGUST 2021

SECOND YEAR (BATCH 2019-22)

Date : 07/08/2021 **CHEMISTRY (Honours)**

Time : 11.00 am – 1.00 pm **Paper : VIII [CC 8]** Full Marks : 50

Group –A (Physical)

[Attempt <u>one</u> from each unit]

<u>UNIT - I</u>

[1×14]

1. a) Prove that $\left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j} = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j}$ [4]

   b) Reason why activity is always less than concentration while fugacity might be greater or less than pressure. [4]

   c) Prove that at constant T, P the chemical potential in a mixture must be uniform at the equilibrium. [4]

   d) Consider a three component liquid mixture, mention the composition at which the entropy of mixing maximizes (no need to derive). [2]

2. a) Mention the criteria/condition at which the following relations are true [4 × 1.5]

   (i) $\sum_i n_i \mu_i = 0$

   (ii) $\mu_i = \mu_i^0 + RT ln p_i$

   (iii) $p_i = p_i^0 x_i$

   (iv) $lnk = lnk_0 + 2AZ_A Z_B \sqrt{I}$

   b) Reason why oil and water do not mix up spontaneously inspite entropy of mixing being negative. [4]

   c) Find out the relation between fugacity and pressure of a gas for which the compressibility factor may be approximated as $z = 1 + aP$. [4]

<u>UNIT - II</u>

[1 × 14]

3. a) (i) Plot of $R_{n,l}(r)$ with r describes the definite value at r = 0, whereas the probability of finding 1s electron at r = 0 is always zero. Explain with equations.

   (ii) Also justify that not only for 1s electron but also for all other functions, the probability is zero. [3+3]

b) $\psi = \frac{1}{\sqrt{32\pi}} z^{5/2} r e^{-zr/2} Sin\theta Sin\phi$ is a solution for 2p function of the H – like atoms. Hence, analyse the given function to show that the function has a nodal plane along XZ plane. [3]

c) Explaining all terms involved, write down the Schrowdinger equation for the harmonic oscillator and convert it to the form of general equation for Hermite function. Then show that

$$C_{n+2} = \frac{\alpha + 2\alpha n - 2mE\hbar^2}{(n+1)(n+2)} C_n$$

[2+3]

4. a) An analytic expression that is a good approximation to an intermolecular potential energy curve is a Morse potential

$$U(l) = D\left(1 - e^{-\beta(l-l_0)}\right)^2$$

D and β are the parameters dependent on molecular system involved. Show that $k = 2D\beta^2$, where k is the force constant, which can be equated to the curvature of the U(x) vs x curve. [Hint: Use the Mclaurin series for U(x)], with a plot of P.E.C. [4]

b) Show that the functions $\psi_+ = \frac{1}{\sqrt{\pi}} Cos(M\phi)$ and $\psi_- = \frac{1}{\sqrt{\pi}} Sin(M\phi)$ constitute the orthonormal set of set of wavefunctions of the particle in a ring. Also show that these two functions are degenerate. [3+2]

c) An H-like orbital is given as

$$\psi = \frac{\sqrt{2}}{81\sqrt{\pi}} z^{5/2} (6 - zr) e^{-zr/3} Cos\theta \text{ (in a.u.)}$$

Determine from inspection, by logical arguments only, the quantum numbers for the wavefunction. And give a radial distribution plot for the function. [3+2]

UNIT - III [1 × 10]

5. a) The equivalent conductance is given by

$$\Lambda = \Lambda_\infty - \left[\frac{82.4}{(DT)^{1/2}\eta} + \frac{8.20x10^5}{(DT)^{3/2}} \Lambda_\infty \right] \sqrt{C}$$

of the two coefficient terms of C, one accounts for the asymmetry, the other the electrophoretic effect. Guess with reasoning which accounts for what. [3]

b) Equivalent conductance is defined as $\Lambda = \frac{1000\kappa}{c}$. Then would it be possible to determine the value Λ from the slope of the line obtained by plotting κ against c ? [3]

c) You are provided with a solution of electrolyte of concentration 10 N and electrodes of area 100 cm^2 each. How far you'd keep the two electrodes inside the cell if you wish to have the measured conductance equal to the equivalent conductance of the electrolyte? [4]

6. a) Why do we use conductance more often than resistance while studying electrolytes ? [2]

b) Why we need to define equivalent conductance in case of electrolytes whereas specific conductance is good enough for metallic conductors. [2]

c) Consider the following reaction :

$$S_2O_8^{-2} + I^- \longrightarrow 2\ SO_4^{-2} + I_2$$

The rate of this reaction has been studied against change in concentration of NaCl present in the solution. Can you guess with proper reasoning how the plot of rate constant against ionic strength of the solution looks? [3]

d) The conductivity of a saturated solution of $BaSO_4$ is 3.48 x 10^{-4} s/m . The conductivity of pure water is 0.50 x 10^{-4} s/m. Calculate the solubility product of $BaSO_4$.(use $K_w = 10^{-14}$) [3]

UNIT - IV [1 × 12]

7. a) The molar polarization of a polar molecule varies with temperature whereas that of a nonpolar molecule is independent of temperature. Explain why it is so. [3]

b) The dielectric constant of a liquid of molecular weight 84.16 is 2.033. Its refractive index (D-line) is 1.427 and its density is 0.7784 g/cm^3 at 20 °C. Determine its molar and electronic polarizations. Comment on the polarity of the molecule from the results. [4]

c) The standard potentials of Cu^{2+}/Cu and Cu^+/Cu are 0.337 V and 0.530 V respectively. Calculate the equilibrium constant for the following reaction: $2Cu^+ = Cu^{2+} + Cu$. [3]

d) Describe pH determination using glass electrode. [3]

8. a) Write down an equation which correlates the polarizability and molar polarization of a polar molecule. How does the molar polarization vary with the temperature? [3]

b) The refractive index of an ideal gas at S.T.P. is 1.000373 and the dielectric constant is 1.00234. Calculate the dipole moment of the molecule assuming atomic polarization to be 5% of electronic polarization. [3]

c) Derive a relation between temperature coefficient $(dE/dT)_p$ and entropy change (ΔS) of an electrochemical cell. [3]

d) For the following cell $E° = 0.222$ V and $E_{cell} = 0.332$ V at 298K. What is the pH of the HCl solution? [3]

$$Pt \mid H_2 (1 \text{ bar}) \mid HCl \mid AgCl(s) \mid Ag$$

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