

- c) Explain why conductivity decreases whereas molar conductivity increases on dilution.
9. Show pictorially and explain how the conductance varies during conductometric titration for the following cases :
- $2\frac{1}{2} \times 2$
- i) A solution of  $\text{MgSO}_4$  with a solution of  $\text{Ba}(\text{OH})_2$ , the later being added from the burette.
- ii) A solution of oxalic acid with a solution of  $\text{NaOH}$ , the later being added from the burette.
10. a) The resistance of a conductivity cell was found to be 60 ohms when filled with a certain  $\text{KCl}$  solution. What resistance will be recorded by the same solution when measured in a new cell having electrodes area twice that of the old cell and the distance between the two electrodes is 75% more than that of the old cell ?  $2\frac{1}{2}$
- b) Solubility of  $\text{CaF}_2$  in water at  $25^\circ\text{C}$  is  $2.04 \times 10^{-4} \text{ mol L}^{-1}$ . Calculate the thermodynamic solubility product and the solubility in 0.01 (M)  $\text{NaF}$  solution. Assume Debye Hückel limiting law to be valid with  $A = 0.509 \text{ L}^{1/2} \text{ mol}^{-1/2}$  at  $25^\circ\text{C}$ .  $3\frac{1}{2}$

**INTER B. SC. EXAMINATION, 2017**

( 2nd Semester )

**CHEMISTRY (HONOURS)****PAPER - VIII****PHYSICAL CHEMISTRY**

Time : Two hours

Full Marks : 50

( 25 marks for each group)

Use a separate Answer-script for each group

**GROUP - A**Answer Q. No. **1** and **any three** from the Q. No. 2 to 6

1. Justify or criticize the following statements with reason(s).

2×5

- a) For an ideally dilute solution, **van't Hoff factor** is always greater than one.
- b) If component 1 in a binary solution behaves non-ideally then component 2 will behave non-ideally.
- c) For one-component system, '**normal boiling point**' and '**triple point**' both are invariant.
- d) At constant pressure, critical point of '**phenol-water system**' is invariant.

[ 2 ]

- e) Composition and boiling point of *Azeotropic mixture* of water and ethanol do not depend on pressure.
2. Derive :  $\pi = C_2RT$  (symbols have their usual meanings), using thermodynamic concept. Mention all the assumption(s) & approximation(s) in proper places. 5
3. a) State and explain '*Nernst distribution law*'. Write about its limitation(s) ?
- b) The steam distillation of chlorobenzene is observed to occur at a temperature of 90.6 °C when the superincumbent pressure is 760 torr. Assuming complete immiscibility of these liquids, calculate the mass of chlorobenzene in 0.1 kg of distillate. The vapor pressure of chlorobenzene is 221.1 torr. 3+2
4. Draw the phase diagram of partially miscible liquid pair of nicotine-water system and label all. Find the number of degrees of freedom of each zone, line & two critical points. What is the '*critical solution temperature*' ?
5. a) Derive 'Duhem-Margules Rule' for a binary solution and mention its significances. 5
- b) Calculate the degree of ionization of  $K_3[Fe(CN)_6]$  in its aqueous solution of 0.01 mol kg<sup>-1</sup> which freezes at -0.06 °C. ( $K_f$  of water = 1.86 K kg mol<sup>-1</sup>) 3+2

[ 3 ]

6. Write notes on : 2+3
- i) Sublimation point
- ii) Freezing mixture.

### GROUP - B

7. a) What do you mean by the mobility of an ion ? On what factors does it depend ? Deduce the relation between the mobility of an ion and its ionic equivalent conductance. 4
- b) Explain any one experimental observation which gives an evidence of the existence of ion atmosphere in an electrolyte solution. 2½
- c) Explain how the conductance of halide ions in water will vary. 2½
8. Answer *any two* : 2½×2
- a) In conductometric titration, the concentration of the titer should be very high compared to the solution to be titrated- Explain.
- b) Which one between DC and AC is used in the measurement of conductance of an electrolyte solution and why ?

[ Turn over