B.Sc. 3rd Semester (Honours) Examination, 2019-20

CHEMISTRY

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

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) Why the term 'Partial molar temperature' is irrelevant?

(b) Which of the following functions are acceptable in quantum mechanics?

(i) Cosec x

(ii) Cos x + Sin x for $0 \leq x \leq \frac{\pi}{2}$

(c) Name one experiment for each, where electron shows particle behavior and wave behavior.

(d) How does the transport number of ions change with temperature?

(e) Define Newtonian fluid.

(f) Define ionic mobility. State its unit.

(g) Draw conductometric titration curve, when an aqueous solution of $AgNO_3$ is titrated by an aqueous solution of KCl.

(h) Plot $\Psi(x)$ versus x curve for a particle at mass m, moving in an one dimensional box at length 'a', having energy $\frac{2h^2}{ma^2}$.

2. Answer *any two* questions. 5×2=10

(a) (i) Show that for a particle in a box of infinite potential wall, the probability of finding the particle outside the box is zero.

(ii) If the equilibrium constant for the reaction
$CO(g) + H_2O(g) = CO_2(g) + H_2(g)$ and
$CH_4(g) + H_2O(g) = CO(g) + 3H_2(g)$; are K_1 and K_2 respectively, find the equilibrium constant for the reaction : $CH_4(g) + 2H_2O(g) = CO_2(g) + 4H_2(g)$.

(iii) Write the expression for distribution co-efficient (K_D) when benzoic acid is equilibrated between a mixture at water and benzene. 2+2+1=5

(b) (i) 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.

(ii) Show that $\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n_{j\neq i}} = -\left(\frac{\partial S}{\partial n_i}\right)_{T,P,n_{j\neq i}}$. (1½+1½)+2=5

(c) (i) The ionic conductance at Li^+ and K^+ are 38·7 mho cm^2/gm-ion and 73·5 mho cm^2/gm-ion, respectively. How long would it take for an ion to more from one electrode to another (2 cm apart) of a conductivity cell when a potential difference of 10 volts is applied between the electrodes?

(ii) Write down the Van't Hoff equation showing the variation of *K*p with temperature T. From the graphical plot of *ln K*p vs $\frac{1}{T}$, explain whether *K*p increases or decreases with temperature. 3+2=5

(d) (i) If $\hat{A}$ and $\hat{B}$ are Hermitian operator, then show that $\hat{A}\hat{B}$ is also Hermitian, if $\hat{A}$ and $\hat{B}$ will commute.

(ii) Explain qualitatively, how the variation of temperature affects the extent of "asymmetry effect" in Debye-Hückcl theory of ion-atmosphere.

(iii) Write down the relation between mobility and transport number of an ion. 2+2+1=5

3. Answer *any one* question. 10×1=10

(a) (i) Calculate ΔG_{mix} and ΔS_{mix} of an ideal solution at 27ºC which contains 0·3 mole of *A* and 0·7 mole of *B*.

(ii) Explain, why amide ion(NH_2^-) in liquid ammonia has abnormally high conductance value.

(iii) Plot t_+ and t_- for KCl solution of widely varying concentration, with proper justification.

(iv) The excited state life time of an atom is 10^{-8}sec. What is the minimum uncertainty in frequency of the radiation emitted by the atom while decaying to ground state?

(v) Define "Stopping Potential" 3+2+2+2+1=10

(b) (i) Consider a particle of mass *m*, moving in an one-dimensional box of length *l*, under the potential $v(x) = 0,\ 0 \leq x \leq l$. Calculate the average value of energy, using $\Psi_n = \sqrt{\frac{2}{l}}\, Sin\frac{n\pi x}{l}$.

(ii) Write down the quantum mechanical energy expression for Harmonic Oscillator system. Give explanation to the fact that the lowest allowed quantum number is 0 for Harmonic Oscillator but it is 1 for particle in 1D box.

(iii) Show that $\left(\frac{\partial G}{\partial ni}\right)_{P,T,n_{j\neq i}} = \left(\frac{\partial A}{\partial ni}\right)_{T,V,n_{j\neq i}}$ (The terms have their usual significance).

(iv) Explain the variation of viscosity of a liquid with temperature. 2+3+3+2=10

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