

## DEPARTMENT OF SCIENCES, MANIPAL UNIVERSITY, MANIPAL

## II SEMESTER M.Sc. END SEMESTER EXAMINATIONS, June-July, 2016 SUBJECT: PHYSICAL CHEMISTRY II [CHM 606]

## **REVISED CREDIT SYSTEM**

Date:04/07/2016

Time: 3 Hours

MAX. MARKS: 50

## Instructions to Candidates:

- Answer ANY FIVE FULL questions.
- Draw diagrams and write equations wherever necessary.
- a) Show that Schrodinger wave equation can be represented as Eigen value equation.
  b) For an electrochemical cell Fe/Fe<sup>2+</sup> (0.02M)//Cd<sup>2+</sup> (1M)/Cd, write the cell reaction and calculate the EMF of the cell. Comment on the spontaneity of the reaction. (The standard reduction potentials of iron and cadmium are -0.44V and -0.40 V respectively)
  c) Highlight the need of comparisons to calculate in quantum chamistry. State and presented as the spontaneous control of th

c) Highlight the need of approximate techniques in quantum chemistry. State and prove two important assumptions of linear variation method.

[2+2+6]

**2. a**) "Cyclic voltammetry is a useful tool to understand the mechanism of redox reaction" Justify the statement with suitable example.

**b)** If a baseball of mass 150g, moves with a velocity of 3000 cm sec<sup>-1</sup>, calculate its de Broglie wavelength. Comment on magnitude of the wavelength. ( $h = 6.624 \times 10^{-34} \text{ J s}$ ) **c)** What is meant by a rigid rotor and harmonic oscillator? Set up Hamiltonian and write Schrodinger wave equation for harmonic oscillator. Write complete solution for the same and comment on its energy Eigen value.

[2+2+6]

- **3.** a) "Energy Eigen value for a free particle and a particle within a box is not same". Justify the statement with appropriate equations and explanations.
  - **b**) Calculate the value of A, if the wave function is  $\psi_x = A \sin(n\pi/L) x$ .
  - c) Define half wave potential. Derive mathematical expression for the same.

[2+2+6]

**4. a**) Justify the following statement: Perturbation factor can-not be neglected while solving Schrodinger wave equation for Helium atom

**b**) If the Tafel constants, a and b, have the values 1.54 V and 0.119 V respectively for the reduction of hydrogen ions at a lead cathode, calculate transfer coefficient and the exchange current density.

c) Set up Schrodinger wave equation for hydrogen and hydrogen like atoms in polar coordinates. Separate the variables and solve for phi equation.

[2+2+6]

**5. a**) Compare and contrast the advantageous and limitations of coulometric titrations over conventional titrations.

**b**) Write the significance of Slater type of orbitals. Calculate screening constant and effective nuclear charge for nitrogen.

c) With an appropriate explanations, explain Huckel molecular orbital theory as applicable to  $\pi$  electron system

[2+2+6]

**6. a**) Justify the following statement: Wave functions and energy eigen values of bonding and antibonding orbitals are different.

**b**) If operators A = d/dx and  $B = 3x^2$  are operating on the function  $f(x) = \sin x$ , show that they are noncommutative

**c**) Assuming Butler Volmer equation, derive Tafel equation. Explain the use of Tafel plots in corrosion rate measurements.

[2+2+6]

\*\*\*\*\*