SH-III/Chemistry-301C-5(T)/19

B. Sc. Semester III (Honours) Examination, 2018-19

CHEMISTRY

Course ID : 31411 **Course Code : SHCHE/301C-5(T)**

Course Title: Physical Chemistry-II

Time: 1 Hour 15 Minutes **Full Marks: 25**

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: 1×5=5

(a) Arrange the ions according to their molar ionic conductance values: Li^+, Na^+, K^+, Rb^+

(b) Draw the ψ(x) vs. *x* plot for the first excited state of an 1-dimensional harmonic oscillator.

(c) Chemical potential is an intensive property of the system. — Comment.

(d) Mention two fundamental difference between molar property and partial molar property.

(e) '$\widehat{p_x}$ is not an eigen operator for the particle-in-a 1-dimensional box wave function.' — What inference you can draw from the above fact?

(f) $y_i P = x_i\, p_i^o$ — Is it Raoult's law or not? x_i is the liquid phase molefraction and y_i is the vapour phase molefraction of the species *i*, *p* is the total pressure of the vapour phase.

(g) State whether $\frac{d}{dx}$ and $\frac{d}{dy}$ will commute or not.

(h) Debye-Hückel law is called a limiting law. — Why?

2. Answer *any two* questions: 5×2=10

(a) (i) Show that if the eigenfunctions of an Hermitian operator have different eigenvalues, then they are orthogonal.

(ii) Find the relation between mean ionic activity and ionic activities of $Na_2\, SO_4$ solution.

(iii) Expand the operator $\left(\frac{d}{dx} + x\right)\left(\frac{d}{dx} - x\right)$ 2+1+2=5

(b) (i) Calculate the $H^+ - ion$ concentration of a solution of HCOOH containing 0.092g of acid per litre. (K_a for HCOOH at 25°C is $2{\cdot}14 \times 10^{-4}$) 2

(ii) Define fugacity. Comment on its unit.

(iii) How would you define ideally-dilute solutions? 2+1½+1½=5

(c) (i) Derive an expression for de-Broglie wavelength of photoelectrons emitted when radiation of frequency ν, falls on an emitter with threshold frequency ν_0.

(ii) Explain the relevant graphical plot for the conductometric titration between HCl and NH_4OH. 3+2=5

(d) (i) For the distribution of a species between two immiscible solvents, thermodynamically derive the Nernst's distribution law. 2½

(ii) The equivalent conductance of a very dilute solution of $NaNO_3$ at 18°C is 105·2 mho cm^2. If the ionic conductance of NO_3^- ions in the solution is 61·7 mho cm^2, calculate the transport number of Na^+ ions in the solution. 2½+2½=5

3. Answer *any one* question: 10×1=10

(a) (i) If $V(x) = V(-x)$, symmetric about the origin, then show that both ψ(*x*) and ψ(–*x*) are solutions of the $\hat{H}$ (Hamiltonian Operator) with the same eigenvalue E.

(ii) Normalize ψ(*x*) = ic (where C is a constant) in the range $-L \leq x \leq L$. $\left(i = \sqrt{-1}\right)$.

(iii) K_p for a gaseous reaction increases by 2% per degree rise in temperature near 600K. Calculate ΔH of the reaction.

(iv) Calculate the molal ionic strength of a solution which is 0.01 m with respect to Na_2SO_4 and 0.02 m with respect to $AlCl_3$.

(v) Find the degeneracy of a particle in a cubical box of dimension '*l*' with energy $\frac{14h^2}{8\,ml^2}$.

2×5=10

(b) (i) In the distribution of succinic acid between ether and water at 15°C, 20 mL ethereal layer contains 0·092g of the acid. Find out the weight of the acid present in 50 mL of the aqueous solution in equilibrium with it if the K_D value for succinic acid between water and ether is 5·2.

(ii) If the percentage error in measurement of the radius of the capillary is '*x*', then show that percentage error in the measurement of the viscosity co-efficient will be equal to 4x.

(iii) If $\hat{A}\psi = a\psi$, then show that σ_a (standard deviation for the measurement of the observable *a*) is zero.

(iv) Prove that for ideal mixing $\Delta V^{mix} = 0$

(v) "Photo-eletric work function is generally less than ionization energy of the electron." — What inference one can draw for it? 3+2+2+2+1=10

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