Oxidation and Reduction

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Classical concept of oxidation and reduction

Oxidation

A chemical process that involves the addition of oxygen or any other electronegative species or removal of hydrogen or any other electropositive species.

i. Addition of Oxygen:

$2Mg + O_2 \longrightarrow 2MgO$ (Mg is oxidized to MgO)

ii. Addition of electronegative Species:

$Ca + Cl_2 \longrightarrow CaCl_2$ (Ca is oxidized to $CaCl_2$)

iii. Removal of Hydrogen:

$H_2S + Cl_2 \longrightarrow 2HCl + S$ (H_2S is oxidized to S)

iv. Removal of electropositive Species:

$2KI + Cl_2 \longrightarrow 2KCl + I_2$ (KI is oxidized to I_2)

Reduction

A chemical process that involves the addition of hydrogen or any other electropositive species or removal of oxygen or any other electronegative species.

i. Addition of hydrogen:

$H_2 + Cl_2 \longrightarrow 2HCl$ (Cl_2 is reduced to HCl)

ii. Addition of electropositive Species

$2KI + Cl_2 \longrightarrow 2KCl + I_2$ (Cl_2 is reduced to KCl)

iii. Removal of oxygen:

$ZnO + C \longrightarrow Zn + CO$ (ZnO is reduced to Zn)

iv. Removal of electronegative Species

$2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$ ($FeCl_3$ is reduced to $FeCl_2$)

Modern or electronic concept of oxidation and reduction

Oxidation is the process in which there is loss of electron.

i. Loss of electron

$Mg \longrightarrow Mg^{++} + 2e^-$

ii. Increase in positive charge

$Fe^{++} \longrightarrow Fe^{+++} + e^-$

Reduction is the process ~~of~~ in which there is gain of an electron.

i. Gain of electron

$Cu^{++} + 2e^- \longrightarrow Cu$

ii. Decrease in positive charge

$Fe^{+++} + e^- \longrightarrow Fe^{++}$

Oxidation Number

It is the charge which appears to be associated with the atom on removing all other atoms as ions from the compound.

Rules for assignment of oxidation number

1. The oxidation ~~sum of the an~~ number of an element in an elementary or free state is zero.

2. The ~~algebric~~ algebraic sum of the oxidation number of all the elements in the compound is zero.

3. The algebraic sum of oxidation numbers of all the elements in an ions is equal to the charge on the ion.

4. The oxidation of alkali metal is +1 and alkaline earth metal is +2 in all the compounds.

5. The oxidation number of hydrogen in compounds is +1 except in metallic hydrides (-1).

6. The oxidation number of oxygen in compounds is -2 except in ~~perodic~~ peroxide (-1) and in superoxides (-1/2)

7. The oxidation number of halogen is (-1) in all it's compound except when they are bonded to more electronegative atoms.

8. The oxidation number of metal in ~~ab~~ amalgam and metal carbonyl~~s~~ is always zero.

Assign the oxidation number of underlined elements.

i. <u>Mn</u> O_2

Solution:

Let O.N of Mn be 'x'

$1x + 2(-2) = 0$

or, $x = +4$

Hence oxidation number of Mn in MnO_2 is +4.

ii. <u>N</u> H_4Cl

Solution:

Let O.N. of N be x

$x + (4 \times 1) + (-1) = 0$

$\therefore x = -3$

iii. $KMnO_4$

Solution:

Let the O.N of Mn be 'x'

$1 + x + (-2 \times 4) = 0$

or, $x = +7$

Hence oxidation number of Mn in $KMnO_4$ is +7

iv. $\underline{C}H_3OH$

Solution:

Let the O.N of C be 'x'

$x + (+1 \times 3) + (-2) + 1 = 0$

or, $x + 3 - 2 + 1 = 0$

$\therefore x = -2$

Hence, oxidation number of C in CH_3OH is −2

v. $\underline{C}Cl_4$

Solution:

Let O.N. of C be 'x'

$x + (-1)4 = 0$

$\therefore x = +4$

Hence, oxidation number of C in CCl_4 is +4

vi. $\underline{N}H_4^+$

Solution:

Let O.N of N be 'x'

i.e. $x + (+1 \times 4) = 1$

$\therefore x = -3$

Hence, oxidation number of N in NH_4^+ is −3

vii. SO_4^{--}

Solution:

Let O.N of S be 'x'

Then, $x + (-2)4 = -2$

$\therefore x = +6$

Hence the oxidation number of S in SO_4 ion is +6.

viii. NO_3^-

Solution:

Let O.N of N be 'x'

Then, $x + (-2)3 = -1$

or, $x = 6 - 1$

$\therefore x = +5$

Hence, the oxidation number of N in NO_3^- is +5.

ix. MnO_4^-

Solution:

Let O.N of Mn be x

Then, $x + (-2)4 = -1$

$\therefore x = +7$

Hence, oxidation number of Mn in MnO_4 ion is +7.

x. $NaNO_3$

Solution:

Let the O.N of N be 'x'

Then, $1 + x + (-2).3 = 0$

or, $1 + x - 6 = 0$

$\therefore x = +5$

Hence, oxidation number of N in $NaNO_3$ is +5.

xi. $\underline{C}HCl_3$

Solution:

Let the O.N of C be 'x'

Then, $x + 1 + (-1)3 = 0$

or, $x + 1 - 3 = 0$

$\therefore x = +2$

Hence, the oxidation number of C in $CHCl_3$ is +2.

xii. $Na_2\underline{S_2}O_3$

Solution:

Let the O.N of S be 'x'

Then, ~~2x +~~ $2 + 2x + (-2)3 = 0$

or, $2 + 2x - 6 = 0$

or, $2x = 4$

$\therefore x = +2$

Hence, the oxidation number of S in $Na_2S_2O_3$ is +2.

xiii. $\underline{N}H_4\underline{N}O_3$

Solution:

Let O.N of N be 'x'

$\underline{N}H_4^+$	$\underline{N}O_3^-$
$x + 4 = +1$	$x + (3\times -2) = -1$
$\therefore x = -3$	$\therefore x = +5$

xiv. $CaO\underline{Cl}_2$

Solution:

Let O.N of Cl be 'x'

Ca^{++}	OCl^-	Cl^-
	$x - 2 = -1$	$= -1$
	$\therefore x =$ ~~0~~ $+1$	

Redox Reaction

The reaction in which oxidation and reduction occur simultaneously is called the redox reaction.

oxidation

$$2\overset{+3}{Fe}Cl_3 + \overset{+2}{Sn}Cl_2 \longrightarrow 2\overset{+2}{Fe}Cl_2 + \overset{+4}{Sn}Cl_4$$

Reduction

Oxidation half-reaction: $Sn^{+2} \longrightarrow Sn^{+4} + 2e^-$

Reduction half-reaction: $Fe^{+3} + e^- \longrightarrow Fe^{+2}$

Steps for balancing redox reaction by oxidation number method.

1. Write the skeleton redox reaction and write the oxidation number of those elements whose oxidation number is changed.

2. Balance those elements whose oxidation number is changed

3. Calculate the change in oxidation number per mole and multiply by the criss-cross method.

4. Balance all other elements and balance hydrogen and oxygen in the end.

Balance the following reaction by oxidation method

1. $Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO + H_2O$

Now,

$Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO + H_2O$

$\overset{0}{Cu} + H\overset{+5}{N}O_3 \longrightarrow \overset{+2}{Cu}(NO_3)_2 + \overset{+2}{N}O + H_2O$

Change in O.N of Cu = 2 - 0 = 2

Change in O.N of N = 5 - 2 = 3

$Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO + H_2O$

2 ⤫ 3

$3Cu + 2HNO_3 \longrightarrow 3Cu(NO_3)_2 + NO + H_2O$

$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + H_2O$ (balancing N)

$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$ (balancing H_2O)

2. $P_4 + NaOH + H_2O \longrightarrow PH_3 + NaH_2PO_2$

Now,

$P_4 + NaOH + H_2O \longrightarrow PH_3 + NaH_2PO_2$

$\overset{0}{P_4} + NaOH + H_2O \longrightarrow \overset{-3}{P}H_3 + NaH_2\overset{+1}{P}O_2$

~~$P_4 + P_4 + NaOH + H_2O \longrightarrow 4PH_3 + 4NaH_2PO_2$~~

Change in O.N from P_4 to PH_3 = $3 \times 4 = 12$

Change in O.N from P_4 to NaH_2PO_2 = $1 \times 4 = 4$

~~$P_4 + P_4 + NaOH + H_2O \longrightarrow 4PH_3 + 12NaH_2PO_2$~~

~~12~~ ⤫ 4

3 1

$P_4 + 3P_4 + NaOH + H_2O \longrightarrow 4PH_3 + 12NaH_2PO_2$

$4P_4 + 12NaOH + H_2O \longrightarrow 4PH_3 + 12NaH_2PO_2$

$4P_4 + 12NaOH + 12H_2O \longrightarrow 4PH_3 + 12NaH_2PO_2$

$P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + 3NaH_2PO_2$ (common 4)

c. $KMnO_4 + H_2SO_4 + H_2C_2O_4 \longrightarrow K_2SO_4 + MnSO_4 + H_2O + CO_2$

Now,

$K\overset{+7}{Mn}O_4 + H_2SO_4 + H_2\overset{+3}{C_2}O_4 \longrightarrow K_2SO_4 + \overset{+2}{Mn}SO_4 + H_2O + \overset{+4}{C}O_2$

Change in O.N of Mn = 5 (i.e. 7 − 2)

Change in O.N of C_2 = 1 (i.e. 4 − 3)

$KMnO_4 + H_2SO_4 + 5H_2C_2O_4 \longrightarrow K_2SO_4 + MnSO_4 + H_2O + 5CO_2$

$2KMnO_4 + H_2SO_4 + 5H_2C_2O_4 \longrightarrow K_2SO_4 + 2MnSO_4 + H_2O + 5CO_2$

$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 \longrightarrow K_2SO_4 + 2MnSO_4 + H_2O + 5CO_2$

$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 2H_2O + 10CO_2$

$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$

d. $KMnO_4 + H_2SO_4 + H_2S \longrightarrow K_2SO_4 + MnSO_4 + H_2O + S$

Now,

$K\overset{+7}{Mn}O_4 + H_2SO_4 + H_2\overset{-2}{S} \longrightarrow K_2SO_4 + \overset{+2}{Mn}SO_4 + H_2O + \overset{0}{S}$

Change in O.N of Mn = 7 − 2 = 5

Change in O.N of S = 2 − 0 = 2

$2KMnO_4 + H_2SO_4 + H_2S \longrightarrow K_2SO_4 + MnSO_4 + H_2O + S$

$2KMnO_4 + 3H_2SO_4 + 5H_2S \longrightarrow K_2SO_4 + 2MnSO_4 + H_2O + 5S$

$2KMnO_4 + 3H_2SO_4 + 5H_2S \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5S$

e. $MnO_4^- + C_2O_4^{--} \longrightarrow Mn^{++} + CO_2$ (acidic medium)

Increase by 1

$\overset{+7}{Mn}O_4^- + \overset{+3}{C_2}O_4 \longrightarrow \overset{+2}{Mn^{++}} + \overset{+4}{C}O_2$

decrease by 5

$MnO_4^- + 5C_2O_4^{--} \longrightarrow Mn^{++} + 5CO_2$

$MnO_4^- + 5C_2O_4^{--} \longrightarrow Mn^{++} + 10CO_2$

$MnO_4^- + 5C_2O_4^{--} \longrightarrow Mn^{++} + 10CO_2 + H_2O$

$MnO_4^- + 5C_2O_4^{--} + 8H^+ \longrightarrow Mn^{++} + 10CO_2 + 4H_2O$

To balance charge

$2MnO_4^- + 5C_2O_4^{--} + 16H^+ \longrightarrow 2Mn^{++} + 10CO_2 + 8H_2O$

f. $Cl_2 \longrightarrow Cl + ClO_3$ (alkaline metal)

Increase by 5

$\overset{0}{Cl_2} \longrightarrow \overset{-1}{Cl^-} + \overset{+5}{ClO_3^-}$

decrease by 1

$3Cl_2 \longrightarrow 5Cl^- + ClO_3^-$

$3Cl_2 + 6OH^- \longrightarrow 5Cl^- + ClO_3 + 3H_2O$

Electrolysis

The process of decomposition of an electrolyte by passing electricity through its aqueous or molten state is called electrolysis.

Qualitative Aspects

The process is carried out in an apporatus called an electrolytic cell. In the cell, two metallic rod or plates are dipped into the electrolyte. These ~~two~~ metallic rod are connected to the direct current (DC) source like battery. These metallic rods are connected to the positive terminal to the battery is called an annode while another electrode that is connected to the negative terminal of battery is called the cathode. A simple diagram for the electrolytic process is given below:

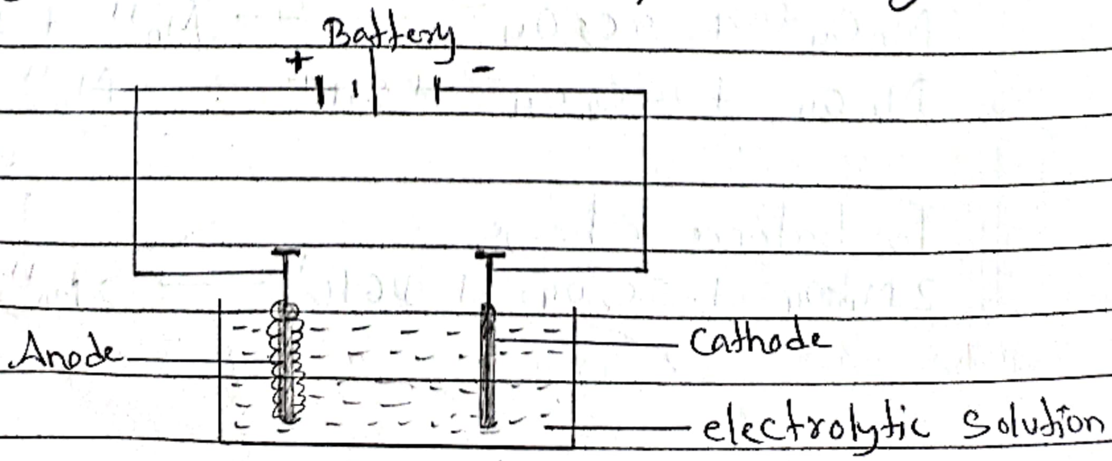


Fig: Electrolytic cell

On passing electricity, cations migrate towards the cathode where they get reduced by gaining electron from the cathode. Similarily, anion migrates towards anode where they get oxidised by losing electrons to the anode.

Quantitative Aspect of Electrolysis

1. Faradays first law of electrolysis

It states that "The mass of substance liberated or deposited on electrodes during electrolysis is directly proportional to the quantity of charge passed through the solution"

i.e. $m \propto Q$

or, $m = ZQ$

or $m = ZIt$ ($i = Q/t$ or, $Q = It$)

Where, m = mass of substance (gm)

I = Current (Amphere)

t = Time (sec)

Q = Charge (columb)

Z = Proportionality constant known as electrochemical equivalent (ECE)

Electrochemical Equivalent (ECE)

From Faraday's first law of electrolysis,

$m = ~~Zt~~ \ ZIt$

If $I = 1$ amp and $t = 1$ sec then $m = Z$

Hence,

ECE is defined as the mass of substance in gram deposited or liberated in electrode during electrolysis on passing 1-amphere current in unit time.

or,

We have, $m = ZQ$

if $Q = 1$ columb, $m = Z$

Hence, ECE is also defined as the mass of substance in gram deposited or liberated in electrode during electrolysis on passing 1 ~~colum~~ coulomb of charge.

2. Faraday's Second Law of Electrolysis

It states that: "When an equal amount of electricity is passed through a different electrolyte, the mass of different substances liberated ~~or~~ deposited on the respective electrode during electrolysis are directly proportional to their chemical equivalent".

Mass of substance (m) $\propto$ chemical equivalent (E)

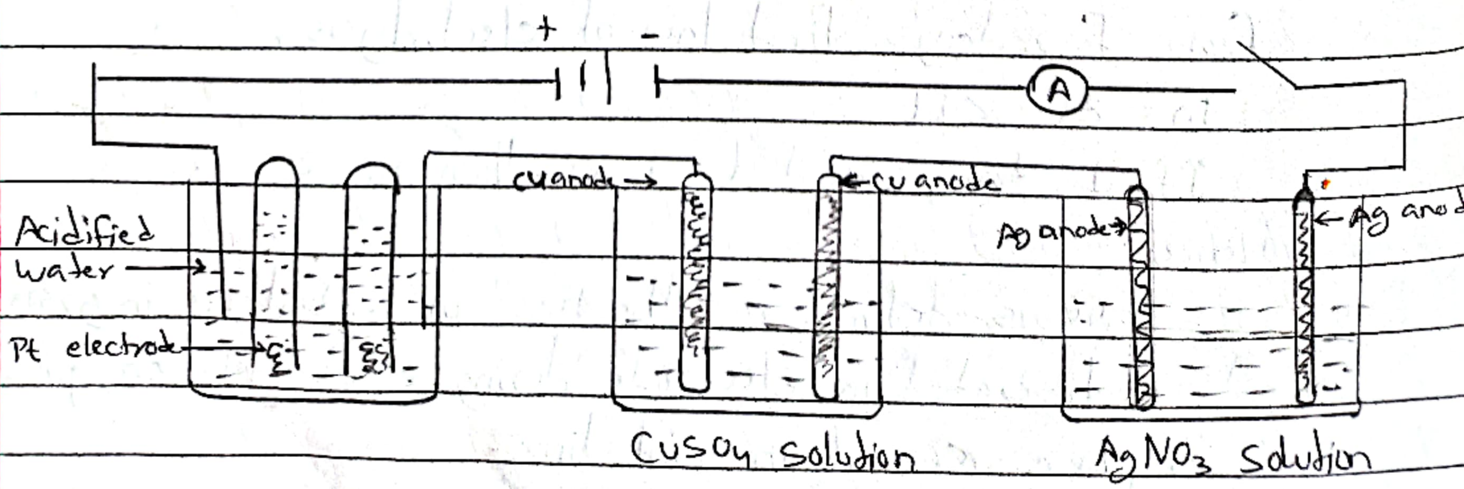
or, $m \propto E$

or, $\frac{m}{E} = k$

$$\frac{\text{mass of substance}}{\text{chemical equivalent}} = \text{Constant}$$

i.e $\frac{m_1}{E_1} = \frac{m_2}{E_2} = \frac{m_3}{E_3}$

Experimental Verification of Faraday's second law of electroly



Let us suppose three electrolytic cells containing acidulated water, an aqueous solution of $CuSO_4$ and an aqueous solution of $AgNO_3$. These three electrolytic cells are connected in series with an electric source as shown in the figure. When the same amount of electricity is passed in three electrolytic cells, after sometime we found that:

$$\frac{\text{Mass of } H_2 \text{ liberated}}{\text{Eq. wt. of } H_2} = \frac{\text{Mass of Cu liberated}}{\text{Eq. wt of Cu}} = \frac{\text{Mass of Ag liberated}}{\text{Eq. wt of Ag}}$$

i.e. $\frac{M_{H_2}}{E_{H_2}} = \frac{M_{Cu}}{E_{Cu}} = \frac{M_{Ag}}{E_{Ag}}$

So, $\frac{\text{Mass of substance}}{\text{Chemical equivalent}} = \text{Constant}$

Thus, faraday's second law of electrolysis is verified.

Faraday

Faradays is defined as the quantity of charge carried by one mole of electron.

We have,

1 mole of electron = 6.023×10^{23} no. of electrons.

Again, charge of 1 electron = 1.602×10^{-19} ~~col~~ Coulumb

Charge carried by one mole of electron = 1 mole of electron × charge of 1 electron

$= 6.023 \times 10^{23} \times 1.602 \times 10^{-19}$

$= 96500$ Columb

∴ 1 faraday = 96500 Columb

Alternatively,

One faraday is defined as the quantity of charge required to deposit or liberate one gram equivalent of any substance on the respective electrode during ~~electro~~ electrolysis.

Relationship between Electrochemical Equivalent and Chemical Equivalent

Let m_A and m_B be the mass of two elements A and B which are discharged at corresponding electrodes on passing the same amount of electricity during electrolysis.

From Faraday's first law of electrolysis:

$M_A = Z_A It$ —— (I)

$M_B = Z_B It$ —— (II)

Where Z_A and Z_B are the ECE of A and B resp.

Dividing (i) by (ii),

$$\frac{M_A}{M_B} = \frac{Z_A}{Z_B} \quad \text{—— (III)}$$

From faraday's second law of electrolysis,

$$\frac{M_A}{M_B} = \frac{E_A}{E_B} \quad \text{—— (IV)}$$

Where E_A and E_B are chemical equivalents of A and B resp.

From (iii) and (iv)

$$\frac{Z_A}{Z_B} = \frac{E_A}{E_B}$$

This shows that electrochemical equivalent (ECE) is directly proportional to chemical equivalent (E).

Relationship between Z, E and F.

As we know that 1 faraday charge (96500 C) discharge 1 gm equivalent of substance at respective electron.

There fore;

96500 C of charge discharge 1 gm. eq. of any substance

Let 1 gm eq. of any substance = E gm

96500 C charge discharge E gm of any substance

1 C charge discharge E/96500 gm of any substance.

Since the mass of substance discharged by passing 1C charge is called ECE (Z).

So, $Z = E/96500$

or $Z = E/F$

a. A current of 2.5 Amphere passes through the solution of a metal sulphate for 30 minutes and diposit 1.52 gm of metal at cathode. Find the equivalent weight of metal.

Solution:

Time (t) = 30×60 sec

= 1800 sec

Current (I) = 2.5 A

Mass (m) = 1.52 gm

From faraday's first Law

$m = ZIt$

or $m = (E/F) It$

or, $1.52 = \frac{E}{96500} \times 2.5 \times 1800$

$\therefore E = 32.59$

Hence, the equivalent weight of metal is 32.59 gm

b. How many coloumbs of electricity are required for the oxidation of one mole of H_2O to O_2?

Solution:

$2H_2O \longrightarrow O_2$ (balancing Oxygen)

$2H_2O \longrightarrow O_2 + 4H^+$ (balancing hydrogen)

$2H_2O$ (2 mole) $\longrightarrow O_2 + 4H^+ + 4e^-$ (4 mole) (balancing charge)

Here, 2 moles of H_2O = 4 moles of electrons

1 mole of H_2O = 2 moles of electrons

Now, Charge of 1 mole of electron = 96500 C

Charge of 2 mole of electron = 2×96500 C

c. How many coulombs of electric charge are required to deposit?

i. 4.6 gm of Sodium   ii. 3 mol of aluminium

Solution:

$Na^+ + e^- \longrightarrow Na$

1 mole of Na = 1 mol e^-

23 gm of Na = 1 mol e^-

4.6 gm of Na = 0.2 mol e^-

1 mol of e^- = 96500 C

0.2 mol of e^- = 19300 C

ii. $Al^{+++} + 3e^- \longrightarrow Al$

Solution:

1 mol of Al = 3 mol of e^-

3 mol of Al = 9 mol of e^-

1 mol of e^- = 96500 C

9 mol of e^- = 868500 C