Model Questions For Semester-IV B.Sc Chemistry Honours

(Physical Chemistry)

1) 'Both osmosis and diffusion are consequence of second law of thermodynamics'.Explain.
2) What is ideal solution? For such a solution deduce thermodynamically can't Hoff equation for osmotic pressure, starting clearly the assumptions and approximations.
3) Discuss the principle of measurement of relative lowering of vapour pressure of a dilute solution by Ostwal-Walker method. Write expression for the same when pure solvent and dilute solution are connected in series.
4) An aqueous solution of potassium sulphate, which is 92% dissociated, exhibits an osmotic pressure of 22 atm at 27^0C. Assuming dissociation to be unaffected by temperature variation, evaluate frzeeing point of the solution taking molarity and molality of the solution are almost same. [Latent heat of fusion of ice = 80cals/gm]
5) Why is the vapour pressure of a solvent lower when a non-volatile non-electrolytic solute is dissolved in it? Why is it necessary that the solute should be non-volatile?
6) Deduce an expression for the lowering of freezing point of a solvent by the dissolution of a non-volatile solute. Hence show that it is a colligative property. Under what conditions an elevation of freezing point is observed?
7) The lowering of freezing point of benzene was 2.33K when $4.12x10^{-4}$ kg of a solute of unknown molar mass was dissolved in 9.31 x 10^{-3} kg of benzene. Calculate the molar mass of the solute. Molar depression constant of benzene = 5.1 K kg /mol.
8) Derive thermodynamically the equation $\pi = CRT$ where the terms have their usual meaning. Mention the assumption and approximations involved in the derivation. What is meant by 'isotonic' solution?
9) Derive the unit of K_f, the molar cryscopic constant from its express units. What does 'K_f" signify?
10) What is van't Hoff factor? How is it related to the degree of ionization of weak electrolyte?
11) The vapour pressure of pure benzene and pure toluene at 86^0C are 1.267 bar and 0.5 bar respectively. Calculate the composition of an ideal mixture of benzene and toluene which smoothly boils at 86^0C at atmospheric pressure of 1.01325 bar.
12) Obtain the relation between the elevation of boiling point of a solvent and the molar concentration of a nonvolatile non-electrolyte solute dissolve in the solvent from the thermodynamic consideration.

13) Compare the processes of osmosis and diffusion. Justify the statement that both the process the consequence of second law of thermodynamics.
14) The aqueous solution of two uni-univalent electrolytes A and B of 0.1 molar strength freeze at – 0.360^0C and -0.208^0C respectively. Calculate the degree of dissociation in each case and comment on the nature of the electrolytes. Calculate also the concentration of A to be required at 37^0C for the preparation of a solution which is isotonic with human blood of a solution at 37^0C (Given K_f for water = 1.86 in usual unit and osmotic pressure of human blood = 7 atm at 37^0C)
15) From thermodynamic considerations derive the expression for Osmotic – pressure of a solution. 4
16) Obtain a relation between osmotic pressure and elevation of boiling point of a solution.
17) The complex compound $K_4[Fe(CN)_6]$ is 45% dissociated in 0.1(M) aqueous solution at 27^0C. What would be the Osmotic pressure of the solution?
18) State the law relating to the vapor pressure lowering and hence explain whether this is a constitutive or colligative property.
19) A certain solution of benzoic acid in benzene boils at 82.6^0C and freezes at 3.1^0C. The boiling point and freezing point of pure benzene are 80.1^0C and 5.5^0C respectively. [k_f = 5.12K kg/mol and k_b =2.67 K kg/mol]. What information about the number of particles and the structure of benzoic acid at the two temperatures can be predicted from the above data?
20) What is activity and activity coefficient?
21) Draw a temperature –composition diagram of a mixture of partially miscible liquids. Indicate one phase and two phase regions.Write lever rules in relation to the diagram.
22) Derive phase rule for reactive and non-reactive system.
23) Triple point is invarient Justify.
24) Draw the phase diagram of a simple eutectic system. Discuss the salient features and determine the degree of freedom in different regions.
25) Deduce phase rule
26) Calculate the number of degree of freedom for water at its triple point.
b) What is an azeotropic mixture? Give two examples.
c) Write notes on steam distrillation.
d) Discuss the fractional distillation of binary mixture of miscible liquids on the basis of the Duhem- Margulees equation.
27) Deduce thermodynamically Duhem-Margules equation.
(b) Explain ‘activity’ and ‘activity coefficient’.
c) Draw a temperature –composition diagram of a mixture of partially miscible liquids. Write ‘Lever Rule” in relation to this diagram.

28) Discuss how the phase diagram of binary alloy system may be constructed by thermal analysis.

29. (a) Define upper critical solution temperature and lower critical solution temperature with one example each.

(b) Explain 'Lever Rule' and its importance.

(30) A mixture of quinoline and water boils at 98.9°C under pressure of 740 mm of Hg. The distillate contains 78 g of quinoline and 1000 g of water. The vapor pressure of quinoline at 98.9°C is 8 mm of Hg. Calculate the molar mass of quinoiine.

30.(a) Define the terms phase, component and degree of freedom. How are the three quantities related? Show that the maximum number of phases that can co-exist in equilibrium for a one component system is three.

(b) Obtain Bragg equation in connection with the X-ray diffraction of a crystal.

(c) Consider a miscible binary liquid mixture of liquid *A* and *B*. Plot schematically on the same graph the vapour pressure of *A*, that of *B*, and the total vapour pressure as a function of mole fraction of *A* when the mixture behaves ideally. Derive the necessary equation. Discuss how the plot will be modified when the components show positive deviation from ideality.

31) Define number of components in a system at equilibrium. Determine the number by components for the following system at equilibrium. $CaCO_3\,(s) = CaO(s) + CO_2$

(c) What is an azeotrope? How does it differ from a pure compound? 100% pure ethyl alcohol cannot be obtained from a mixture of ethyl alcohol and water by distillation—explain with phase diagram. d) What is meant by the mean activity co-efficient of an electrolyte? Explain the necessity of defining such a quantity.

32. (a) How can the thermodynamic probability be related to entropy?

(b) Derive Gibbs' phase Rule.

(c) Draw a phase diagram of two partially miscible liquids with description. Indicate the change in the diagram on addition of a solute that dissolves only in one liquid. Justify the change indicate

33) A silver dipped in a 0.1 M KCl solution saturated with AgCl when coupled with a 0.1N calomel electrode gives e.m.f 0.0495V at 25^0C. Calculate activity solubility product of AgCl at this temperature.

Given: Mean activity coefficient for 0.1M KCl is 0.77V: $E_{cal}(ox) = -0.3338$V and the standard oxidation potential of Ag-electrode is –0.795V.

34) What is ionic product of water and how can you determine it potentiometrically?

35) We cannot a voltmeter be used for the measurement of E. M.F. of a reversible cell? What are the essential requirements for the construction of a cell without transference?

How the E^0 value of Ag(s) /AgCl(s) electrode can be determined very accurately? What is the method of determining mean activity coefficients of HCl of any desired concentration?

36) What are the electrodes utilized for the determination of H^+ ion concentration of solution? Draw and explain the potentiometric titration curve of a N/100 oxalic acid with N/10 NaOH as titrant.

37) Following the usual convention, a cell written as Zn/Zn^{++} (a_{Zn2+}= 0.1) || Cl^- (a_{Cl^-}= 0.2) /Hg_2Cl_2(s) /Hg [$E^0_{Zn2+/Zn}$ = – 0.70 V and E^0_{Hg2Cl2}(s) /Hg = 0.268V]

i) Indicate the flow of electron in the external circuit.

ii) Write each of the half-cell reaction and hence the net cell reaction.

iii) Calculate the E of the cell.

38) For the concentration cell with transference ($a_1 > a_2$)

Pb, $PbSO_4$(s)/$CuSO_4$(a_1) / $CuSO_4$(a_2) /$PbSO_4$(s), Pb

i)Write the various processes at two electrodes and at the liquid junction.

ii)Derive expression for ΔG and e.m.f. of the cell

iii) Write the corresponding cell without liquid junction.

39) Given that E^0 = –0.152V for AgI +e = Ag +I^- at 25^{0}C and E^0 = +0.80 V for Ag^+ + e = Ag at 25^{0}C Calculate K_{SP} for AgI.

40) Why is salt-bridge used? What is the parameter of utmost importance when an electrolyte is chosen for construction of a salt-bridge? Give reasons in support of your answer. 3

41) A cell is set up with an aqueous solution containing 80% Ce^{4+} and 20% Ce^{3+} coupled with an aqueous solution containing 10% Fe^{3+} and 90% Fe^{2+}. The observed emf at 25^{0}C is 0.93V. Find the equilibrium constant of the reaction: Ce^{4+} +Fe^{2+} = Ce^{3+} + Fe^{3+} at 25^{0}C. Can this reaction be used for quantitative estimation?

42) Construct the galvanic cell for each of the following reaction and write down the corresponding expression for the cell potential.

i) 2Cr(s) +3Hg_2Cl_2(s) = 2Cr^{+3}(aq) + 6Cl^-(aq) + 6H_2O(l)

ii) Zn + H_2SO_4 = $ZnSO_4$(aq) +H_2

iii) AgCl(s) +I^-(aq) = AgI(s) +Cl^-

43) Write down the Nernst equation for an electrochemical cell reaction and define standard e.m.f of a cell.

44) Justify the use of KCl in the construction of a salt bridge.

45) How would you determine the PH of a solution using quinhydrone electrode?

46) Derive the Nernst equation for the electrode process from thermodynamic consideration.

47) Construct a complete cell with quinhydrone and calomel electrodes. Write the cell reactions at each electrode. Indicate the ions that are responsible for the reversibility of the electrodes

48) Calculate the solubility product of AgCl at 25^0C given the standard reduction potentials of silver-silver ion and silver-silver chloride to be 0.79 and 0.22 volts respectively at 25^0C. Derive the necessary relation.

49) Calculate the P^H of 1 litre buffer solution which is 0.1 M in acetic acid and 0.4M in sodium acetate. What changes in P^H?

50) 1 ml of 10 N HCl acid and ii) 2 ml of 5N NaOH is added to 1 litre of buffer solution ? (assuming no change of volume). What change in P^H would occur if the original buffer solution is diluted by a factor of 10? Explain your result.

51) A solution contains 0.1gm mole Cl^- and 0.002 gm CrO^- per litre. Decimolar $AgNO_3$ is added gradually to this solution.

i) State whether AgCl or Ag_2CrO_4 will be precipitated first

ii) Calculate the concentration of Cl^- ion in solution when Ag_2CrO_4 beings to precipitate (K_{sp} for AgCl = 1.5 x 10^{-10}, K_{sp} for Ag_2CrO_4 = 2.4 x 10^{-12} at 25^0C). 2+2

52) Calculate i) the P^H of a 0.2 M solution of NH_4Cl and ii) the P^H of a 10^{-9} N HCl solution at 25^0C K_b NH_4OH = 1.8 x 10^{-5} at 25^0C. 2

53) Explain with examples the terms buffer solution and buffer capacity. Can you prepare a buffer solution with sodium acetate and HCl? The P^H value of a half neutralized weak acid is 4.74 What is the K_a of the acid.

54) Calculate the P^H of a saturated solution of $Mg(OH)_2$. Give solubility product of $Mg(OH)_2$ at 25 ^{0} C = 1.2 x10^{-11}.

55) Estimate the mean activity coefficient ($\gamma_\pm$) for $CaCl_2$ solution at 25^0C with molality = 0.01.

56) Derive the Henderson's equation for calculating the P^H of a buffer solution indicating the various assumptions involved and its condition of applicability.

b) To each of 25 ml of a 0.1(M) KH_2PO_4 solution, are added i) 5 ml and ii) 25 ml of a 0.1(M) NaOH solution respectively. Calculate the P^H values of the resulting solutions.
(Given for phosphoric acid P_{k1} = 2.1, P_{k2} = 7.2 and P_{K3} = 12.3)

57) Show that the degree of hydrolysis of ammonium acetate is independent of concentration.

58) What is buffer solution? Explain the buffer action of a mixture of ammonium hydroxide and ammonium chloride solution.

59) Calculate the ionic strength of a mixture of 0.008 M $BaCl_2$ and 0.005 M KCl solution.

60) The P^H scale ranges from 0— 14 ——— Explain.

61. a) Calculate the pH in each of the following solutions assuming complete ionisation:

i) 5.1xl0^{-4}MHCl.

ii) 0.0025 M NaOH.