Chapter 8

Redox Reactions and Electrochemistry

REDOX REACTIONS

CONCEPT OF OXIDATION & REDUCTION

Oxidation	Reduction
(i) Loss of electron	(i) Gain of electron
(ii) Loss of hydrogen	(ii) Gain of hydrogen
(iii) Gain of oxygen	(iii) Loss of oxygen
(iv) Increase in oxidation number	(iv) Decrease in oxidation number

OXIDATION NUMBER

Oxidation number change is defined as the change (real or imaginary) which an atom appears to have undergone when it is present in redox reaction. There are certain rules laid down in order to determine the oxidation number.

(a) Oxidation number of an atom in free elements is zero.

(b) Oxidation number of oxygen is –2, while in peroxides it is –1, in OF_2 it is +2.

(c) Oxidation number of hydrogen is +1, while in metal hydrides it is –1.

(d) Oxidation number of an ion is equal to the electrical charge present on it.

(e) Oxidation number of group IA elements is +1 and that of group IIA elements is +2.

(f) For complex ions, the algebraic sum of oxidation numbers of all the atoms is equal to the net charge on the ion.

(g) In case of neutral molecules the algebraic sum of the oxidation number of all the atoms present in the molecules is zero.

(h) Oxidation number of an atom never be greater than its valence electron. *e.g.*, valence electron for Cr is 6.

Increase in oxidation number of an element in a reaction is known as oxidation while decrease in oxidation number of an element in a reaction is known as reduction.

Besides +ve and -ve values, fractional values of oxidation number (as average) are also possible.

Balancing of H_2O can also be done as per the medium given

(1) **Acidic Medium :** Add H_2O on that side of reaction where oxygen are deficient and double number of H^+ on opposite side of reaction.

(2) **Basic Medium :** Add H_2O on that side of reaction where oxygen are excess and double number of OH^- on opposite side of reaction.

ELECTROCHEMISTRY

STANDARD ELECTRODE POTENTIAL

Standard Electrode Potential : The potential difference developed between metal electrode and the solution of its ions of unit molarity (1 M) at 298 K is called standard electrode potential.

> ***Note :*** *Standard reduction potential = – (Standard oxidation potential)*
>
> *or Standard oxidation potential = – (Standard reduction potential)*

Standard Hydrogen Electrode – (SHE)

SHE Half Reaction	Electrode Potential
$H_2 \rightarrow 2H^+ + 2e^-$	0.0 V (anode)
$2H^+ + 2e^- \rightarrow H_2$	0.0 V (cathode)

With the help of SHE - the SRP values of all the electrodes has been determined and are placed in electrochemical series.

> ***Note :*** E_{Cell} *= O.P. of anode + R.P. of cathode.*
>
> *or* E_{Cell} *= R.P. of cathode – R.P. of anode.*

ELECTROCHEMICAL SERIES

Table in which the standard reduction potentials of various electrodes have been arranged in the increasing order is called electrochemical series or activity series or electromotive series.

Electrode	Electrode reaction	E°(volts)
Li^+/Li	$Li^+ + e^- = Li$	– 3.045 (Lowest)
Zn^{+2}/Zn	$Zn^{+2} + 2e^- = Zn$	– 0.763
H^+/H_2, Pt	$2H^+ + 2e^- = H_2$	0.0 (Standard)
Cu^{+2}/Cu	$Cu^{+2} + 2e^- = Cu$	+ 0.34
F_2/F^-, Pt	$F_2 + 2e^- = 2F^-$	+ 2.887 (Highest)

Applications of Electrochemical Series :

The important applications of electrochemical series are:

(a) Relative strength of oxidising and reducing agents. In the series, the elements are arranged in the increasing order of reduction potentials or decreasing order of oxidation potential. Therefore, the elements at the top are good reducing agents while those at the bottom are good oxidising agents.

(b) **Calculating e.m.f. of the cell :** The e.m.f. of the cell can be determined by knowing the standard electrode potentials from the series as:

$E^\circ_{cell} = E^\circ_{(cathode)} \quad E^\circ_{(anode)}$ (If standard reduction potential are given)

$E^\circ_{cell} = E^\circ_{(anode)} \quad E^\circ_{(cathode)}$ (If standard oxidation potential are given)

(c) **Predicting feasibility of a redox reaction :** In general, a redox reaction is feasible only if the species which has higher reduction potential is reduced i.e., accepts the electrons and the species which has lower reduction potential is oxidised i.e. loses the electrons. Otherwise, a redox reaction is not feasible. In other words, the species to release electrons must have lesser reduction potential as compared to the species which has to accept electrons.

(d) To predict whether a metal can liberate hydrogen from acid or not, only the metals which have negative reduction potentials, can liberate hydrogen from the acids.

EMF OF GALVANIC CELL

In galvanic cells, current is generated as a result of a spontaneous chemical reaction that occur in the cell. The main characteristics of galvanic cell are given below

		Cathode	**Anode**
(i)	Sign	Positive	Negative
(ii)	Half reaction	Reduction	Oxidation
(iii)	Direction of electron movement	Into the cell	Out of the cell

Note : *Flow of currrent from cathode to anode.*

GIBB'S ENERGY CHANGE AND CELL POTENTIAL

The electrical work done from the cell = nFE

$– \ G = nFE$

$G = –nFE$

or $G^o = – \ nFE^o$

where, G = Gibb's energy change

G° = Standard Gibb's energy change

E = emf of cell/electrode potential

E° = Standard emf of cell/standard electrode potential.

Type of Electrode Potential

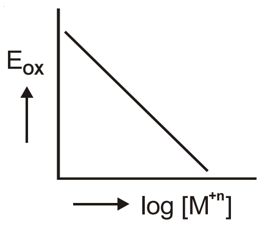
1. Oxidation Potential
2. Reduction Potential

1. **Oxidation Potential :** When electrode is negatively charged w.r.t. solution then it acts as anode, and oxidation takes place.

$$M \quad \rightarrow M^{+n} + ne^-$$

$$E_{ox} = E_{\ ox} \quad \frac{2.303RT}{nF} . \log[M^{+n}]$$

$$\text{Intercept} = E°_{ox} \quad \text{and} \quad \text{Slope} = \frac{2.303RT}{nF}$$

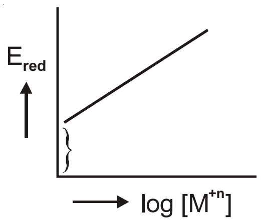


2. **Reduction Potential :** When electrode is positively charged w.r.t. solution then it acts as cathode, and reduction takes place.

$$M^{+n} + ne^{-} \rightarrow M$$

$$E_{red} = E_{\ red} \quad \frac{2.303RT}{nF} . \log \frac{1}{[M^{+n}]}$$

$$E_{red} = E_{\ red} + \frac{2.303RT}{nF} . \log [M^{+n}]$$



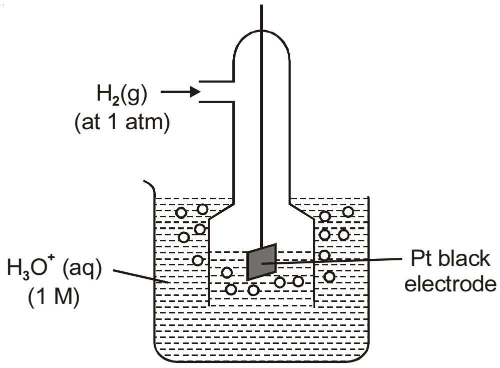
Intercept = $E°_{red}$

Slope = $\frac{2.303RT}{nF}$.

Various Types of electrodes

Different types of half cells are used to make complete cell with spontaneous reaction in forward direction.

1. **Hydrogen Electrode :** The standard hydrogen electrode (S.H.E.) consists of a Pt electrode coated with Pt black. The electrode dipped in a solution of 1 M and hydrogen gas bubbled through it at 1 bar.



Hydrogen electrode

$$Pt, \underset{1\,bar}{H_2(gas)}|H^{+}(aq).\,1M$$

$$H_2(g) \rightarrow 2H^{+} + 2e^{-}$$

$$E°_{SHE} = 0$$

$$E = \frac{0.059}{1} \log H^{+} = E = \frac{0.059}{1} pH$$

2. **Metal-Metal ion Half Cell** :

$Ag \mid Ag^{+}(aq)$

$Ag(s) \rightarrow Ag^{+}(aq) + e^{-}$

$E = E° - 0.0591 \log [Ag^{+}]$

3. **Metal-Metal-Insoluble Salt anion Half Cell :**

$Ag \mid AgCl \mid Cl^{-}(aq)$

$Ag + Cl^{-}(aq) \rightarrow AgCl(s) + e^{-}$

$$E = E° - 0.0591 \log \frac{1}{[Cl\ \ ]}$$

$$E = E° + 0.0591 \log [Cl^{-}]$$

4. **Calomel Electrode :**

$Hg, Hg_2Cl_2 \mid Cl^-(aq)$

$2Hg(l) + 2Cl^-(aq) \rightarrow Hg_2Cl_2(s) + 2e^-$

$$E = E \quad \frac{0.0591}{2}\,.\log\frac{1}{[Cl^-]^2}$$

$E = E° + 0.0591 \log [Cl^-]$.

5. **Metal-Metal Oxide Hydroxide Half Cell :**

$Hg,HgO \mid OH^-(aq)$

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

$$E = E \quad \frac{0.0591}{2}\,.\log\frac{1}{[OH^-]^2}$$

$E = E° + 0.0591 \log [OH^-]$.

6. **Oxidation-Reduction Half Cell :**

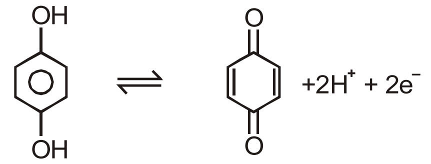
$Pt \mid Fe^{+2}(aq), Fe^{+3}(aq)$

$Fe^{+2}(aq) \rightarrow Fe^{+3}(aq) + 1e^-$

$$E = E \quad \frac{0.0591}{1}\,.\log\frac{[Fe^{+3}]}{[Fe^{+2}]}.$$

7. **Quinhydrone Half Cell :**

$Pt \mid Quinhydrone \mid H^+(aq)$



Hydroquinone Quinone

$$E = E \quad \frac{0.0591}{2}\,.\log[H^+]^2$$

$$E = E \quad \frac{0.0591}{1}\,.\log[H^+].$$

ELECTROLYSIS

(a) The decomposition of the electrolyte due to the passage of electricity is known as electrolysis.

(b) During electrolysis, electrical energy changes into chemical energy.

(c) To have electrolysis we must use direct current.

(d) Electrolysis is a redox phenomenon.

Faraday's laws of electrolysis

(a) First Law : The weight of substance deposited at the electrode is directly proportional to the quantity of electric charge passed through the electrolytic solution

$W \quad Q$ W = Weight in g

Q = Quantity of charge

$\Rightarrow$ W = ZQ Z = Constant known as electrochemical equivalent

$\Rightarrow$ W = ZIt I = Current in ampere

t = Time in second

$$Z = \frac{\text{E(equivalent mass)}}{96500}$$

(b) Second law : If the same quantity of current is passed through different electrolytic solutions then the weights of different substances deposited at the respective electrodes is directly proportional to their chemical equivalents.

$$\frac{\text{Weight of electrolyte (A)}}{\text{Eq. wt. of (A)}} = \frac{\text{Weight of electrolyte (B)}}{\text{Eq. wt. of (B)}}$$

ELECTROLYTIC CONDUCTION

Molten true electrolyte and the aqueous solution of electrolytes contain free ions and conduct electricity due to the movement of ions.

According to Ohm's law,

$$R \quad \frac{l}{a} \qquad \text{or} \qquad R = \quad \frac{l}{a}$$

$$= R\;\frac{a}{l}$$

$$\frac{1}{\;} = \frac{1}{R}\;\frac{l}{a}$$

where R = Resistance of solution

l = Length

a = Area of cross-section of the solution

= Resistivity of solution

If *l* = 1 unit of length and a = 1 unit of area

then $\boxed{R = \quad}$

Conductance (G) = $\frac{1}{R}$

Unit of conductance = ohm^{-1} or siemens (S)

Specific conductance (K) = $\frac{1}{\ } = \frac{1}{R}\,\frac{l}{a} = \frac{\text{Cell constant}}{\text{Resistance}}$ ($\frac{l}{a}$ is called cell constant)

K = Conductance if l = 1 unit (length) and a = 1 unit (area)

S.I. Unit of K = Sm^{-1}

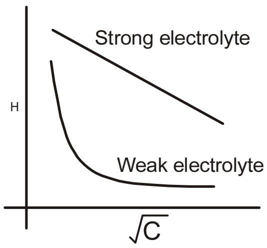
Note : *Specific conductance is now-a-days called conductivity.*

MOLAR CONDUCTIVITY ($_m$)

The conducting power of all the ions furnished by one mole of an electrolyte in any solution is termed as its molar conductivity

$$_m = \frac{\text{Conductivity (K) [}^{-1}\text{ cm}^{-1}]}{\text{Concentration of solution in moles per unit volume (cm}^3)}$$. Unit of $_m$ = $\text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$

Molar conductivity of weak electrolyte increases with increase in dilution or decrease in concentration due to increase in ionisation but specific conductivity decreases with increase in dilution because number of ions per cm^3 of solution decreases.



KOHLRAUSCH'S LAW

It states that at infinite dilution the molar conductivity of an electrolyte [known as limiting molar conductivity] can be expressed as the sum of the contribution from its individual ions.

$^o_m = V_+\ ^o_+ + V\ \ ^o$ (where V_+ and $V\_$ are the number of cations and anions per formula unit of electrolyte respectively and $^o_+$ and $\ ^o$ are limiting molar conductivities of the cation and anion respectively).

Application

Some typical applications of Kohlrausch's law are

(i) Determination of ^o_m for weak electrolyte

(ii) Determination of degree of dissociation ( ) of a weak electrolyte

$$= \frac{^c_m}{^o_m}$$

(iii) Determination of ionisation constant of weak electrolyte of (AB) type

$$K = \frac{C(\ ^c_m)^2}{^o_m(\ ^o_m\quad ^c_m)}$$

(iv) Determination of solubility of a sparingly soluble salt

Concentration of sparingly soluble salt $(C_m) = \frac{1000.K_{salt}}{(V_+\ ^o_+ + V\ \ ^o)}$

IMPORTANT POINTS

(1) Degree of dissociation ( ) can be related with conductance. *i.e.*, $= \frac{m}{{}^{o}_{m}}$

(2) $G^{\circ} = -nFE_{cell}$ n = Number of electrons

F = Faraday

(3) Concentration cells are made up of same electrode but dipped in different concentration of its own ion.

e.g., $Cu\,|\,Cu^{+2}_{(0.01M)}\,||\,Cu^{+2}_{(0.2M)}\,|\,Cu$

(4) For spontaneity of reaction, $E_{cell} > 0$ *i.e.*, $G < 0$.

(5) **Primary Cells :** The reaction occurs in one direction only and the cell cannot be recharged. *e.g.*, Mercury cell.

(6) **Secondary Cells :** The cells that can be recharged by passing current through it. *e.g.*, Lead storage cell.

Fuel Cell : Energy is obtained by combustion of fuels.

(7) Rusting of iron is the example of corrosion which is a electrochemical process.

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