B.Sc. 3rd Semester (Honours) Examination, 2018 (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 from the following: 2×5=10

(a) Justify that 1 CGS unit = 0·1 SI unit for viscosity coefficient, η.

(b) The Fick's law of diffusion may be written as : $J_Z = D\left(-\frac{\partial c}{\partial z}\right)$. Identify the flux and force in the above equation.

(c) State the conditions of validity of Nernst distribution law.

(d) If the standard free energy charge ($\Delta G°$) of a reaction is positive, can the reaction proceed to forward direction? —Explain.

(e) The term 'partial molar volume' is relevant, but, 'partial molar temperature' is irrelevant. — Explain.

(f) How equivalent conductance (Λ_c) and molar conductance (Λ_m) are related for the electrolytes:

(i) KCl

(ii) $Al_2(SO_4)_3$

(g) Evaluate the expression of the operator $\left(\frac{d}{dx} + x\right)^2$.

(h) Calculate the de Bröglio wavelength associated with a particle of 1 mg mass moving with a velocity of 5×10^5 cm sec^{-1}.

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

(a) (i) Starting from Ostwald dilution law, derive a suitable expression to obtain the equivalent conductance value at infinite dilution (Λo) and dissociation constant (K_a) of acetic acid from conductance measurement.

(ii) State the SI unit of ionic mobility. (2+2)+1=5

(b) Starting from the expression for $\Delta G_{mix} = nRT\sum_i x_i \ln x_i$, deduce expressions for ΔS_{mix}, ΔH_{mix} and ΔV_{mix}, in case of ideal mixing. Comment on the value of ΔH_{mix}.

(2+1+1)+1=5

(c) (i) Show that $\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \left(\frac{\partial V}{\partial n_i}\right)_{S,V,n_{j\neq i}}$.

(ii) A base ball $(m = 200\ g)$ is moving with a velocity of 3000 cm sec^{-1}. If it's position is located with an uncertainty of 500 nm, what will be the uncertainty in velocity? Comment on the answer. 2+(2+1)=5

(d) (i) Show that $[\widehat{x^n}, \widehat{p_x}] = -\frac{h}{2\pi i}.n.x^{n-1}$.

(ii) Does equilibrium constant of a chemical reaction depend on

(A) choice of standard state for reactants and products and

(B) stoichiometric representation of the reaction?

Justify your answer. 3+(1+1)=5

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

(a) (i) Temperature has different effects on variation of viscosities of liquids and gases. Explain.

(ii) Explain whether the principle of falling sphere method works if a wooden sphere is used in measuring η of water.

(iii) In the gas phase reaction,

$2A + B \leftrightharpoons 3C + 2D$,

it was found that when 1·00 mol A, 2·00 mol B and 1·00 mol D were mixed are allowed to come to equilibrium at 25°C, the resulting mixture contained 0·90 mol of C at a total pressure of 1 bar. Calculate

(A) the mol fraction of each species at equilibrium,

(B) the equilibrium constant Kp and

(C) $\Delta G°$. 3+2+(2+1+2)=10

(b) (i) The normalised wavefunction of a particle moving in a one dimensional box of length 'a' is given by

$$\psi_n = \left(\frac{2}{a}\right)^{1/2} \sin\left(\frac{n\pi x}{a}\right).$$

(A) Comment whether the value of $n = 0$ is permitted in this case.

(B) Find the energy of the n^{-th} state using the above wavefunctions (ψ_n).

(ii) Draw conductometric titration curves with explanation for the titrations of

(A) KCl solution by A_gNo_3 and

(B) CH_3COONa solution by HCl .

(iii) Deduce van't Hoff equation $\frac{d\ln K_p}{dT} = \frac{\Delta H°}{RT^2}$, starting from van't Hoff reaction isotherm.

(1+3)+(1½+1½)+3=10

(c) (i) State and explain Kohlrausch's law of independent migration of ions. Write down the relation between mobility and transport number of an ion.

(ii) Why is Walden's rule not obeyed by ions with smaller sizes?

(iii) Prove that the operator $\hat{P}_x$ is hermitian.

(iv) Show that $e^{-\alpha x^2}(\alpha = \text{constant})$ is an eigenfunction of the operator $\frac{1}{x}\frac{d}{dx}$ but not of $\frac{d^2}{dx^2}$.

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

(d) (i) Explain the term asymmetric effect in connection with Debye-Hückel theory of ion-atmosphere. Discuss qualitatively, how the variation of dielectric constant of the medium affect the extent of this effect.

(ii) Estimate the wavelength of light absorbed when a pi-electron of butadiene is excited from the highest occupied energy level to the lowest vacant energy level. Assume that the pi-electron of butadiene move in a one dimensional box of length 7·0 Å ($m_e = 9 \cdot 1 \times 10^{-28}\ g$)

(iii) The work function for metallic cesium is 2·14 eV. Calculate the kinetic energy of the electrons ejected by light of wavelength 300 nm. (2+2)+3+3=10
