

## B.Sc. (Honours) Examination, 2019

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) Prove that the EMF of the Daniell cell can be expressed as the sum of the potential difference between the phases in contact. 1.5  
b) Describe the principle for the determination of EMF of a galvanic cell using the potentiometer. 1.5  
c) Express the activity of an electrolyte in terms of the activity of its ions. Also express the activity of the electrolyte in terms of its concentration and mean ionic activity co-efficient. 1+1  
d) Using an example demonstrate the principle for the determination of standard EMF of a cell. Why this principle is adopted in general? 1.5+1  
e) The EMF of the cell  $\text{Ag}|\text{Cd}|\text{CdCl}_2(1\text{m})|\text{AgCl}|\text{Ag}$  is 0.675 volts at  $25^\circ\text{C}$ . The temperature co-efficient of the cell EMF is  $-6.5 \times 10^{-4}$  Volt/ $^\circ\text{C}$ . Find  $\Delta H$  and  $\Delta S$  for the cell reaction when 1 F of electricity is drawn from it. 2.5
2. a) State the strategy for the calculation of mean ionic activity co-efficient for an electrolyte. 1.5  
b) To execute the above strategy solve the Poisson equation for any point in the ionic atmosphere for a dilute solution. 3.5  
c) Using the solution of the Poisson equation find an expression for mean ionic activity co-efficient in terms of concentration of the electrolyte. 2.5  
d) Considering an example state the principle for the determination of composition of a complex through EMF measurement. 2.5
3. a) Define polarizability ellipsoid of a molecule? What is the most essential criteria for a molecule to be Raman active? 1+1  
b) Discuss classical theory of Raman effect, briefly. 2  
c) Write the selection rule for rotational Raman Spectra. For rotational find structure in vibrational Raman Spectra, find the energy expression for Q, S and O-branch lines. 2  
d) Why does the chemical shift arises in NMR spectroscopy? Why we require TMS in nmr spectroscopy? 2+1  
e) Sketch the proton NMR spectra of  $(\text{CH}_3)_2\text{CHCOCH}_3$  molecule. 1
4. a) In ESR spectroscopy the coupling constant is related to electron density as  $A = R\rho$ . Calculate the electron density at each atoms of a  $\cdot\text{CH}_3$  radical. (Given that  $R = 0.05 \text{ T}$ ). Also sketch its ESR spectrum. 1.5+0.5  
b) Schematically show how the electronic excitation can lead to dissociation of molecules. Calculate the maximum value of the vibrational energy of HCl molecule. (Given that  $\omega_e = 2990 \text{ cm}^{-1}$ ,  $x_e = 0.0174$ ). 1+2  
c) The phosphorescence quantum yield is higher for molecules containing heavier atoms as compared to that of molecules containing lighter atoms – Explain why? 1  
d) What is photosensitized reaction? Give one example of such reaction. 1.5  
e) The percentage transmittance of an aqueous solution of disodium fumarate at 250 nm and  $25^\circ\text{C}$  is 19.2% for a  $5 \times 10^{-4} \text{ Mol L}^{-1}$  solution in a 1 cm cell.  
(i) Calculate the absorbance and the molar absorption co-efficient, (ii) What will be the percentage transmittance of a  $1.75 \times 10^{-5} \text{ Mol L}^{-1}$  solution in a 10 cm cell? 2.5

P.T.O.

5. a) Determine the Miller indices of the plane that intersects the crystal axes at (i) (a, 2b, 3c), (ii) (a, b, -c), (iii) (2a, b, c) [where a, b and c are the standard intercepts]. 1.5
- b) For a 2d cubic crystal of edge length a, show that the distance ( $d_{hk}$ ) between two parallel (hk) planes is given by

$$d_{hk} = \frac{a}{\sqrt{h^2 + k^2}}. \quad 2$$

- c) The x-ray diffraction pattern of a cubic crystalline substance shows data that correspond to reflection from the 110, 200, 220, 310, 222 and 400 planes. What type of cubic unit cell does the substance have? 1.5
- d) For a primitive cubic crystal with  $a = 3 \times 10^{-10}$  m, what are the smallest diffraction angle ' $\theta$ ' for (i) 100, (ii) 110, (iii) 111 planes for  $\lambda = 1.5 \times 10^{-10}$  m? 3
- e) How many crystal systems and crystal classes are there in the solid? On which basis the crystal system and crystal classes are classified? 2
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