B.Sc. 3rd Semester (Honours) Examination, 2019 (CBCS)

Subject : Chemistry

(Physical Chemistry-II)

Paper : CC-5

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

The figures in the margin indicate full marks.

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

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

(a) Define Newtonian and non-Newtonian fluid.

(b) Transport number of Cl^- ion in the solution of HCl and NaCl is same, if the solutions are of same molarity.—Comment.

(c) If the resistance of a 0·1(N) aqueous solution of KCl is measured in conductivity cells having different cell constants, will the values of conductance and specific conductance change? — Justify.

(d) Using van't Hoff equation, obtain the value of $(d\ln K_p/d(1/T))$. Comment on its sign for an exothermic reaction.

(e) Plot $\mu - \mu^\circ$ vs. $ln(P/P^\circ)$ for an ideal gas ($P^\circ = 1$ bar). [The terms have their usual significance.]

(f) Find the degeneracy of a quantum particle in a cubic box having energy four times that of the lowest energy.

(g) If the position of a 5 KeV electron is located within 2 Å, what is the uncertainty in its momentum?

(h) Define 'partial molar volume' of a component in a mixture. When will it become equal to corresponding molar volume?

2. Answer *any two* questions of the following: 5×2=10

(a) (i) Define 'fugacity' and 'fugacity coefficient'.

(ii) The distribution coefficient (K_D) of I_2 between CCl_4 and water is given by the ratio of molarities $\frac{C_{CCl_4}}{C_{H_2O}} = 85$. How much ml of CCl_4 is required for 95% of the I_2 to be extracted from 100 ml of aqueous solution in one step? 2+3=5

(b) (i) Derive the relation between 'ionic mobility' and 'ion-conductance' at infinite dilution.

(ii) Plot t_+ and t_- for KCl solution of widely varying concentration. (t_+ and t_- are the transport numbers of K^+ and Cl^- ions respectively.) 3+2=5

(c) (i) Three real functions Ψ_1, Ψ_2 and Ψ_3 are individually normalised and mutually orthogonal. Find the normalisation constant of the combined wave function:

$$\Psi = \Psi_1 - \frac{1}{\sqrt{2}}\Psi_2 + \frac{\sqrt{3}}{\sqrt{2}}\Psi_3$$

(ii) Determine, whether or not, the following pair of operators commute:

$$\hat{A} = \frac{d}{dx}, \hat{B} = \frac{d^2}{dx^2} + 2\frac{d}{dx}$$

2+3=5

(d) (i) Determine the average momentum ($\bar{p}_x$) for an electron moving in a one-dimensional box of length 'a'.

(ii) For a certain liquid the $\log \eta$ vs. $(1/T)$ plot (η =viscosity) yields a slope of 600 K. Estimate the activation energy for the flow.

2·5+2·5=5

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

(a) (i) Draw conductometric titration curve with brief explanation, when an aqueous solution of $Ba(OH)_2$ is titrated by an aqueous solution of $MgSO_4$.

(ii) Electrophoretic effect, being a viscous effect, is necessarily present, whether a solution be ideal or not.—Justify or criticize.

(iii) Explain briefly the 'Wien effect'.

(iv) The resistance of a conductivity cell is 2,20,000 ohms with water, 100 ohms with 0·02 (N) KCl and 1,02,000 ohms with water saturated with AgCl at 25°C. Neglecting the variation of Λ with concentration, calculate (A) cell constant (B) specific conductivity of the saturated solution of AgCl (C) solubility product of AgCl at 25°C. (Given $\Lambda_{AgCl} = 126{\cdot}8, \Lambda_{KCl} = 138{\cdot}3$ at 25°C)

2+2+2+(1+1+2)=10

(b) (i) Deduce the van't Hoff reaction isotherm for the general reaction $aA + bB = lL + mM$ using the concept of chemical potential.

(ii) Deduce an expression for the variation of the chemical potential of a component 'i' in a mixture, with pressure.

(iii) The equilibrium constants for the reactions, $CH_4(g) + 2H_2O(g) = CO_2(g) + 4H_2(g)$ and $CO(g) + H_2O(g) = CO_2(g) + H_2(g)$ are K_1 and K_2 respectively. Find the equilibrium constant for the reaction $CH_4(g) + H_2O(g) = CO(g) + 3H_2(g)$, in terms of K_1 and K_2.

4+3+3=10

(c) (i) Show that $\cos(ax)\cos(by)\cos(cz)$ is the eigenfunction of the operator

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}.$$

Find the eigenvalue.

(ii) Show that the maximum probability of finding the simple harmonic oscillator at the ground state is at its mean position (i.e. at $x = 0$).

(iii) Plot the graph of wave function having energy $(0{\cdot}5h^2/ma^2)$ for particle in a one-dimensional box. Locate the position of node, if any (Symbols have their usual meaning).

(3+1)+3+(2+1)=10

(d) (i) Prove that the kinetic energy operator $\hat{T} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$ is hermitian.

(ii) Explain the variation of specific and equivalent conductance with dilution, in case of an aqueous solution of acetic acid.

(iii) Write the phenomenological equation for flow of a fluid against a pressure gradient. Identify the flux and force terms in the equation with brief reason. 3+3·5+3·5=10