Roll No. 2131123002 55 Exam Code : D-22

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Subject Code—58413

B.Sc. EXAMINATION

(Main/Reappear) (Batch 2018 Onwards)

(Third Semester)

CHEMISTRY

CCL-304, Course-V

Physical Chemistry-II

(Solutions, Phase Equilibrium, Conductance and Electrochemistry)

Time : 3 *Hours* *Maximum Marks* : 80

Note : Attempt *Five* questions in all, selecting *one* question from each Unit. Q. No. 1 is compulsory. Q. No. 1 consists of eight short answer type questions of 2 marks each. All questions carry 16 marks each.

(Compulsory Question)

1. (a) Which out of Molarity and Molality is preferred method of expressing the concentration and why ?

   (b) When are chloroform and acetone mixed, the vapour pressure is less than that expected from Raoult's Law. Why ?

   (c) Why there can't be a quadruple point on a phase diagram for one component system ? Give reason.

   (d) Define stable and metastable equilibrium.

   (e) What do we mean by pK_w ? Give its value at 25°C.

   (f) Define Walden's rule. Write its mathematical expression.

   (g) Give mathematical expression for relationship between EMF of a cell and equilibrium constant.

   (h) Define Liquid Junction Potential How can it be minimized ? $2 \times 8 = 16$

Unit I

2. (a) 1 g of a solute dissolved in 100 g of solvent gave depression in freezing point = 0.2 K. Calculate the molecular mass of the solute. The cryoscopic constant for water is 5.0 K kg mol^{-1}. 2

   (b) Using boiling point composition diagram, explain the fractional distillation of azeotropic mixtures showing a minimum in the boiling point. 4

   (c) Define consolute temperature. Show its existence with the help of a labelled diagram of Phenol-Water system. 8

   (d) Why equimolar NaCl and Glucose solutions do not have same osmotic pressure ? 2

3. (a) Derive thermodynamic relation between depression in freezing point and molality of a solution. Why there is depression in freezing point when non-volatile solute is dissolved in a solvent ? 8

(b) Define Konowaloff's rule. Give its mathematical expression. 2

(c) Explain the isotopic effect on critical solution temperature. 2

(d) A mixture of water and aniline boils at a temperature of 98.5°C at a pressure of 760 mm Hg. The vapour pressure of water at this temperature is 717 mm Hg. Find the composition of distillate. 4

Unit II

4. (a) Draw a well labeled diagram of sulphur system and discuss its salient features. 8

(b) Explain, why the fusion curve of ice has a negative slope whereas sublimation curve has a positive slope in the phase diagram of water ? 4

(c) Calculate the number of components present in the following systems : 4

(i) $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$

(ii) $MgCO_3(s) \rightleftharpoons MgO(s) + CO_2(g)$

5. (a) What is meant by triple point of water ? Why is it different from normal melting point of ice ? 2

(b) Sketch and explain the phase diagram of Pb-Ag system. 8

(c) What is the criterion for phase equilibrium for a multi-component system ? 3

(d) Water boils at 373 K at 1 atm pressure. At what temperature will it boil when atmospheric pressure becomes 528 mm of Hg at some space station ? Latent heat of water = 2.28 kJ/kg. 3

Unit III

6. (a) The transport number of Cl^- ion in an aqueous solution of NaCl is more than that its value in an aqueous solution of HCl. Explain. 2

Roll No. 213112300 253

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(b) Define ionic product of water. How can it be determined using conductance measurement ? 4

(c) What is the principle underlying conductometric titration ? Discuss the titration curve obtained in the conductometric titration of the following : 10

(i) Strong acid against strong base

(ii) Weak acid against strong base

(iii) Strong acid against weak base

(iv) A mixture of strong acid and weak acid against strong base.

7. (a) Discuss graphically, how does molar conductivity of a strong electrolyte and a weak electrolyte vary with concentration ? Give reasons for the variation in each case. 4

(b) Define pH of a solution. What will be hydronium ion concentration of a solution whose pH is zero ? 2

(c) Calculate the pH of a buffer containing 0.5 m propionic acid (C_2H_5COOH) and 0.1 m sodium propionate (C_2H_5COONa). The dissociation constant of propionic acid is 1.34×10^{-5}. 6

(d) State Kohlrausch's Law. How can it be used to determine the solubility and solubility product of a sparingly soluble salt ? 6

Unit IV

8. (a) Derive the Nernst Equation for measuring EMF of a cell. Describe its utility. 5

(b) Taking example of Daniel Cell, explain why the EMF of the cell drops to zero after some time. 5

(c) Define concentration cells. Derive an expression for the EMF of a concentration cell with transference. 8

9. (a) Derive expressions for ΔG, ΔH and ΔS in terms of EMF of a cell and the temperature coefficient of EMF. **8**

(b) Describe the construction and working of a quinhydrone electrode. How is it useful in determining the pH of a solution ? **6**

(c) Can a solution of 1 M $CuSO_4$ be stored in a vessel made of nickel metal ? Given that $E^{\circ}_{Ni,Ni^{2+}} = +0.25$ V, $E^{\circ}_{cu,cu^{2+}} = +0.34$ V. **2**