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DEPARTMENT OF SCIENCES, MANIPAL UNIVERSITY, MANIPAL

II SEMESTER M.Sc. END SEMESTER EXAMINATIONS, MAY 2016

SUBJECT: PHYSICAL CHEMISTRY II [CHM 604]

REVISED CREDIT SYSTEM

Time: 3 Hours Date: 09/05/2016 MAX. MARKS: 50

Instructions to Candidates:

- Answer **ANY FIVE FULL** questions.
- Draw diagrams and write equations wherever necessary.

1. a) "Shape of 's' orbital is spherical and that of 'p' orbital is dumbbell". Justify the statement with appropriate equations and explanations.

b) Comment on the origin of liquid junction potential. Calculate the liquid junction potential associated with the following cell: Ag(s), AgCl(s), HCl (m_1 = 1.0, γ_1 = 0.809): HCl (m_2 = 0.05, γ_2 = 0.830), AgCl(s), Ag(s), if the transference number of H^+ is 0.83.

c) Setup and solve Schrodinger wave equation for a particle in a box of definite length and infinite height. Give schematic representation of energy levels.

[2 + 2 + 6]

2. a) "Inhibitors can control both anodic and cathodic reactions of corrosion process". Justify the statement with suitable examples and explanations.

b) Show that d^2/dx^2 is a Hermitian operator, when operated on two acceptable Eigen functions $\psi = e^{ix}$ and $\phi = \sin x$.

c) Discuss molecular orbital theory of chemical bonding by taking molecular hydrogen ion as an example. Give schematic representation of bonding and antibonding orbitals.

[2 + 2 + 6]

3. a) Justify the following statement: Evaluation of potential energy Hamiltonian is difficult for multi-electron system.

b) A wave function is given by $\psi = \sin x$. Is it acceptable? Is it normalized? Explain.

c) Explain the principle of ampherometric titrations. Explain the ampherometric titration between lead and chromate solutions using acetate buffer solution of pH=4.2, under different applied potentials. **[2 + 2 + 6]**

4. **a)** Justify the following statement: Effective nuclear charge is always less than the actual nuclear charge.

b) For the electrode equilibrium $Cu^{2+} + 2e^{-} \rightleftharpoons Cu$, the transfer coefficient is 0.5 and the exchange current density is 2.5×10^{-5} A cm^{-2}. Calculate the Tafel constants at 298 K and estimate the overpotential to deposit copper from a solution of unit activity at this temperature at a current density of 5×10^{-3} A cm^{-2}.

c) Set up Schrodinger wave equation for particle rotating in a sphere in polar coordinates. Separate the variables and solve for phi (ϕ) equation.

[2+2 +6]

5. **a)** "With the knowledge of half wave potential it is possible to separate ions from its mixture" Justify the statement with appropriate example and explantions.

b) Derive quantum mechanical expression for momentum operator.

c) Describe the essential features of the Huckel Molecular Orbital treatment of linear conjugated system.

[2 +2 + 6]

6. **a)** Justify the following statement: Pauli's exclusion principle can be explained by using Slater determinants.

b) Applying classical treatment, derive an expression for energy of a particle executing simple harmonic oscillation.

c) Write short notes on the following:

(i) Principles of cyclic voltametric technique.

(b) Applications of coulumetric titrations

[2 +2+ 6]

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