8. Show that (i) $\hat{A} \equiv \frac{d}{dx}$ & $\hat{B} \equiv x^2$ do not commute and

   (ii) $\hat{H} \equiv -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$ is a Hermitian operator. 2+2

9. Write down the normalized wave function of a free particle in 1-D box having length L and show that its average linear momentum, $\langle p_x \rangle = 0$ for any quantum states.

   4

10. Solve the equation : $\frac{d^2x}{dt^2} + \omega^2 x(t) = 0$; with conditions

    $x(0) = A$ & $\left(\frac{dx}{dt}\right)_{t=0} = 0.$

    What will be the nature of plot of 'x' versus 't' ? 3+1

11. Tunneling effect is possible for quantum particles, not for classical ones. Explain with reason/s. Show that classical turning point of SHO at v = 0 are $\pm\frac{1}{\sqrt{\alpha}}$; where $\alpha = \frac{\mu\omega}{\hbar}$; symbols have their usual meanings. 4

12. The normalized wave function for 1s-orbital of H-atom is, $\psi_{1s} = (\pi a_0)^{-\frac{3}{2}} e^{-r/a_0}$ (a_0 = Bohr radius). Depict graphically the plots of (a) $|\psi_{1s}^2|$ *vs.* 'r' and (b) $4\pi r^2 |\psi_{1s}^2|$ *vs.* 'r'. What are values of (i) probability density and (ii) probability of finding the 1s electron on the nucleus ? 4

Ex/CHEM/H/31/XI/A/34/2019

FINAL B.SC. EXAMINATION, 2019

(1st Semester)

CHEMISTRY (HONOURS)

PHYSICAL CHEMISTRY

PAPER - XI

Time : Two hours Full Marks : 50

(25 marks for each group)

Use separate answerscript for each group.

GROUP - A

1. Answer ***any three*** from the following : 4×3

   a) By thermodynamical consideration, show that the amount of free energy change is equal to the amount of electrochemical work for a reversible electrochemical cell under a condition of constant pressure and temperature. Hence, explain why does the electrochemical cell offers possibilities for efficient production of electrical energy from chemical sources that are unequalled by any other devices ?

   b) How can pH of an aqueous solution be determined by exploiting the quinone to hydroquinone reduction process? Mention the basic limitation of this method with proper reasoning. Why is the calibration of glass electrode with known buffer medium essential for measuring accurate pH of an aqueous medium ?

c) Briefly explain the connection between *"overvoltage"* and *"irreversibility"* in an electrolytic cell. Why is the decomposition potential of diulte HCl solution largely different than that of dilute H_2SO_4 solution ? "For clean-cut separation of one metal from another, a difference of about 0.2 V metal deposition potential is essential between them." Justify the statement.

d) Why is the rate of an electron transfer reaction depends on external electrical potential ? What is *"activation overpotential"* and explain its significance on electro-kinetic processes ?

2. a) Cell : Pt / H_2 (g, 1 atm) / HA_2 ($pK_a = 6$), C_1 at 25°C // HA_1 ($pK_a = 4$), C_1 at 25°C / H_2 (g, 1 atm) / Pt.

Calculate the emf of the above cell at 25°C. What are the assumptions which must be made in order to solve the problem ? 3

b) Construct a cell where the following reactions take place :

i) $Ag^+ + Br^- = AgBr$

ii) $CuSO_4(C_1) = CuSO_4(C_2)$ 2

GROUP - B

3. Derive Gibbs adsorption isotherm. What does this expression really imply ? 5+1

4. What is peptization ? How would you justify peptization ? 2+2

5. How would you rationalize the formation of land at the junction of a river and a sea ? 3

6. How would you determine the molar mass of a polymer using osmometry ? Does it represent number average or weight average molar mass ? 3+1

GROUP - C

Answer ***any four*** questions

7. a) Derive the unit of $\rho_v(T)dv$ (in SI system) using the following equation for Blackbody radiation. 2

Planck distribution equation : $\rho_v(T)dv = \frac{8\pi h}{c^3}\frac{v^3 dv}{e^{hv/k_BT} - 1}$

b) A household light bulb is a blackbody radiator. Many light bulbs use tangsten filaments that are heated by an electric current. What temperature is needed so that $\lambda_{max} = 550$ nm ? 2