9. a) The resistance of a conductivity cell was 257·3 ohms when filled with 0·01 (M) KCl solution (specific conductance $1·41 \times 10^{-3}$ S cm^{-1}) and 508.6 ohms when filled with 0·2 N acetic acid solution ($\Lambda^0_{HOAc} = 390·7$ S cm^2 g-eqv^{-1}) at 25°C. Calculate the degree of dissociation of acetic acid at that temperature.   3

    b) A solution of hydrochloric acid is electrolyzed in a conductivity cell using platinum electrodes. 20·175 g of the cathode solution contained 0·175 g of Cl$^-$ ion before electrolysis and 18·466 g of the cathode solution contained 0·146 g Cl$^-$ ion after electrolysis. A silver coulometer connected in series had a deposit of 0·2508 g Ag (Molar mass of Ag is 107·88 g). Calculate the transport numbers of Cl$^-$ and H$^+$ ions.   3

INTER B.SC. EXAMINATION, 2018

(2nd Semester)

CHEMISTRY (HONOURS)

PAPER - VIII

PHYSICAL CHEMISTRY

Time : Two hours   Full Marks : 50

Use separate answer scripts for each Group

GROUP - A

Answer *Q. No. 1* and *any three* from the Q.No. 2 to 5.

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

                                                                    2×5

    a) The magnitude of *elevation of boiling point* does not depend on nature of the solvent, only depends on the concentration of solution.

    b) Solid substance *sublimes* in an open container only when its triple point pressure is greater than the atmospheric pressure.

    c) the compositions of binary solution and its vapor phase, in equilibrium, *never are same*.

    d) Critical point of *'phenol-water system'* is invariant.

    e) Composition and melting point of *Eutectic mixture* do not depend on pressure.

2. Derive : $\Delta T_b = k_b \, m_2$ (symbols have their usual meanings), using thermodynamic concept. Mention all the assumptions & approximations. 5

3. The molal freezing-point depression constant of benzene is $5.07 \text{ K kg mol}^{-1}$. A 0.45 (m/m) of monoclinic sulfur in benzene freezes 0.088 K below the freezing point of pure benzene. Find the molecular formula of sulfur in benzene. 5

4. Draw the phase diagram of partially miscible liquid pair system : nicotine-water system, and label. Find the number of degrees of freedom of each zone, line & point. 5

5. Write notes on - (i) Boiling point, (ii) Azeotropic mixture.

2+3

GROUP - B

6. What is an electrophoretic effect ? Explain how the viscosity of the medium affects the conductance of an electrolytic solution and hence deduce the Walden's rule. 4

7. Answer *any four* : $2\frac{1}{2} \times 4$

   a) Equivalent conductance increases while the specific conductance decreases with increase in dilution – Explain.

   b) Conductance ratio may be used to determine the degree of dissociation of weak electrolyte in solution. Justify.

   c) Arrange NaOH, NaCl, CH_3COOH and HCl in the ascending order of Λ_m^0 values at a given temperature and explain.

   d) Explain why the conductivity of an electrolytic solution is increased when a very high frequency of electric field is employed.

   e) Do you expect that the solubility of CaF_2 in aq. KNO_3 solution to be same as, lower than or higher than its solubility in pure water at a given temperature ? Give reasons.

8. Explain qualitatively the difference in the nature of the conductometric titration curves when (i) NH_4OH is titrated with HCl taken in the burette and (ii) HCl is titrated with NH_4OH taken in the burette. $2\frac{1}{2} \times 2$