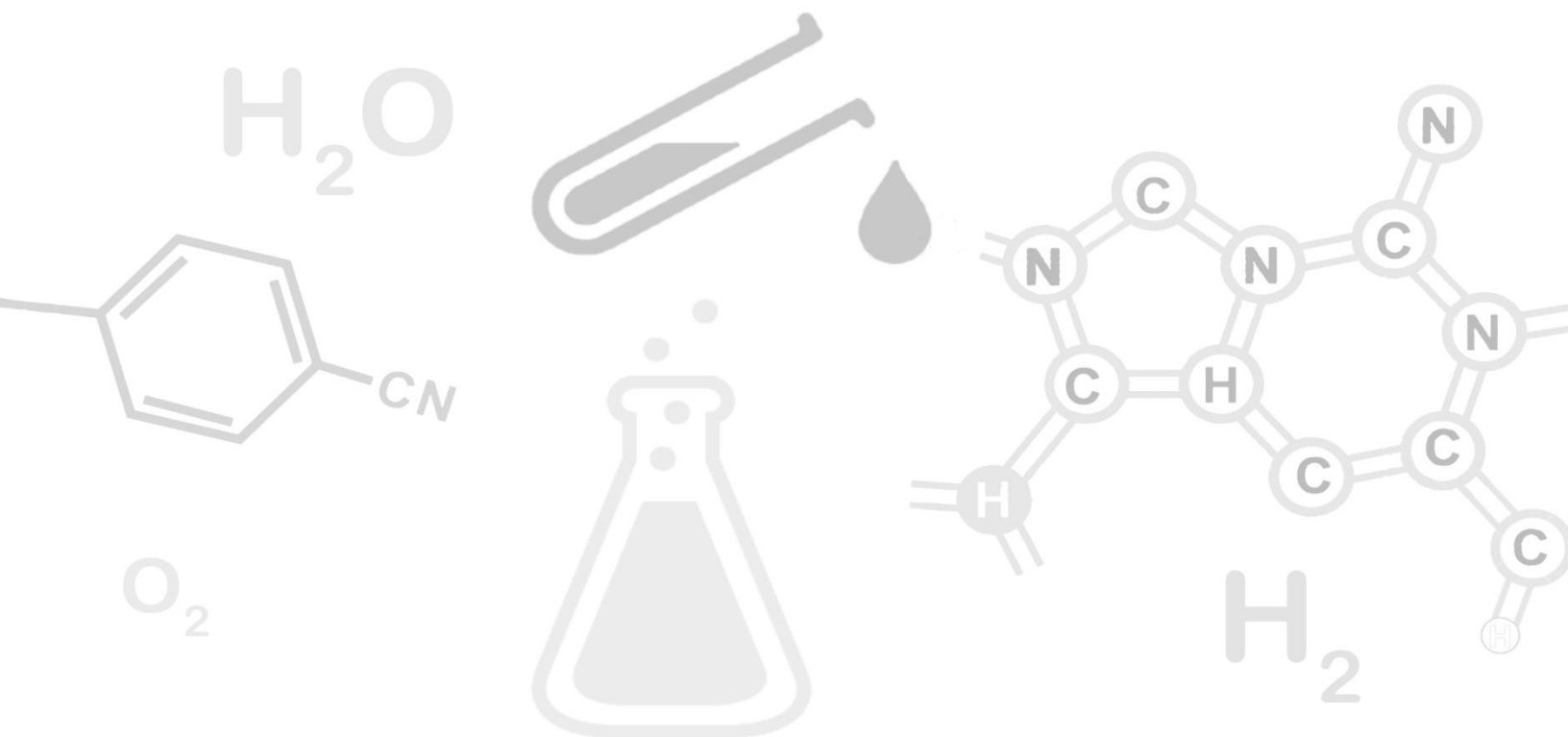# CHEMISTRY

Electrochemistry

1. Oxidation is defined as a loss of electrons, while reduction is defined as a gain of electrons.

2. In a redox reaction, both oxidation and reduction reactions occur simultaneously.

3. Direct redox reaction: In a direct redox reaction, both oxidation and reduction reactions occur in the same vessel. Chemical energy is converted to heat energy in a direct redox reaction.

4. Indirect redox reaction: In indirect redox reactions, oxidation and reduction occur in different vessels. In an indirect redox reaction, chemical energy is converted into electrical energy.

5. In an indirect redox reaction, the device which converts chemical energy into electrical energy is known as an electrochemical cell.

6. In an electrochemical cell:
   a. The half cell in which oxidation occurs is known as an oxidation half cell.
   b. The half cell in which reduction occurs is known as a reduction half cell.
   c. Oxidation occurs at the anode which has negative potential with respect to solution and reduction occurs at the cathode which has positive potential with respect to solution.
   d. Transfer of electrons occurs from the anode to the cathode, while the electric current flows in the opposite direction.
   e. An electrode is made by dipping the metal plate into the electrolytic solution of its soluble salt.
   f. A salt bridge is a U-shaped tube containing an inert electrolyte in agar-agar and gelatine.

7. A salt bridge maintains electrical neutrality and allows the flow of electric current by completing the electrical circuit.

8. Representation of an electrochemical cell:
   a. The anode is written on the left, while the cathode is written on the right.
   b. The anode represents the oxidation half cell and is written as Metal/Metal ion (concentration)
   c. The cathode represents the reduction half cell and is written as
      Metal ion (concentration)/Metal
   d. The salt bridge is indicated by placing double vertical lines between the anode and the cathode.
   e. The electrode potential is the potential difference which develops between the electrode and its electrolyte. The separation of charges at the equilibrium state results in the potential difference between the metal and the solution of its ions. It is the measure of tendency of an electrode in the half cell to lose or gain electrons.

9. When the concentration of all the species involved in a half cell is unity, the electrode potential is known as standard electrode potential. It is denoted as $E^{\ominus}$.

10. According to the present convention, standard reduction potentials are now called standard electrode potential.

11. There are two types of electrode potentials: Oxidation potential and reduction potential.

12. Oxidation potential is the tendency of an electrode to lose electrons or get oxidised.

13. Reduction potential is the tendency of an electrode to gain electrons or get reduced.

14. Oxidation potential is the reverse of reduction potential.

15. The electrode with a higher reduction potential has a higher tendency to gain electrons. So, it acts as a cathode.

16. The electrode with a lower reduction potential acts as an anode.

17. The standard electrode potential of an electrode cannot be measured in isolation.

18. According to convention, the Standard Hydrogen Electrode is taken as a reference electrode, and it is assigned a zero potential at all temperatures.

19. The standard calomel electrode can also be used as a reference electrode.

20. The standard hydrogen electrode consists of a platinum wire sealed in a glass tube and carries a platinum foil at one end. The electrode is placed in a beaker containing an aqueous solution of an acid with 1 molar concentration of hydrogen ions. Hydrogen gas at 1 bar pressure is continuously bubbled through the solution at 298 K. The oxidation or reduction occurs at the platinum foil. The standard hydrogen electrode can act as both anode and cathode.
    When the standard hydrogen electrode acts as an anode:
    H_2 (g) → $2H^+$ (aq) + $2e^-$
    When the standard hydrogen electrode acts as a cathode:
    $2H^+$ (aq) + $2e^-$→ H_2 (g)

21. In the electrochemical series, various elements are arranged according to their standard reduction potential values.

22. A substance with a higher reduction potential value means that it has a higher tendency to get reduced. So, it acts as a good oxidising agent.

23. A substance with a lower reduction potential value means that it has a higher tendency to get oxidised. So, it acts as a good reducing agent.

24. The electrode with a higher reduction potential acts as a cathode, while the electrode with a lower reduction potential acts as an anode.

25. The potential difference between the two electrodes of a galvanic cell is called the cell potential and is measured in volts.

26. The cell potential is the difference between the reduction potential of the cathode and that of the anode.
    $$E_{cell} = E_{cathode} - E_{anode}$$
    The cell potential is called the electromotive force (EMF) of the cell when no current is drawn through the cell.

27. Nernst studied the variation of electrode potential of an electrode with the temperature and the concentration of an electrolyte.

28. Nernst formulated a relationship between standard electrode potential $E^⊖$ and electrode potential E.

$$E = E^⊖ - \frac{2.303RT}{nF} \log \frac{1}{[M^{n+}]}$$

$$E = E^⊖ - \frac{0.059}{n} \log \frac{1}{[M^{n+}]} \quad \text{(At 298 K)}$$

29. The electrode potential increases with increase in the concentration of the electrolyte and decrease in temperature.

30. Nernst equation when applied to a cell:

$$E_{cell} = E^{\ominus}{}_{cell} - \frac{2.303RT}{nF} \log \frac{[\text{Anode ion}]}{[\text{Cathode ion}]}$$

This helps in calculating the cell potential.

31. At equilibrium, the cell potential E_{cell} becomes zero.

32. The relationship between the equilibrium constant K_c and the standard cell potential $E^{\ominus}{}_{cell:}$

$$E^{\ominus}{}_{cell} = \frac{0.059}{n} \log K_c \text{ (At 298 K)}$$

33. The work done by an electrochemical cell is equal to the decrease in Gibbs energy:
$\Delta G^{\ominus} = -nFE^{\ominus}{}_{cell}$

34. Substances which allow the passage of electricity through them are known as conductors.

35. Every conducting material offers some obstruction to the flow of electricity which is called resistance. It is denoted by R and is measured in ohm.

36. The resistance of any object is directly proportional to its length **l** and inversely proportional to its area of cross section **A**.

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

ρ is called specific resistance or resistivity. Its SI unit is ohm metre.

37. The inverse of resistance is known as conductance, G

$$G = \frac{1}{R}$$

The unit of conductance is ohm^{-1} or mho. It is also expressed in siemens denoted by S.

38. The inverse of resistivity is known as conductivity. It is represented by the symbol κ. The SI unit of conductivity is Sm^{-1}. However, it is also expressed in Scm^{-1}.

$$\kappa = \frac{1}{\rho} = \frac{1}{R}\left(\frac{l}{A}\right) = G \frac{l}{A}$$

So, Conductivity = Conductance × Cell constant

39. For measuring the resistance of an ionic solution, there are two problems:
    a. First, passing direct current changes the composition of the solution.
    b. Second, a solution cannot be connected to the bridge such as a metallic wire or a solid conductor.

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

41. A conductivity cell consists of two Pt electrodes coated with Pt black.
They have an 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 all the ions produced by dissolving 1 mole of an electrolyte in the solution.

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

where κ is conductivity and M is the molarity.
Unit of Molar conductivity is $Scm^2 \, mol^{-1}$

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

Equivalent conductivity $\Lambda_{e} = \dfrac{\kappa \times 1000}{N}$

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_+^0 and that of the anions by λ_-^0, then the limiting molar conductivity of the 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 the 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. $K_a = \dfrac{c\alpha^2}{1-\alpha}$, where K_a is acid dissociation constant, 'c' is concentration of electrolyte and α is degree of ionisation.

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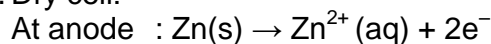
49. Faraday's second law of electrolysis: If the same quantity of electricity is passed through different electrolytes, then the mass of the substance deposited will be proportional to their equivalent weights.

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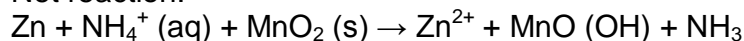The products of electrolysis also depend on the electrode potentials of oxidising and reducing species. Some of the electrochemical processes although feasible but slow in their rates at lower voltage, and hence do not take place at low voltages. They require extra voltage, i.e. over voltage at which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

51. Primary cells: A primary cell is a cell in which electrical energy is produced by the reaction occurring in the cell. Examples: Daniell cell, dry cell and mercury cell. It cannot be recharged.
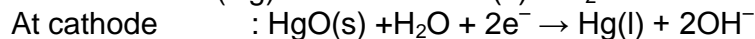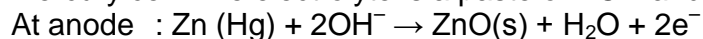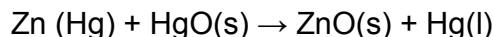
52. Dry cell:
At anode : $Zn(s) \rightarrow Zn^{2+} (aq) + 2e^-$
At cathode : $MnO_2(s) + NH_4^+(aq) + e^- \rightarrow MnO(OH) + NH_3$
Net reaction:
$Zn + NH_4^+ (aq) + MnO_2 (s) \rightarrow Zn^{2+} + MnO (OH) + NH_3$

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 : $HgO(s) + H_2O + 2e^- \rightarrow Hg(l) + 2OH^-$
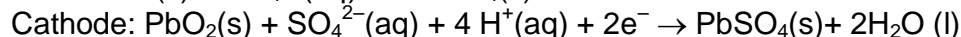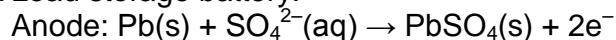Net reaction:
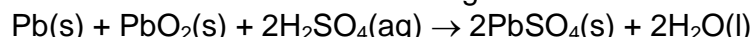$Zn (Hg) + HgO(s) \rightarrow ZnO(s) + Hg(l)$

54. Secondary cells: These cells are used for storing electricity. Examples: 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
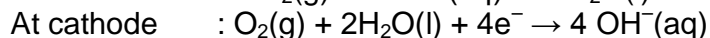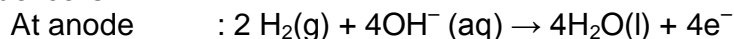$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$
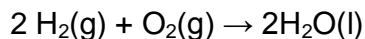On recharging the battery, the reaction is reversed.

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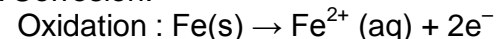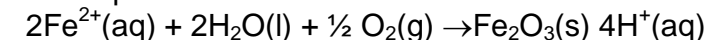$Cd(s) + 2 Ni(OH)_3(s) \rightarrow CdO(s) + 2Ni(OH)_2(s) + H_2O(l)$

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:
$2Fe^{2+}(aq) + 2H_2O(l) + ½ O_2(g) \rightarrow Fe_2O_3(s) 4H^+(aq)$

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

60. Cathodic protection: Instead of coating a more reactive metal on iron, this metal is made to act as sacrificial anode and the protected metal such as iron is made to act as cathode..

TOP Formulae:

1. $E_{cell} = E_{cathode} - E_{anode}$

2. $E = E^{\ominus} - \dfrac{0.059}{n} \log \dfrac{1}{[M^{n+}]}$ (At 298 K)

3. $E_{cell} = E^{\ominus}{}_{cell} - \dfrac{2.303RT}{nF} \log \dfrac{[\text{Anode ion}]}{[\text{Cathode ion}]}$

4. $E^{\ominus}{}_{cell} = \dfrac{0.059}{n} \log K_c$ (At 298 K)

5. $\Delta G^{\ominus} = -nFE^{\ominus}{}_{cell}$

6. $R = \rho \dfrac{l}{A} = \dfrac{1}{\kappa} \dfrac{l}{A}$

7. $G = \dfrac{1}{R}$

8. Conductivity = Conductance × Cell constant

9. $\kappa = \dfrac{1}{\rho} = \dfrac{1}{R}\left(\dfrac{l}{A}\right) = G\,\dfrac{l}{A}$

10. Cell constant is denoted by the symbol G^{*}.

11. $\Lambda_m = \dfrac{\text{Specific conductance}}{\text{Molarity}} = \dfrac{\kappa}{C}$

   $\Lambda_m = \dfrac{\kappa \times 1000}{C}$

   Remember: The unit of Λ_m in the above formula is Scm^2mol^{-1}.

12. $\alpha = \dfrac{\Lambda_m^c}{\Lambda_m^0}$

13. $K_a = \dfrac{c\alpha^2}{1-\alpha}$

14. $m = ZIt$

15. $\dfrac{w_1}{E_1} = \dfrac{w_2}{E_2} = \dfrac{w_3}{E_3} = \ldots$