b) Show that the zero-point energy of a particle moving in a one dimensional box freely is in accordance with Heisenberg's uncertainty principle. 2

9. Answer ***any two*** of the following questions : 3×2

a) Calculate the probability that the electron will be found somewhere within a sphere of radius a_0 for H-atom in its ground state. Given normalized ground state wave function.

$$\Psi_{1s} = \left(\frac{1}{\pi a_0^3} \right)^{\frac{1}{2}} \exp\left(- \frac{r}{a_o} \right) \text{ ; where } a_0 = \text{Bohr radius.}$$

b) In the IR spectrum of $H^{79}Br$, there is an intense line at 2559 cm^{-1}. Calculate the period of vibration of $H^{79}Br$.

c) Show that two eigenfunctions of a Hermitian operator that corresponds to different eigen values must be orthogonal.

Ex/FCH/I/XI/34/2017

FINAL B. SC. EXAMINATION, 2017

(3rd Semester)

CHEMISTRY (HONOURS)

PHYSICAL CHEMISTRY

PAPER - XI

Time : Two hours Full Marks : 50

(25 marks for each unit)

Use a separate answerscript for each group.

GROUP - A

1. a) What is the difference in chemical potential and electrochemical potential ? "The electrochemical potential of metal ions between electrode and electrolyte are different to each other." — Justify or criticised. 1+2

b) Briefly explain a suitable method for determining the reversible *emf* of an electrochemical cell. Highlight the reasons for choosing such method.

Or

Suggest a cell from whose *emf*, the value of solubility product of AgCl can be determined. 3

c) An aqueous solution containing 0.01 (M) $Fe(ClO_4)_3$, 0.01 (M) $Fe(ClO_4)_2$ and 0.01 (M) $HClO_4$ was titrated with a concentrated NaOH solution at room temperature

(30^oC), so that changes in volume were negligible. Calculate the redox potential of Fe^{2+}/Fe^{3+} system at pH values 2·2, 4·2 6·0, and 10 assuming new species formed during titration were $Fe(OH)_3$ and $Fe(OH)_2$ only.

[Given : $E^0 (Fe^{2+} / Fe^{3+}) = 0·77$ V ; solubility product of $Fe(OH)_3 = 10^{-37.1}$ and that of $Fe(OH)_2 = 10^{-18·4}$]

4

2. a) Briefly explain the connection between *"overvoltage"* and *"irreversibility"* in an electrolytic cell ? "The deposition of Ag from aqueous $AgNO_3$ solution of pH 7·0 does not depend on the presence of hydrogen overvoltage, whereas the deposition of Cd from $Cd(NO_3)_2$ solution at the same pH may depend" – Explain. 1+2

b) What do you mean by the electrochemical cell with and without liquid junction potential (LJP) with suitable example ? Why the LJP is removed almost completely by use of proper electrolyte in a *"salt-bridge"* ?

Or

Why does the rate of an electron transfer reaction depend on external electrical potential ? What is *"activation overpotential"* and explain its significance on electro-kinetic processes ? 2+2

GROUP - B

3. Describe the Bredig's method for the preparation of a gold sol. Is it a "top-down" or a "botton-up" approach ? 3+1

4. Explain "Gold number" of a liophilic sol. What does it signify relating to the property of the colloidal system ? 2+1

5. Deduce Langmiur adsorption isotherm. Show when and how can it be considered same as Freundlich isotherm.

5+2

6. Describe a method for the determination of number average molecular weight of a polymer. 3

GROUP - C

7. a) Derive Wien's displacement law that $\lambda_{max} T$ is a constant from Planck's formula for black-body radiation and deduce an expression for the constant. 3

b) Calculate the de Broglie wavelength of an electron accelerated from rest through a potential difference of 100V. 2

8. a) Evaluate the commutator, 3

$$\left[d/dx - x, d/dx + x \right]$$