B.Sc. (Honours) Examination, 2017

Semester-VI

Chemistry (Honours)

Course: BCHC-63

(Physical Chemistry)

Time: Three Hours **Full Marks: 30**

Questions are of value as indicated in the margin.

Answer ***any three*** questions.

1. a) Discuss classical theory of Raman Effect and show that the change in polarizability during internal motion is the essential criteria for a molecule to be Raman active. 3
   b) Write the energy expression and selection rule for rotational Raman Spectra of symmetric top molecules. 2
   c) Sketch the rotational Raman spectra of symmetric top molecules and label the lines according to branch names. 3
   d) Sketch the nmr spectrum of $(CH_3)_2 - CH - OH$ and explain the splitting of the peaks by family tree method. 2

2. a) Prove that for an electrolyte like AxBy, $a = x^x y^y c^{(x+y)} \gamma_{\pm}^{(x+y)}$ (symbols have usual significance). 1.5
   b) Calculating the charge density at a distance r from the central ion in the ionic atmosphere, write the Poisson equation for the point at r. Solving the equation determine the electrical potential at r. Using this expression prove that the mean activity coefficient of an electrolyte is proportional to the square root of the ionic strength of the solution. 1.5+1+2.5
   c) Express the EMF of the following cell

      $$Pt_L \left| H_2(g) \right| HCl(aq; m) \left| AgCl(S) \right| Ag(S) \left| Pt_R \right.,$$

      in terms of mean activity co-efficient of HCl. Using this cell describe the principle of determination of E^o of the cell. 1+2.5

3. a) The EMF of the cell,

      $$Pt_L \left| H_2(1atm) \right| HBr(a=1) \left| AgBr(S) \right| Ag \left| Pt_R \right.,$$

      is given by $E = \left[0.0713 - 0.5 \times 10^{-4} (t - 25) \right]$ volt, t in ^oC. Calculate ΔH for the reaction, $H_2 + 2AgBr(S) = 2Ag + 2HBr$ at 25^oC for the given EMF. Calculate the maximum efficiency of the cell. Comment on the result. 2+0.5+1
   b) One of the classifications of the Galvanic cells is (i) chemical cells (ii) concentration cells. Justify the classification with proper examples. 1+1
   c) What is the relation between entropy changes of a system and the surroundings when the Nernst equation is valid? 1.5
   d) In the relation, $\Delta G = -nFE$, ΔG, n and E are intensive properties – comment on the statement. 1.5
   e) Define emulsion with an example. Identify the dispersed phase and dispersion medium in your example. 1.5

4. a) State and illustrate the law of rational intercepts and show how the concept of Miller indices comes. 1+1+1
   b) The electron diffraction studies can be used for the determination of the structure of a crystal – Justify the statement. 2.5

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c) The structure factor F(hk*l*) for a unit cell of a crystal is given by

$F(hkl) = \sum_i f_i \, e^{i2\pi(hx_i + ky_i + lz_i)}$ (Symbols have their usual meaning).

Using this formula show that for a bcc lattice there will be reflections only from (hk*l*) planes with either h, k, *l* all are odd or even. 2

d) Using X-ray radiation of $\lambda = 154.2\,\text{pm}$, a fcc lattice produces reflections from the 111 and 200 planes. If the density of copper, which is fcc is 8.935 g/cm^3, at what angles will the reflection from copper appear? (Atomic weight of Cu = 63.5 g/mol). 2.5

5. a) A 0.1 M solution of compound A shows 50% transmission when a cell of 1 cm width is used at $\lambda_1$nm. Another 0.1 M solution of compound B gives the optical density value of 0.1761 using 1 cm cell at $\lambda_1$nm. What will be the transmission of solution that is a mixture of 0.1 M in A and 0.1 M in B using the same cell and at the same wavelength? 2

b) Using the mechanism of excitation by light absorption and subsequent decay of excited singlet state, establish a relationship between fluorescence life time and its quantum yield in absence of any quencher. 2

c) The study of phosphorescence should always be done at very low temperature – explain why. 1

d) The photodecompotion of HI vapour was carried out with $\lambda = 2070\,\text{Å}$ radiation. Absorption of each calorie gave $1.44 \times 10^{-5}\,\text{g}$ of hydrogen. What is the quantum yield? 2

e) A particular n.m.r. instrument operates at 30.256 MHz, what magnetic field are required to bring ^{1}H and ^{13}C nuclei to resonance at this frequency? (given that g value for ^{1}H = 5.585 and ^{13}C = 1.404, $\beta_N = 5.05 \times 10^{-27}\,\text{J T}^{-1}$) 2

f) The four lines from an AX spectrum are observed at δ = 5.8, 5.7, 1.1, 1.0 (measured from TMS). What are the chemical shift position (in δ) of the A and X nuclei, and the coupling constant (in hertz) between them? (the instrument is operating at 100 MHz). 1

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