RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. FOURTH SEMESTER EXAMINATION, JUNE 2022

SECOND YEAR (BATCH 2020-23)

Date : 21/06/2022 **CHEMISTRY (HONOURS)**

Time : 11.00 am – 1.00 pm **Paper : VIII [CC8]** Full Marks : 50

[Attempt **one** question from **each unit**]

Unit : I

[14 marks]

1. a) Two ideal gases are at the same T but at different P. If n_A moles of gas A and n_B moles of gas B are mixed isothermally, what will be the $\Delta_{mix}G$?

   b) Calculate the $\Delta_{mix}G$, $\Delta_{mix}H$ and $\Delta_{mix}S$ at 25°C and 1 atm pr, - when 10 moles of Ne are mixed with 20 moles of equimolar mixture of Ne and He.

   c) A gas obeys the equation of state $P(V_m - b) = RT$. For this gas, b = 0.0391 dm^3mol^{-1}. Calculate f and ϕ (ratio of f and P) for the gas at 1000°C and 1000 atm. Also calculate $\mu_{real} - \mu_{ideal}$.

   d) By increasing the number of moles of one of the components of the mixture at constant T and P, its μ increases, while, simultaneously, μ for other components decrease. Explain with expression of rate of change of μ with number of moles.2. [3+3+4+4]

2. a) How does the $\Delta_{mix}G/nRT$ and $\Delta_{mix}H$ vary with mole fraction? (Show by qualitative plot)

   b) Show that the molar free energy of mixing in a binary ideal gas mixture is minimum when two gases are present in the equimolar ratio, i.e $x_1 = x_2 = ½$.

   c) True pressure is the geometric mean of the fugacity and the ideal pressure. Explain.

   d) Use Gibbs-Duhem equation to show that $\mu_i = \left(\frac{\delta E}{\delta n_i}\right)_{S,V,n_{j\neq i}}$. And comment on the fact that this does not represent partial molar internal energy. [4+3+3+4]

Unit : II

[14 marks]

3. a) A H-atom wave function has the following structure:

   $$\psi_{nlm}(r,\theta,\phi) = \frac{1}{4\sqrt{2\pi}}\left(\frac{z}{a_0}\right)^{3/2}(2-\sigma)e^{-\sigma/2}cos\theta$$

   (i) Find out the set of quantum number n, l, m for the state represented by the above wave function.

   (ii) With the aid of qualitative plots show how the wave function, probability density and radial probability density changes with σ (scaled form of the distance of electron from the nucleus). [3+4]

   b) Write down the Schrodinger's equation (time independent form) for simple harmonic oscillator. Show that the function $\psi = \sqrt{2\alpha}\left(\frac{\alpha}{\pi}\right)^{1/4} xe^{-\alpha x^2/2}$ is a solution to it (x is the distance from the equilibrium position). Find out the corresponding energy eigenvalue. [2+3+2]

4. a) Consider the following wave functions :

$$\psi_{nlm}(r,\theta,\phi) = \frac{1}{\sqrt{64\pi}}\left(\frac{z}{a_0}\right)^{\frac{3}{2}} \sigma e^{-\frac{\sigma}{2}} sin\theta e^{i\phi}$$

and

$$\psi_{nlm}(r,\theta,\phi) = \frac{1}{\sqrt{64\pi}}\left(\frac{z}{a_0}\right)^{\frac{3}{2}} \sigma e^{-\frac{\sigma}{2}} sin\theta e^{-i\phi}$$

Construct a pair of real orbitals from these complex ones. Comment whether these newly constructed orbitals would give the same value for energy, angular momentum and z-component of angular momentum. [3+3]

b) Calculate the zero point energy of a linear simple harmonic oscillator consisting of a particle of mass 2.33 x10^{-26} kg and force constant 155 Nm^{-1}. [2]

c) Calculate the value of classical turning point of a harmonic oscillator in the ground state in terms of frequency ν . Is it possible to find a quantum oscillator outside this turning point? [3]

d) The wave function of 1s orbital has the form, $\psi_{1s}(r,\theta,\phi) = \frac{1}{\sqrt{\pi}}\left(\frac{z}{a_0}\right)^{\frac{3}{2}} e^{-\sigma}$, find out the distance at which the radial probability is maximum. [3]

Unit : III

[10 marks]

5. a) Conductance, specific conductance, equivalent conductance, equivalent conductance at infinite dilution **:** mention how each of these quantities depend on concentration? [4]

b) A moving boundary experiment is done to measure the transference number of Li^+ in 0.01 mol/L LiCl. In a tube having a cross sectional area of 0.125 cm^2, the boundary moves 7.3 cm in 1490 s using a current of 1.80 x 10^{-3} A. Calculate $t_{+.}$ [3]

c) Establish a relation between ion conductance and ionic mobility of an ion. [3]

6. a) Derive a relation that shows how the equivalent conductance of an weak electrolyte changes with concentration. Also mention how this equation helps to determine the dissociation constant of the weak electrolyte. [3+1]

b) The specific conductance of a saturated solution of $BaSO_4$ is 3.48 x 10^{-6} S/cm and that of pure water is 5 x 10^{-7} S/cm. The ionic conductance values of Ba^{2+} and SO_4^{-2} ions are 127.26 and 160.04 S cm^2/mol. Calculate the solubility product of $BaSO_4$. [3]

c) The equivalent conductance of LiCl at infinite dilution is 115.03 ×10^{-4} S m^2/mol. The cationic transport number is 0.336. Calculate the mobility of the cation and its velocity if the applied potential difference across two electrodes, 0.4 cm apart, is 6.0 volt. [3]

Unit : IV

[12 marks]

7. a) If molar polarization of NH_3(g) obeys equation P_m = a + b/T, where the constant a and b have the values 5.6 and 12.000 $cm^{-3}mol^{-1}$, respectively, what is the relative permittivity of ammonia gas at STP? [$P_m = \left(\frac{\epsilon_r - 1}{\epsilon_r + 2}\right) V_m$]

b) A cell is given as Cd | Cd^{+2} (a = 1) | | H^+ (a = 1) | H_2 (1 atm) | Pt, where displacement of H^+ ions from solution occurs by Cd metal. Using standard condition, show that ΔG° is an extensive property, whereas E° is an intensive property. [E_{cell} = 0.403 V at 25°C]

c) (i) Use Gibbs-Helmholtz equation to find out the expression of ΔH in terms of temperature coefficient of EMF.
(ii) For the cell, $Pb \mid PbCl_2(s) \mid 0.1N\ KCl \mid Hg_2Cl_2(s) \mid Hg$, $E_{cell} = 0.5356$ V. Write the cell reaction for 1F current. If the $(\delta E/\delta T)_P = 1.45 \times 10^{-4}$, find out the values of ΔH and ΔG for the same condition. [3+4+(2+3)]

8. a) If dipole moment of the monosubstituted benzene C_6H_5X, derive expressions for the 1,2-disubstituted benzene, and 1,4-disubstituted benzene, symbolically represented as $C_6H_4X_2$.

b) Metallic Pb cannot displace Sn^{+2} ions from solution to form metallic Sn, at standard condition. What will happen, if Pb is placed in a solution with $a_{Sn^{+2}} = 1.0$ gm ion lit^{-1} and that of $a_{Pb^{+2}} = 0.1$ gm ion lit^{-1}? Also write down the cell structure for the spontaneous process at this condition. [Given, $E^0(Pb/Pb^{+2}) = 0.126$ V and $E^0(Sn/Sn^{+2}) = 0.140$ V]

c) At 25°C, for the cell $Ag \mid AgCl(s) \mid 0.1N\ KCl \mid Hg_2Cl_2(s) \mid Hg$, $E_{cell} = 0.0455$ V. Calculate the activity (or concentration) of Ag^+ in saturated solution of AgCl in 0.1 N KCl.

d) Show that every 10 fold decrease in the ratio of activities or roughly concentrations, of the cations results in the oxidation potential becoming more +ve by 0.0592/n V, at 25°C. And further comment on the fact that a change from 1 gm ion to 0.1 gm ion per lit produces the same change as in decrease from 10^{-6} to 10^{-7} gm ion per lit. [3+3+2+4]

———— × ————