Name :.....
Time : 6 hr

Total Marks = 192
Date: 23/10/2017

Q1. A spinel is an important class of oxides consisting of two types of metal ions with the oxide loss arranged in ccp layers. The normal spinel has 1/8th of the tetrahedral void occupied by one type of metal and one half of the octahedral voids occupied by another type of metal ions. Such a spinel is formed by Zn^{2+}, Ai^{3+} and O^{2-} with Zn^{2+} in tetrahedral void. Give the simplest formula of the spinel. 3

Q2. KF has NaCl type structure. What is the distance between $K^{\oplus}$ and $F^{\ominus}$ in KF if density is 2.48 g cm^{-3}? 3

Q3. Silver has atomic mass 108 a.m.u. and density 10.5 g cm^{-3}. If the edge length of its unit cell is 409 pm, identify the type of unit cell. Also calculate the radius of an atom of silver. 3

Q4. Calculate the value of Avogadro constant from the following data: 3
Density of NaCl = 2.165 g cm^{-3}, Distance between Na^+ and Cl^- in NaCl = 281 pm (Molar mass of NaCl = 58.5 g mol^{-1}).

Q5. Calculate the distance between Na^+ and Cl^- ions in NaCl crystal if its density is 2.165 g cm^{-3}. 3
[Molar mass of NaCl = 56.5 g mol^{-1}; N_A = 6.02 $\times 10^{23}$ mol^{-1}]

Q6. How would you account for the following? 3
(a) Frenkel defects are not found in alkali metal halides.
(b) Schottky defects lower the density of related solids.
(c) Impurity doped silicon is a semiconductor.

Q7. Explain the following terms with suitable examples: 3
(a) Schottky defect (b) Frenkel defect (c) Interstitials (d) F-centres.

Q8. What is a semiconductor? Describe the two main types of semiconductors and contrast their conduction mechanisms. 3

Q9. Calculate the mole fraction of ethylene glycol ($C_2H_6O_2$) in a solution containing 20% of $C_2H_6O_2$ by mass. 3

Q10. Calculate (a) molality (b) molarity and (c) mole fraction of KI if the density of 20% (mass/mass) aqueous solution KI is 1.202 g mL^{-1}. 3

Q11. A sample of drinking water was found to be severely contaminated with chloroform $CHCl_3$, supposed to be carcinogen. The level of contamination was 15 ppm (by mass) 3
(a) Express this in parcent by mass.
(b) Determine the molality of chloroform in the water sample.

Q12. A solution of glucose in water is labelled as 10% w/w, what would be the molality and mole fraction of each component in the solution? If the density of the solution is 1.2 g ml^{-1}, then what shall be the molarity of the solution? 3

Q13. Heptane and Octane form ideal solution. At 373 K, the vapour pressure of the two liquid components are 105.2 kPa and 46.8 kPa, respectively. What will be the vapour pressure of a mixture of 25.0 g of Heptane and 35.0 g of Octane? 3

Q14. 100 g of liquid A (molar mass of 140 g mol^{-1}) was dissolved in 1000 g of liquid B (molar mass 180 g mol^{-1}).The vapour pressure of pure liquid B was found to be 500 torr. Calculate the vapour pressure of pure liquid A and its vapour pressure in the solution if the vapour pressure of the solution is 475 torr. 3

Q15. Two liquid *A* and *B* on mixing form an ideal solution in two following composition. 3

(a) In 1st composition 4 mol of *A* mix with 2 mol of *B* and vapour pressure of solution 750 mm of Hg.

(b) In 2nd composition 6 mol of *A* mix with 2 mol of *B* and vapour pressure of solution 770 mm of Hg.

What is pure vapour pressure of *A* and *B* of given temperature?

Q16. Benzene and toluene form ideal solution on over the entire range of composition. The vapour pressure of pure benzene and toluene at 300 K are 50.71 mm Hg and 32.06 mm Hg respectively. Calculate the mole fraction of benzene in vapour phase if 80 g benzene is mixed with 100 g of toluene. 3

Q17. An aqueous solution containing 144 g of non-volatile solute having molecular formula $C_xH_{2x}O_x$ is prepared by using 180 g of water. If the solution boils at 101.24°C at one atm pressure. Find out the exact molecular formula of the compound. [K_b(water) = 0.512°C kg mol^{-1}] 3

Q18. The vapour pressure of pure water at 298 K is 23.8 mm Hg. If 50 g of urea (NH_2CONH_2) is dissolved in 850 g of water. Calculate the vapour pressure of water for this solution and its relative lowering. 3

Q19. A 5% solution (by mass) of cane sugar in water has freezing point of 271 K. Calculate the freezing point of a 5% glucose in water if freezing point of pure water is 273.15 K. 3

Q20. Two elements *A* and *B* form compounds having molecular formula AB_2 and AB_4. When dissolved in 20 g of C_6H_6, 1 g of AB_2, lowers the freezing point by 2.3 K, while 1.0 g of AB_4, lowers it by 1.3 K. The molar depression constant for benzene is 5.1 K kg mol^{-1}. Calculate atomic masses of *A* and *B*. 3

Q21. At 300 K, 36 g of glucose present per litre in its solution has an osmotic pressure of 4.98 bar. If the osmotic pressure of solution is 1.52 bar at the same temperature, what would be its concentration? 3

Q22. (a) Urea forms an ideal solution in water. Determine the vapour pressure of an aqueous solution containing 10% by mass of urea at at 40°C. 3
[Vapour pressure of water at 40°C = 55.3 mm of Hg]

(b) Why is freezing point depression of 0.1 M sodium chloride solution nearly twice that of 0.1 M glucose solution?

Q23. Calculate the amount of KCl which must be added to 1 kg of water so that the freezing point is depressed by 2 K. Assume KCl is 100% dissociated. 3

$K_{f\,Water}$ = 1.86 K kg/mol.

Q24. A decimolar solution of $K_4[Fe(CN)_6]$ at 300 K is 50% dissociation. Calculate the osmotic pressure of the solution. 3

Q25. The standard reduction potential of the reaction: 3

$$2H_2O + 2e^- \rightleftharpoons H_2(g) + 2OH^- \text{ is } -0.8277\,V$$

Calculate equilibrium constant for the reaction

$$2H_2O \rightleftharpoons H_2O^+ + OH^- \text{ at } 25°\,C.$$

Q26. Write the Nernst equation and the e.m.f. of the following cells at 298 K: 3

(a) $Sn\,(s) \mid Sn^{2+}_{(0.050\ M)} \| 2H^+_{(0.020\ M)} \mid H_2(g)_{(1\ bar)} \mid Pt\,(s)$

(b) $Pt\,(s) \mid Br_2(1) \mid Br^-_{(0.010\ M)} \| H^+_{(0.030\ M)} \mid H_2(g)_{(1\ bar)} \mid Pt\,(s)$

Given: $E^{\ominus}_{Sn^{2+}/Sn} = -0.14\,V$, $E^{\ominus}_{Br^2/Br^-} = +1.08\,V$.

Q27. Write the Nernst equation and the e.m.f. of the following cells at 298 K: 3

(a) $Mg\,(s) \mid Mg^{2+}_{(0.001\ M)} \| Cu^{2+}_{(0.0001\ M)} \mid Cu\,(s)$

(b) $Fe\,(s) \mid Fe^{2+}_{(0.001\ M)} \| H^+ \mid (1\ M)\ H_2(g)_{(1\ bar)} \mid Pt\,(s)$

Given: $E^{\ominus}_{Mg^{2+}/Mg} = -2.37\,V$, $E^{\ominus}_{Cu^{2+}/Cu} = +0.34\,V$, $E^{\ominus}_{Fe^{2+}/Fe} = -0.44\,V$.

Q28. $E^{\ominus}$ of some elements are given as: 3

$$I_2 + 2e^- \longrightarrow 2I^{\ominus} \qquad E^{\ominus} = 0.54\ V$$

$$MnO^{4\ominus} + 8H^{\oplus} + 5e^- \longrightarrow Mn^{2\oplus} + 4H_2O, \qquad E^{\ominus} = 1.52\ V$$

$$Fe^{3\oplus} + e^- \longrightarrow Fe^{2\oplus} \qquad E^{\ominus} = 0.77\ V$$

$$Sn^{4\oplus} + 2e^- \longrightarrow Sn^{2\oplus} \qquad E^{\ominus} = 0.1\ V$$

(a) Select the strongest reductant and weakest oxidant among these elements.

(b) Select the weakest reductant and strongest oxidant among these elements.

Q29. A current of 1.70 amp was passed through 300 ml of 0.160 M solution of $ZnSO_4$ for 230 sec with a current efficiency of 90%. Find the molarity of zinc (Zn^{+2}) after the deposition of zinc. Assume that volume of solution remains constant during electrolysis. 3

Q30. The resistance of a conductivity cell when filled with 0.02 M KCl solution is 164 ohm at 298 K. However, when it is filled with 0.05 M $AgNO_3$ solution its resistance is found to be 78.50 ohms. If conductivity of 0.02 M KCl is 2.768×10^{-3} ohm^{-1} cm^{-1}, calculate 3

(a) The conductivity of 0.05 M $AgNO_3$ (b) the molar conductivity of $AgNO_3$ solution.

Q31. A current of 4 amp was passed for 1.5 hours through a solution of copper sulphate when 3.0 g of copper was deposited. Calculate the current efficiency. 3

Q32. Write Nernst equation and calculate the e.m.f. of the cell at 298 K 3

$$Cu\,(s) \mid Cu^{2+}\,(0.130\ M) \| Ag^+(1.0 \times 10^{-4}\ M)/Ag(s)$$

Given the value of $E^{\ominus}_{Cu^{2+}/Cu}$ and $E^{\ominus}_{Ag^+/Ag}$ as 0.34 V and 0.80 V respectively.

Q33. A galvanic cell is constructed with Ag^+/Ag and Fe^{3+}/Fe^{2+} electrodes. Find the concentration of Ag^+ at which the e.m.f. of the cell is zero at equimolar concentrations of Fe^{2+} and Fe^{3+} ions. 3

$$(E^{\ominus}_{Ag^+/Ag} = 0.80\ V;\ E^{\ominus}_{Fe^{2+}/Fe^{3+}} = 0.77\ V).$$

Q34. Given the following cell $Al/Al^{3+}(0.01\ M) \| Fe^{2+}(0.02\ M)/Fe$ calculate the value of ΔG and E_{cell} at 298 K when $E^{\ominus}_{cAl^{3+}/Al}$ and $E^{\ominus}_{cFe^{2+}/Fe}$ are −1.66 and −0.44 respectively. 3

Q35. The standard reduction potential for the half cell. 3

$$NO_3^- + 2H^+ + e^- \longrightarrow NO_2(g) + H_2O \text{ is } 0.78\,V$$

(a) Calculate the reduction potential in 8M H^+ solution.

(b) What will be the reduction potential of the half cell in a neutral solution?

Assume other species to be at unit concentration.

Q36. Calculate the standard cell potentials of galvanic cell in which the following reactions take place: 3

(a) $2Cr(s) + 3Cd^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + 3Cd$

(b) $Fe^{2+}(aq) + Ag^+(aq) \longrightarrow Fe^{3+}(aq) + Ag(s)$

Calculate the $\Delta_r G^\ominus$ and equilibrium constant of the reactions.

Given, $E^\ominus_{Cr^{3+}/Cr} = -0.74\,V$, $E^\ominus_{Cd^{2+}/Cd} = 0.40\,V$, $E^\ominus_{Ag^+/Ag} = 0.80\,V$, $E^\ominus_{Fe^{3+}/Fe^{2+}} = 0.77\,V$

Q37. The conductivity of a solution containing 1.0 g of anhydrous $BaCl_2$ (barium chloride) in 200 cm^3 of the solution has been found to be 0.0058 S cm^{-1}. Calculate the molar and equivalent conductivity of the solution. (Atomic masses: Ba = 137 and Cl = 35.5). 3

Q38. Three electrolytic cells *A*, *B*, *C*, containing solution of $ZnSO_4$, $AgNO_3$ and $CuSO_4$, respectively are connected in series. A steady current of 1.5 amperes was passed through them until 1.45 g of silver deposited at the cathode of cell *B*. How long did the current flow? What mass of copper and of zinc were deposited? At. masses of Ag, Cu, Zn are 108 u, 63.5 u and 65 u respectively. 3

Q39. The conductivity of NaCl at 298 K has been determined at different concentrations and the results are given as under: 3

Concentration (M):	0.001	0.010	0.020	0.050	0.100
$k\,(S\,m^{-1}) \times 10^2$:	1.237	11.85	23.15	55.53	106.74

Calculate Λ_m for all concentrations and draw a plot between Λ_m and $C^{1/2}$. Find the value of Λ°_m from the graph.

Q40. How much electricity in terms of Faraday is required to produce 3

(a) 20.0 g of Ca from molten $CaCl_2$ (b) 40.0 g of Al from molten Al_2O_3.

Q41. The resistance of 0.01 M acetic acid solution when measured in a conductivity of cell constant 0.366 cm^{-1}, is found to be 2220 Ω. Calculate degree of dissociation of acetic acid. given that values of $\lambda^\ominus_{H^+}$ and $\lambda^\ominus_{CH_3COO^-}$ are 349.1 and 40.9 $\Omega^{-1}\,cm^2\,mol^{-1}$ respectively. 3

Q42. How much charge is required for the following reduction of 3

(a) 1 mol of Al^{3+} to Al. (b) 1 mol of Cu^{2+} of Cu (c) 1 mol of MnO^{4-} to Mn^{2+}

Q43. How many coulombs of electricity are required for 3

(a) Oxidation of 90 g of water. (b) Reduction of 0.2 mols of CrO_7^{2-} to Cr^{3+}.

(c) Complete reduction of MnO_4^- ions in 500 ml of 0.5 M solution to Mn^{2+} ions.

Q44. Silver is electrodeposited on a metallic vessel of surface area 900 cm^2 by passing a current of 0.5 ampere for 2 hours. Calculate the thickness of the silver deposited. Given the density of silver as 10.50 g/cc (Atomic mass of Ag =108 u). 3

Q45. A solution containing 30 g of a non-volatile solute exactly in 90 g of water has a vapour pressure of 2.8 kPa at 298 K. Further 18 g of water is then added to solution, new vapour pressure becomes 2.9 kPa at 298 K. Calculate (a) molar mass of the solute (b) vapour pressure of water at 298 K. 5

Q46. A liquid mixture containing 26 g of C_6H_6 and 46 g of C_7H_8 at 50°C has a vapour pressure of 163.75 mm. When another 52 g of C_6H_6 are added, the vapour of mixture is increased to 211.57 mm of Hg. Calculate the vapour pressures of pure components. Also find the values of *A* and *B* if the vapour pressure of the mixture is represented by $P = A + B$. X_T is the mole fraction of toluene. **5**

Q47. What is meant by positive and negative deviations from Raoult's law and how is the sign of ΔH_{mix} related to positive and negative deviations from Raoult's law? **5**

Q48. Vapour pressure of Chloroform ($CHCl_3$) and dichloromethane (CH_2Cl_2) at 298 K are 200 mm Hg and 415 mm Hg respectively. **5**

(a) Calculate the vapour pressure of the solution prepared by mixing 25.5 g of $CHCl_3$ and 40 g of CH_2Cl_2 at 298 K.

(b) Mole fraction of each component in vapour phase.

Q49. Vapour pressure of pure acetone and chloroform at 328 K are 632.8 mm Hg and 741.8 mm Hg. respectively. Assuming that they form ideal solution over the entire range of composition, plot p_{total}, $p_{chloroform}$ and $p_{acetone}$ as a function of $x_{acetone}$. The experimental data observed for different compositions of mixture is **5**

$100 \times x_{Acetone}$	$p_{Acetone}$ (mm Hg)	$p_{Chloroform}$ (mm Hg)
0	0	632.8
11.8	54.9	548.1
23.4	110.1	469.4
36.0	202.4	359.7
50.8	322.7	257.7
58.2	405.9	193.6
64.5	454.1	161.2
72.1	521.1	120.7

Plot the above data on a same graph paper. Indicate it has positive deviation or negative deviation from the ideal solution.

Q50. (a) Which aqueous solution has higher concentration: 1 molar or 1 molal solution of the same solute? Give reason. **5**

(b) How many mL of a 0.1 M HCl are required to react completely with 1 g mixture of Na_2CO_3 and $NaHCO_3$ containing equimolar amounts of the two?

Q51. (a) Explain why on addition of 1 mol of NaCl to 1 litre of water, the boiling point of water increases, while addition of 1 mol of methyl alcohol to one litre of water decreases its boiling point. **5**

(b) Components of a binary mixture of two liquids *A* and *B* were being separated by distillation. After some time separation of components stopped and composition of vapour phase became same as that of liquid phase. Both the components started coming in the distillate. Explain why this happened.

(c) What is the significance of Henry's Law constant K_H?

(d) Amongst the following compounds, identify which are insoluble, partially soluble and highly soluble in water? (i) Phenol (ii) Toluence (iii) Formic Acid (iv) Ethylene Glycol (v) Chloroform (vi) Pentanol.

(e) Based on solute-solvent interactions, arrange the following in order of increasing solubility in *n*-octane. Cyclohexane, KCl, CH_3OH, CH_3CN.

Q52. (a) Draw a neat diagram of standard hydrogen electrode. **5**

(b) Describe the electrochemical phenomenon of rusting of iron.

Q53. (a) How long will it take an electric current of 0.15 A to deposit all the copper from 500 ml of 0.15 M copper sulphate solution? **5**

(b) What is corrosion? What are the factors which affect corrosion? CO_2 is always present in natural water. Explain its effect (increases, stops or no effect) on rusting of Fe.

Q54. (a) How many coulombs of electricity are required for **5**

(i) oxidation of 1 mol of H_2O to O_2 (ii) Oxidation of 1 mol of FeO to Fe_2O_3

(b) An aqueous sloution of an unknown salt of palladium is electrolysed by a current of 3.0 A passing for 1 hr. During electrolysis, 2.977 g of a palladium ions are reduced at the cathode. What is the charge on the palladium ions in solutions?

Q55. (a) For the cell, $Mg|Mg^{2+}(aq)||Ag^{+}(aq)|Ag$, calculate the equilibrium constant at 25 °C and also the maximum work that can be obtained by operating the cell. **5**

$$E^{\ominus}(Mg^{2+} | Mg) = -2.37\ V \text{ and } E^{\ominus}(Ag^{+} | Ag) = +0.80\ V.$$

(b) Explain the following in brief.

(i) What is the use of platinum foil in hydrogen electrode?

(ii) Electrolysis of fused KHF_2 gives fluorine at anode but hydrogen at cathode.

Q56. (a) What are secondary cells? Give the anode and cathode reaction of Nickel-Cadmium storage cell. **5**

(b) What is disproportionation reaction? Calculate the equilibrium constant for the disproportionation of copper (I) ion in aqueous solution.

[Given $E^{\circ}_{Cu^{2+}/Cu} = +0.34\ V$ and $E^{\circ}_{Cu^{+}/Cu} = +0.52\ V$]