

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
- Justify that 1 CGS unit = 0.1 SI unit for viscosity coefficient, η .
 - 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.
 - State the conditions of validity of Nernst distribution law.
 - If the standard free energy change (ΔG°) of a reaction is positive, can the reaction proceed to forward direction? —Explain.
 - The term 'partial molar volume' is relevant, but, 'partial molar temperature' is irrelevant. — Explain.
 - How equivalent conductance (Λ_c) and molar conductance (Λ_m) are related for the electrolytes:
 - KCl
 - $\text{Al}_2(\text{SO}_4)_3$
 - Evaluate the expression of the operator $\left(\frac{d}{dx} + x \right)^2$.
 - Calculate the de Bröglie wavelength associated with a particle of 1 mg mass moving with a velocity of $5 \times 10^5 \text{ cm sec}^{-1}$.
2. Answer *any two* questions from the following: 5×2=10
- Starting from Ostwald dilution law, derive a suitable expression to obtain the equivalent conductance value at infinite dilution (Λ_0) and dissociation constant (K_a) of acetic acid from conductance measurement.
 - State the SI unit of ionic mobility. (2+2)+1=5
 - 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 ($m = 200 \text{ g}$) 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 $[\widehat{x}^n, \widehat{p}_x] = -\frac{h}{2\pi i} \cdot n \cdot x^{n-1}$.

- (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

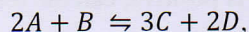
3. Answer any two questions from the following:

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,



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 K_p and

(C) ΔG° .

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 AgNO_3 and

(B) CH_3COONa solution by HCl .

- (iii) Deduce van't Hoff equation $\frac{d \ln K_p}{dT} = \frac{\Delta H^\circ}{RT^2}$, 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 \AA ($m_e = 9.1 \times 10^{-28} \text{ g}$)
- (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
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