B.Sc. (Honours)Examination, 2018

Semester-V

Chemistry (Honours)

Course: BCHC-53

(Physical Chemistry)

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

Questions are of value as indicated in the margin.

Answer ***any three*** questions.

1. a) Why Onsager equation is to be regarded as a limiting expression applicable to very dilute solutions only? 2

   b) What are the two factors that retard the motion of an ion in solution? 2

   c) Why the conductance of the $\overset{\ominus}{OH}$ ion in water is less than that of the H^+ ion? 2

   d) Show that the degree of ionization of a weak electrolyte is given by

   $\alpha = \sqrt{\frac{k_a}{C}}$; (terms have standard meanings) 2

   e) Calculate the solubility of calcium oxalate in pure water without any hydrolysis.

   [Given: $k_{sp}^{o}(CaOx) = 2.3\times10^{-9}$, for oxalic acid, $k_{a_1}^{o} = 5.4\times10^{-2}$, $k_{a_2}^{o} = 5.1\times10^{-5}$] 2

2. a) Derive the locations of two maxima in the RDF plot of

   $$\psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{z}{a_0}\right)^{3/2}\left(2-\frac{zr}{a_0}\right)e^{-zr/2a_0}$$

   (Symbols have usual meaning). 3+2

   b) Discuss, how the energy levels of hydrogen like atoms are split in presence of an external magnetic field. In this context show the normal Zeeman spectrum of hydrogen atom for $1s \rightarrow 2p$ transition. 2+3

3. a) Construct, by suitable linear combinations of $2p_{+1}$ and $2p_{-1}$ orbitals of hydrogen-like atoms, the $2p_x$ and $2p_y$ orbitals. In this context, discuss which of the four orbitals viz. $2p_{+1}$, $2p_{-1}$, $2p_x$ and $2p_y$ will be eigenfunctions of both $\hat{L}^2$ and $\hat{L}_z$ operators. 1.5+1.5+2

   b) Prove that the surface tension of a liquid is numerically same as the surface energy of the liquid. Is it consistent with their definitions? 1.5+1

   c) If two gases A and B undergo non-dissociative adsorption on the same surface then prove that the Langmuir assumptions give

   (i) $\theta_A = \frac{k_A p_A}{1+k_A p_A + k_B p_B}$ (ii) $\frac{v}{v_{mono}} = \frac{k_A p_A + k_B p_B}{1+k_A p_A + k_B p_B}$

   Where the symbols have usual meaning. What will be these relations if the n-components undergo non-dissociative adsorption on the same surface? 1+1+0.5

4. a) What is the definition of solution? 0.5

   b) Find an expression of chemical potential of the solvent in an ideal liquid solution. Is it consistent with your expectation? 1.5+1

   c) Find an expression to calculate the depression of freezing point in terms of molality of the solute in a dilute solution. Based on this derive an expression of ideal law of solubility assuming that the ideal solution is a saturated solution of the solute. 4+1

P.T.O.

d) For CCl_4, $k_b = 5.03$ k kg mol^{-1} and $k_f = 31.8$k Kg mol^{-1}. If 3.0 g of a substance in 100g CCl_4 raises the boiling point by 0.60 K, calculate the freezing point depression, the relative vapor pressure lowering, the osmotic pressure at 25°C, and the molar mass of the substance. The density of CCl_4 is 1.59g Cm^{-3} and molar mass of CCl_4 is 153.823 g mol^{-1}. 2

5. a) What is the most important factor for increasing the resolving power of a spectrometer? How does it affect the signal-to-noise ratio? 2

b) Which factor determines the minimum possible linewidth of a spectrum? 1

c) Sketch the curves of population distribution against different rotational levels in case of two different B values. Derive the expression of J_{max}. (Symbols have usual meaning). 2

d) The rotational spectrum of $^{79}Br^{19}F$ shows a series of equidistant lines 0.71433 cm^{-1} apart. Calculate the number of revolution per second which the molecule undergoes when in J=0 and J=10 states. Given that the atomic masses of ^{79}Br = 131.03×10^{-27} kg and $^{19}F = 31.55 \times 10^{-27}$ kg. 2

e) Discuss the concept of 'hot band' in vibrational spectroscopy. Obtain the energy expression for 'hot band'. 1.5

f) Sketch a diagram showing all possible vibrational modes of H_2O molecule. Label the vibrational frequencies according to the convention and identify the $||^{\ell}$ and $\perp^{r}$ modes. 1.5
