POINTS ON ELECTROCHEMISTRY - III

40. This can be resolved by using a source of alternating current and the second problem is resolved by using a specially designed vessel called conductivity cell.

41. A conductivity cell consists of 2 Pt electrodes coated with Pt black. They have area of cross section A and are separated by a distance l. Resistance of such a column of solution is given by the equation:

$$R = \rho \frac{l}{A} = \frac{1}{\kappa}\frac{l}{A}$$

$\frac{l}{A}$ is called cell constant and is denoted by the symbol G^*

42. Molar conductivity of a solution is defined as the conducting power of the ions produced by dissolving 1 mole of an electrolyte in solution.

Molar conductivity $\Lambda_m = \frac{\kappa \times 1000}{M}$

Where κ = Conductivity and M is the molarity

Unit of Molar conductivity is $S cm^2 mol^{-1}$

43. Equivalent conductivity is the conductivity of all the ions produced by dissolving one gram equivalent of an electrolyte in solution.

Equivalent conductivity $\Lambda_e = \frac{\kappa \times 1000}{N}$

Unit of equivalent conductivity is $S\ cm^2 (g\ equiv)^{-1}$

44. Kohlrausch's Law of independent migration of ions: According to this law, molar conductivity of an electrolyte, at infinite dilution, can be expressed as the sum of individual contributions from its individual ions. If the limiting molar conductivity of the cations is denoted by λ_+^o and that of the anions by λ_-^o then the limiting molar conductivity of electrolyte is:

$$\wedge_m^0 = v_+\lambda_+^0 + v_-\lambda_-^0$$

Where v_+ and v_- are the number of cations and anions per formula of electrolyte

45. Degree of dissociation: It is ratio of molar conductivity at a specific concentration 'c' to the molar conductivity at infinite dilution. It is denoted by α.

$$\alpha = \frac{\wedge_m^c}{\wedge_m^0}$$

46. $K_a = \frac{c\alpha^2}{1-\alpha}$ where K_a is acid dissociation constant, 'c' is concentration of electrolyte, α is degree of ionization.

47. Faraday constant: It is equal to charge on 1 mol of electrons. It is equal to 96487 C mol^{-1} or approximately equal to 96500 C mol^{-1}.

48. Faraday's first law of electrolysis: The amount of substance deposited during electrolysis is directly proportional to quantity of electricity passed.

49. Faraday's second law of electrolysis: If same charge is passed through different electrolytes, the mass of substance deposited will be proportional to their equivalent weights.

50. Products of electrolysis: The products of electrolysis depend upon the nature of electrolyte being electrolyzed and the nature of electrodes. If electrode is inert like platinum or gold, they do not take part in chemical reaction i.e. they neither lose nor gain electrons. If the electrodes are reactive then they will take part in chemical reaction and products will be different as compared to inert electrodes. The products of electrolysis also depend upon the electrode potentials of oxidizing and reducing species. Some of the electrochemical processes although feasible but slow in their rates at lower voltage, these do not take place. They require extra voltage, i.e. over voltage at which these processes will take place. The products of electrolysis also differ in molten state and aqueous solution of electrolyte.

51. Primary cells. A primary cell is a cell in which electrical energy is produced by the reaction occurring in the cell, e.g. Daniell cell, dry cell, mercury cell. It cannot be recharged.

52. Dry Cell:

At anode : $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

At cathode : $MnO_2(s) + NH_4^+(aq) + e^- \rightarrow MnO(OH) + NH_3$

The net reaction:

$Zn + NH_4^+(aq) + MnO_2(s) \rightarrow Zn^{2+} + MnO(OH) + NH_3$

53. Mercury Cell. The electrolyte is a paste of KOH and ZnO.

At anode : $Zn(Hg) + 2OH^- \rightarrow ZnO(s) + H_2O + 2e^-$

At cathode : $HgO(s) + H_2O + 2e^- \rightarrow Hg(l) + 2OH^-$

The net reaction :

$Zn(Hg) + HgO(s) \rightarrow ZnO(s) + Hg(l)$

54. Secondary cells. Those cells which are used for storing electricity, e.g., lead storage battery, nickel – cadmium cell. They can be recharged.

55. Lead storage battery:

Anode : $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$

Cathode: $PbO_2(s) + SO_4^{2-}(aq) + 4\,H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O\,(l)$

The overall cell reaction consisting of cathode and anode reactions is:

$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

On recharging the battery, the reaction is reversed.

56. Nickel cadmium cell: It is another type of secondary cell which has longer life than lead storage cell but more expensive to manufacture. The overall reaction during discharge is:

$Cd(s) + 2\,Ni(OH)_3(s) \rightarrow CdO(s) + 2Ni(OH)_2(s) + H_2O(l)$

57. Fuel cells:

At anode : $2\,H_2(g) + 4OH^-\,(aq) \rightarrow 4H_2O(l) + 4e^-$

At cathode : $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4\,OH^-(aq)$

Overall reaction:

$2\,H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

58. Corrosion:

Oxidation: $Fe(s) \rightarrow Fe^{2+}\,(aq) + 2e^-$

Reduction: $O_2(g) + 4H^+\,(aq) + 4e^- \rightarrow 2H_2O(l)$

Atmosphere oxidation:

$2Fe^{2+}(aq) + 2H_2O(l) + \frac{1}{2}\,O_2(g) \rightarrow Fe_2O_3(s)\ 4H^+(aq)$

59. Galvanization. It is a process of coating zinc over iron so as to protect it from rusting.

60. Cathodic protection: Instead of coating more reactive metal on iron, the use of such metal is made as sacrificial anode.

Source : http://ciseche10.files.wordpress.com/2013/12/6-electrochemistry.pdf