B.Sc. 3rd Semester (Honours) Examination, 2023 (CBCS)

Subject : Chemistry

Course : CC-V

(Physical Chemistry-II)

Time: 2 Hours **Full Marks: 40**

Candidates are requested to give their answers in their own words as far as practicable.

1. Answer *any five* questions: 2×5=10

(a) Show that the error in the de Broglie wavelength (λ) is related to the error in velocity (v) by the relation $d\lambda = -(\lambda/v)\ dv$.

(b) Derive a relation between ionic mobility and ionic conductance.

(c) State and explain Walden's rule.

(d) The conductivity of pure water at 25°C is 5.5×10^{-6} S m^{-1}, calculate the value of molar conductance of pure water at that temperature. Given the density of pure water is 0.997 g/mL at 25°C.

(e) If there is 1% error in the value of '*r*', the radius of capillary, what will be the error in the viscosity coefficient value calculated by using Poiseuille equation?

(f) The IR spectrum of $^{75}Br^{19}F$ consists of an intense line at 380 cm^{-1}. Calculate the force constant of $^{75}Br^{19}F$ considering SHO approximation.

(g) Depict schematically the normalized harmonic-oscillator wave functions and corresponding probability densities for first two states of a SHO.

(h) Ice melts at lower temperature under higher pressure. – Explain according to Le Chatelier's principle.

2. Answer *any two* questions: 5×2=10

(a) (i) Prove $\left(\frac{\partial A}{\partial n_i}\right)_{V,T,n_{j\neq i}} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_{j\neq i}}$

(ii) 2 mol of N_2 and 2 mol of He gas are mixed at 300 K. Considering the gases as ideal, calculate ΔS_{mix} and ΔG_{mix} and hence arrive at the value of ΔH_{mix} using the value of ΔG_{mix} and ΔS_{mix}. 2+3

(b) (i) If Z = Z(X,Y), where Z is a thermodynamic state function with natural variables X and Y, write the expression of 'partial molar Z' and the expression of 'chemical potential' in terms of Z for an open system.

(ii) Derive an expression for the fugacity of a gas that obeys the equation of state: P(V-b)=RT, where b is a constant and V refers to molar volume.

(iii) What is the significance of Gibbs-Duhem equation? 2+2+1

(c) (i) Show that the length of the 1D box is an integral multiple of $\lambda/2$ where λ is the wavelength associated with the particle–wave for the particle in 1D box.

(ii) Normalise the wave function $N_1(a^2 - x^2)$ within $-a \leq x \leq a$.

(iii) Starting from Newton's law, arrive at the dimension of viscosity coefficient. 2+2+1

(d) (i) Determine the degrees of degeneracy of the level with energy $38h^2/8ma^2$ for a particle of mass 'm' moving in a cubical box of side length 'a'.

(ii) Find out the dimension of the wave function for the 'particle in 1D box' system with proper justification.

(iii) Name the phenomenon that proves the 'particle like behavior of light' and the 'wave like behavior electron'. 2+2+1

3. Answer *any two* questions: 10×2=20

(a) (i) State and explain Ostwald dilution law and hence derive the following relation: $1/\Lambda = 1/\Lambda° + c\Lambda/K\Lambda°^2$, [$\Lambda°$ = molar conductance at infinite dilution, K = dissociation constant and c = concentration] and comment on its utility.

(ii) Draw the curves for the conductometric titration of oxalic acid with NaOH and NH_4OH in two separate diagrams with proper explanation.

(iii) If the equivalent conductances of solutions with varying concentrations of sodium acetate, sodium chloride and hydrochloric acid are plotted against $\sqrt{c}$, the intercepts obtained are 91.0, 128 and 425 respectively in $ohm^{-1}\ cm^2\ eqv^{-1}$ unit at 25°C. If the resistance of 0.02 molar solution of acetic acid in a cell with cell constant 0.2061 cm^{-1} be 888 ohms at 25°C, what is the degree of dissociation of the acid at 25°C.

(iv) What is meant by Newtonian fluid? Define the viscosity coefficient of such a fluid. 3+2+3+2

(b) (i) Show that e^{ikx} is an eiganfunction of the operator $P_x = -ih\,(\partial/\partial x)$. Find the eigenvalue.

(ii) Derive the expression for the operator $[(d/dx + x)(d/dx - x)]$.

(iii) Calculate the wavelength of the photon absorbed when a particle of mass 10^{-27}g confined to move freely in a 1D box of length 6Å undergoes a transition from n=2 to n=3 level.

(iv) The classical turning point of a SHO, by definition, is a point at which E-V(x)=0. Find out the value of the classical turning point of a SHO at its ground state in terms of the fundamental frequency of the oscillator.

(v) What is meant by the term 'action'? What is its utility? Write its unit & dimension.

2+2+2+2+2

(c) (i) Show that the equilibrium condition for a chemical reaction is give by $\Sigma \nu_i \mu_i = 0$, where the symbols have their usual significance.

(ii) The dissociation constant of $CaCO_3$ at 900°C and 1000°C are measured to be 790 mm and 2940 mm respectively. Calculate the heat dissociation at this temperature range.

(iii) Discuss about the relative values of the total ion conductance of the pair of dilute solutions of the same strong electrolyte in each of the cases below with short explanations:

(I) Solution 1 and solution 2 having molar concentration c_1 and c_2 [$c_1 > c_2$] at same temperature in same solvent.

(II) Solution 3 and solution 4 having same molar concentration at temperature T_3 and T_4 respectively [$T_3 > T_4$] in same solvent.

(III) Solution 5 and solution 6 having same molar concentration in two different solvents with same viscosity but varying di-electric constants ε_5 and $\varepsilon_6 [\varepsilon_5 > \varepsilon_6]$ at same temperature.

(IV) Solution 7 and solution 8 having same molar concentration in two different solvents with same di-electric constants but varying viscosity coefficients η_7 and η_8 [$\eta_7 > \eta_8$] at same temperature.

(iv) How is it possible to approach to the value of 'conductance at infinite dilution' without dilution of a dilute solution of a strong electrolyte? Explain with reference to Debye-Huckel theory.

2+2+4+2

(d) (i) The partial molar volumes of the components for an ideal solution are equal to the respective molar volumes of the pure components. —Justify the statement.

(ii) Prove that the addition of inert gas to a gaseous reacting system at constant volume keeping the temperature fixed, does not affect the equilibrium.

(iii) Write down the standard expression of reaction isotherm. From it, derive the Reaction Isochore.

(iv) Find the value of the commutator of $\hat{x}$ and $\widehat{p_x}$.

(v) If we like to extract at a time 51% of the iodine present in 100 ml of an aqueous solution of the same, what volume of CCl_4 is needed? Given that at the experimental temperature, the distribution coefficient of iodine between CCl_4 and water is 85. 2+2+2+2+2
