MANIPAL UNIVERSITY

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DEPARTMENT OF SCIENCES, II SEMESTER M.Sc (CHEMISTRY)
END SEMESTER EXAMINATIONS, JUNE 2017

PHYSICAL CHEMISTRY II [CHM 606]

(REVISED CREDIT SYSTEM)

Time: 3 Hours Date: 19-6-2017 MAX. MARKS: 50

Note: (i) Answer any **FIVE FULL** questions
(ii) Draw diagrams, and write equations wherever necessary

1. **(a)** Justify the following statement: According to quantum mechanical treatment, a particle can have zero rotational energy, but not zero vibrational energy.

   (b) The exchange current density for the reaction $H^+ + e^- \rightleftharpoons \frac{1}{2} H_2$ on nickel at 298 K is 1.00×10^{-5} A cm^{-2}. Calculate the current density required to obtain an overpotential of 0.100 V using the Butler-Volmer equation. ($\alpha = 0.50$)

   (c) Obtain the conditions for degeneracy of energy level by solving Schrödinger wave equation. Give an explanatory note on quantum mechanical tunneling effect. **[2 + 2+6]**

2. **(a)** Given reason:- A very low concentration of a surface active material must be present in the analyte subjected to polarographic analysis.

   (b) If operators A and B are made to operate on the function $f(x) = \sin x$, show that they are not commutative. Find the value of commutator.

   (c) Apply Valence Bond theory to elucidate the structure of molecular hydrogen ion.

   [2 + 2+6]

3. **(a)** Justify the following statement with an example: Effective nuclear charge of an atom is always less than the actual nuclear charge.

   (b) A ball of mass 1 g, confined to a one dimensional box of length 0.1m, moves with a velocity of 0.01m s^{-1}. Calculate the quantum number *'n'*.

   (c) What are concentration cells? Derive an expression for the EMF of an electrolyte concentration cell with transference. **[2 + 2+6**

4. **(a)** Prove that Perturbation method is used to determine the energy Eigen value of helium atom

(b) Consider an electrochemical cell

$$Fe/Fe^{2+}\ (0.02\ M)//Cd^{2+}\ (1\ M)/Cd$$

(i) Write the cell reaction and (ii) calculate the EMF of the cell and determine the direction of the spontaneous reaction. Given the standard reduction potentials of iron and cadmium are -0.44 and -0.40 V respectively.

(c) Set up and solve Schrödinger wave equation for a particle executing simple harmonic oscillation. **[2 + 2+6]**

5. **(a)** Give Reason:- Pourbaix diagram is a very good tool for control the corrosion of metal.

(b) Calculate the de Broglie wave length of an electron moving with a velocity of 1.20 $x10^5$ m sec^{-1}. If it can be located in an atom within a distance of $0.1A^0$, what is the uncertainty involved in the measurement of its velocity?

(c) Explain the following:

(i) Application of Huckel Molecular orbital theory to 1,3 butadiene

(ii) Spherical harmonics. **[2 + 2+6]**

6. **(a)** Set up and solve Schrödinger wave equation for a free particle. Comment on its energy Eigen value.

(b) Derive the equation for half wave potential in the polarogram. Draw the polarogram and explain the following:-

(i) Limiting current (ii) Diffusion current (iii) Residual current (iv) Decomposition potential

[4 +6]

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