Welcome to

Aakash + BYJU'S LIVE

Redox Reactions

Classical Concept of Oxidation

01 Addition of **Oxygen**

02 Removal of **Hydrogen**

03 Loss of **electron**

04 Addition of an **electronegative element**

05 Removal of an **electropositive element**

$$2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$$

$$2H_2S(g) + O_2(g) \longrightarrow 2S(s) + 2H_2O(l)$$

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$$

Classical Concept of Reduction

01 Addition of **Hydrogen**

02 Removal of **Oxygen**

03 Gain of **electron**

04 Addition of an electropositive element

05 Removal of an electronegative element

$C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$

$2HgO(s) \xrightarrow{\Delta} 2Hg(l) + O_2(g)$

$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

Oxidation Number

It is an **imaginary or apparent charge** developed over the atom of an element when it goes from its elemental **free state to combined state** in a molecule.

It is based on the assumption that a **complete transfer** of an electron takes place from a **less electronegative atom** to a **more electronegative atom**.

Concept of Oxidation

Oxidation

Process in which there is an increase in the oxidation number of the element from reactant to product in chemical reaction.

Increase in oxidation number

$$\overset{0}{H_2} + O_2 \longrightarrow \overset{+1}{2H_2O}$$

Increase in oxidation number

$$2\overset{0}{Na} + \tfrac{1}{2}O_2 \longrightarrow \overset{+1}{Na_2}O$$

Concept of Reduction

Reduction

Process in which there is a decrease in the oxidation number of the element from reactant to product in chemical reaction.

Decrease in oxidation number

$$\overset{+2}{Mg}H_2\,(s) \longrightarrow \overset{0}{Mg}\,(s) + H_2\,(g)$$

Decrease in oxidation number

$$2Na\,(s) + \frac{1}{2}\overset{0}{O_2}\,(g) \longrightarrow Na_2\overset{-2}{O}\,(s)$$

Rules for Finding Oxidation Number

For **single monatomic ions**, the oxidation number is equal to the **charge on the ion.**

O.N. of **Na^+** = **+ 1**

Examples

H^+ **Ca^{2+}** **Cl^-**

More E.N. = Negative O.N.

Less E.N. = Positive O.N.

Rules for Finding Oxidation Number

In general, the oxidation number of **halogens (F, Cl, Br, I) is – 1**

If any **halogen** atom is attached to a more electronegative atom, then it will have a **positive oxidation number.**

Fluorine is the most E.N. atom (known). It always has an oxidation number equal to **-1** in all its compounds.

Examples

Cl_2O ClF_3 HIO_4 $HClO_4$

Rules for Finding Oxidation Number

Generally, the oxidation number of **hydrogen is +1**

O.N. of **H** = **+ 1**

Examples

HCl

H_2S

H_2O

In **Metal - Hydrides**
(As metals are electropositive)

O.N. of **H** = **- 1**

Examples

LiH

NaH

CaH_2

Rules for Finding Oxidation Number

In **neutral compounds**, the sum of oxidation numbers of all the atoms of different elements is equal to **zero.**

In **complex ions or polyatomic ions**, the sum of oxidation numbers of all the atoms is equal to the **net charge on the ion**.

For elements in their **native or free state**, the oxidation number is **zero**. Example: H_2, N_2, Cl_2, Cu, Zn etc.

Rules for Finding Oxidation Number

The oxidation number of oxygen is **–2 in oxides** in most of its compounds (generally)

O.N. of **O** = – 2

Examples

H_2O

CO_2

SO_2

The oxidation number of oxygen is **–1 in Peroxides (O_2^{2-})**

Examples

H_2O_2

Na_2O_2

BaO_2

Rules for Finding Oxidation Number

The oxidation number of oxygen is
– (½) in superoxides (O_2)

Examples

KO_2

RbO_2

CsO_2

The oxidation number of **oxygen**
is +1 or +2 in oxy-fluorides depending
upon the bonding state.

Rules for Finding Oxidation Number

In their compounds, the oxidation number of alkali metal is **+1** and the oxidation number of alkaline earth metal is **+2.**

O.N. of **Na^+** = + 1

O.N. of **Mg^{2+}** = + 2

Examples

NaCl

KF

CaO

Rules for Finding Oxidation Number

Alkali Metals (1st Group)	Alkaline Earth Metals (2nd Group)
Lithium (Li)	Beryllium (Be)
Sodium (Na)	Magnesium (Mg)
Potassium (K)	Calcium (Ca)
Rubidium (Rb)	Strontium (Sr)
Caesium (Cs)	Barium (Ba)

Range of Oxidation Numbers

Generally, Oxidation Number

Maximum O.N.

=

Electrons in valence shell

Minimum O.N.

=

Electrons in valence shell - 8

Range of Oxidation Numbers

Generally, for p-block elements

$n - 18 \leq$ Oxidation number $\leq n - 10$

n: Group number of element in modern periodic table

O.S. of Some Oxygen Containing Compounds

H_2SO_5 (Peroxymonosulphuric acid)

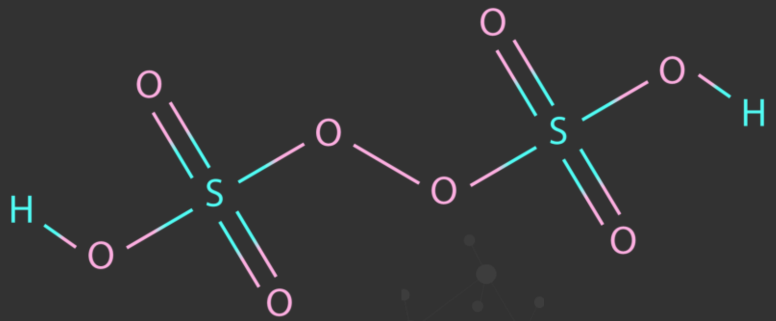
Calculated O.S.	=	8
Maximum O.S.	=	6

O.S. of Some Oxygen Containing Compounds

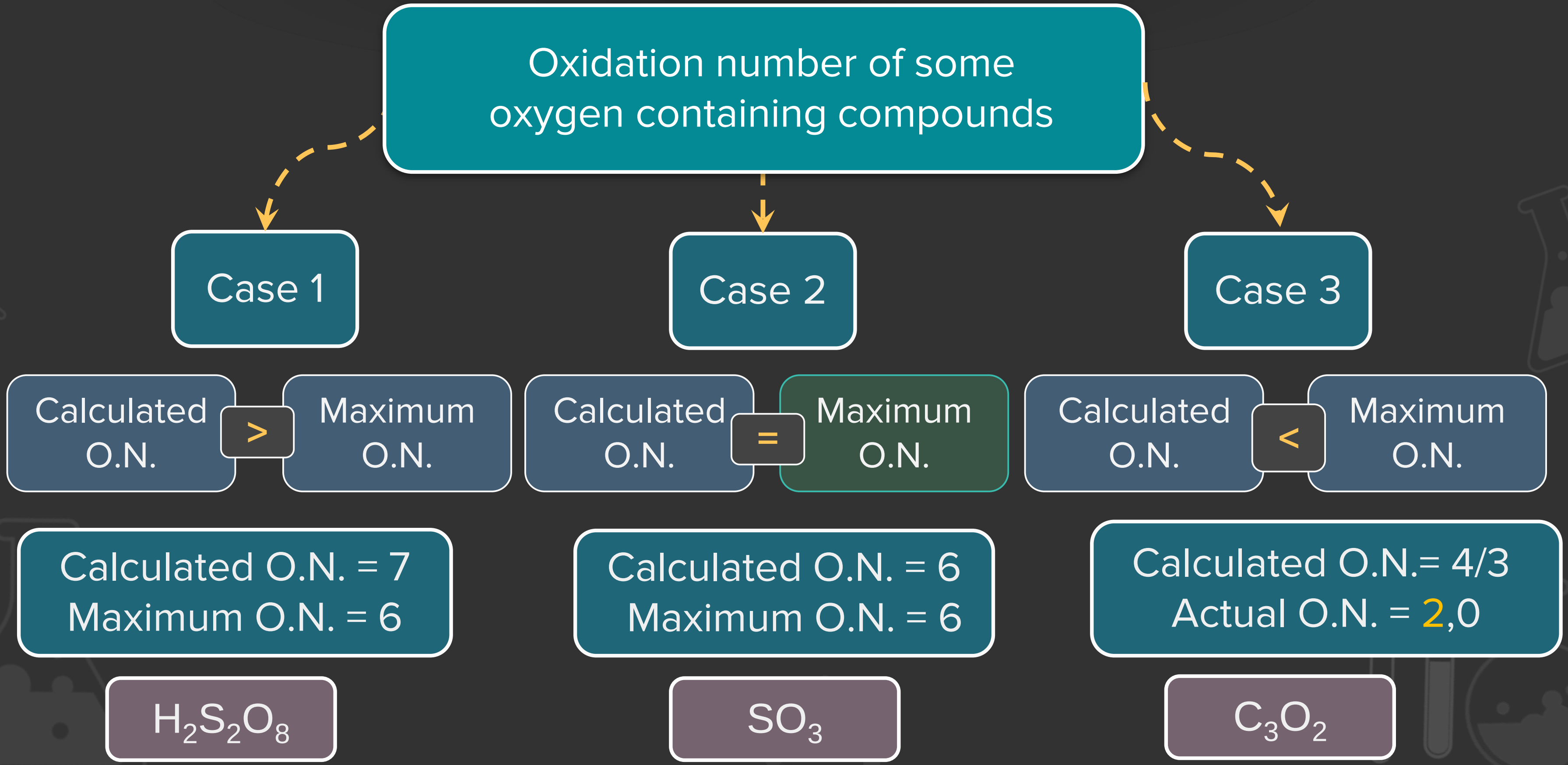
$H_2S_2O_8$

Calculated O.S. = 7

Maximum O.S. = 6



O.S. of Some Oxygen Containing Compounds



Oxidation number of some oxygen containing compounds

Case 1

Calculated O.N. > Maximum O.N.

Calculated O.N. = 7
Maximum O.N. = 6

$H_2S_2O_8$

Case 2

Calculated O.N. = Maximum O.N.

Calculated O.N. = 6
Maximum O.N. = 6

SO_3

Case 3

Calculated O.N. < Maximum O.N.

Calculated O.N.= 4/3
Actual O.N. = 2,0

C_3O_2

Paradox of Fractional Oxidation Number

In certain compounds, the oxidation number of a particular element is a **fraction** and not a whole number

The actual oxidation numbers of these elements are whole numbers, but the **average of those can be fractional.**

Paradox of Fractional Oxidation Number

C_3O_2 Carbon suboxide

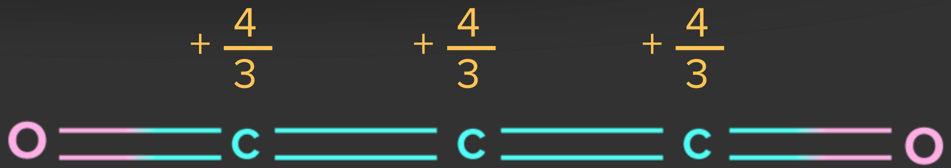
$$O=C=C=C=O$$

$$3x - 4 = 0 \Rightarrow x = \frac{4}{3}$$

Average Oxidation number of Carbon $= \frac{4}{3}$

Paradox of Fractional Oxidation Number

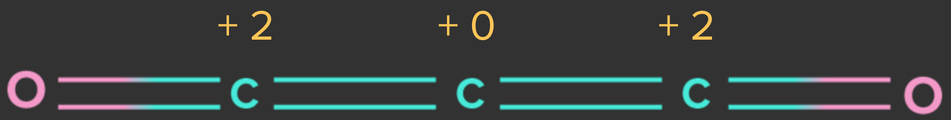
Average oxidation number of C atoms



$$O=\overset{+\frac{4}{3}}{C}=\overset{+\frac{4}{3}}{C}=\overset{+\frac{4}{3}}{C}=O$$

The actual oxidation number of the elements can be determined on the basis of the **bonds** present in their molecules.

Actual oxidation number of C atoms



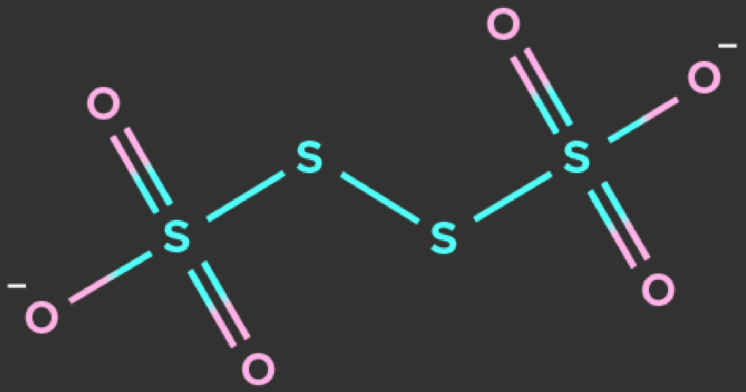
$$O=\overset{+2}{C}=\overset{+0}{C}=\overset{+2}{C}=O$$

Paradox of Fractional Oxidation Number

$(S_4O_6)^{2-}$ Tetrathionate ion

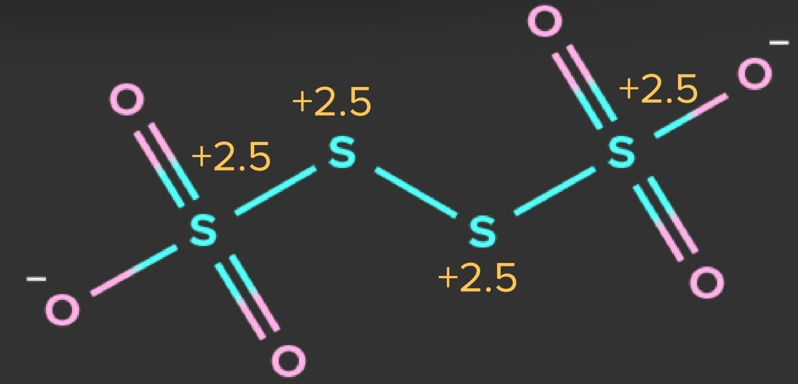
$4x - 12 = -2 \Rightarrow x = \frac{5}{2}$

Average Oxidation number of Sulphur $= \frac{5}{2}$

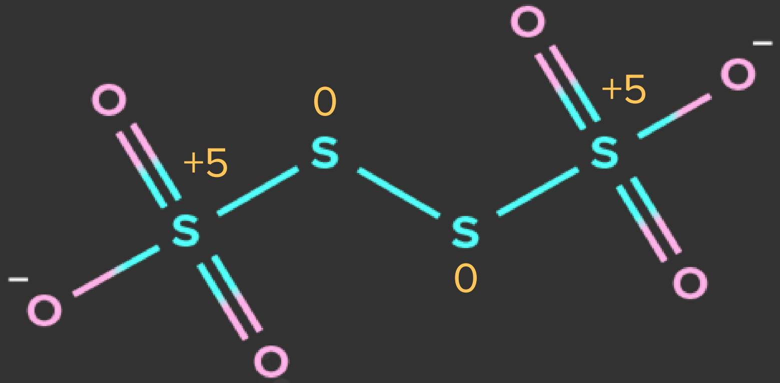


Paradox of Fractional Oxidation Number

Average oxidation number of S atoms



Actual oxidation number of S atoms



Oxidising and Reducing Agent

Oxidising Agent/Oxidant

Substance which **oxidises** others and itself gets **reduced**

Examples

$KMnO_4$, H_2O_2, $K_2Cr_2O_7$

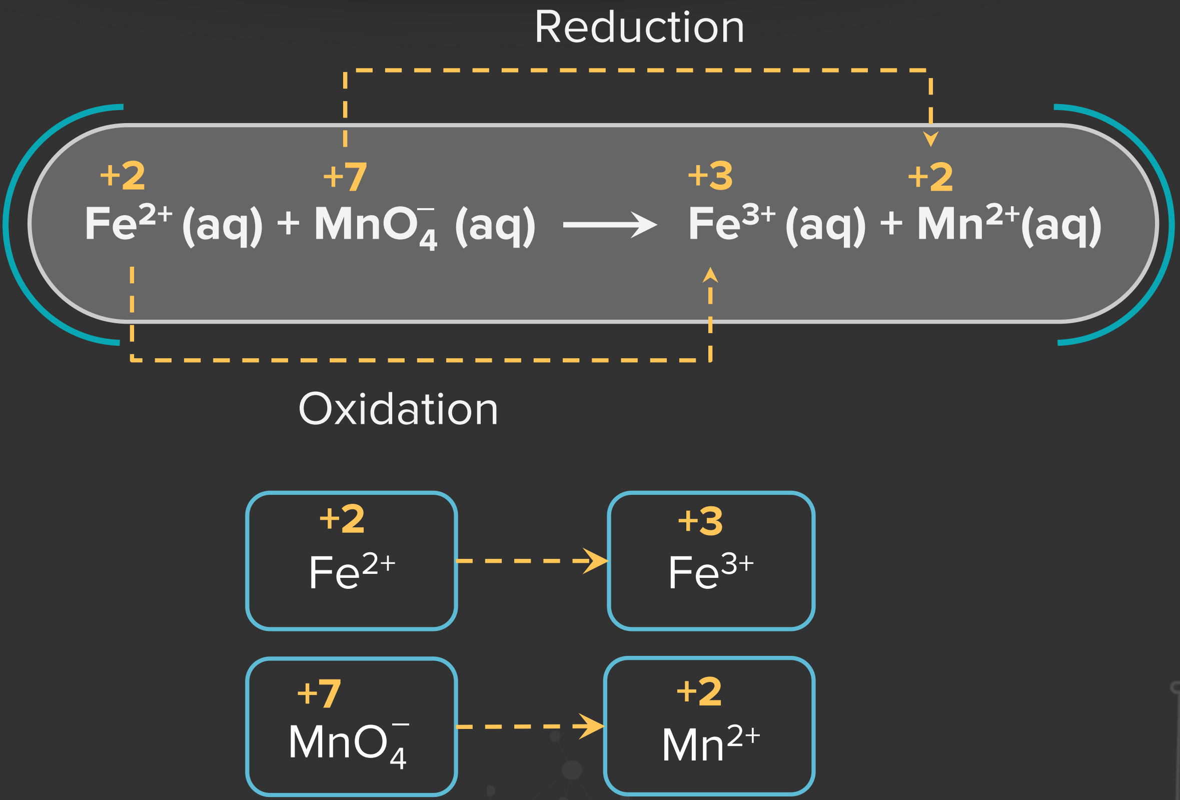
Reducing Agent/Reductant

Substance which **reduces** others and itself gets **oxidised**

Examples

$Na_2S_2O_3$, H_2O_2

Oxidising and Reducing Agent



Reduction

$$\overset{+2}{Fe^{2+}}(aq) + \overset{+7}{MnO_4^-}(aq) \longrightarrow \overset{+3}{Fe^{3+}}(aq) + \overset{+2}{Mn^{2+}}(aq)$$

Oxidation

$$\overset{+2}{Fe^{2+}} \dashrightarrow \overset{+3}{Fe^{3+}}$$

$$\overset{+7}{MnO_4^-} \dashrightarrow \overset{+2}{Mn^{2+}}$$

Redox Reactions

- Combination
- Decomposition
- Displacement
- Disproportionation
- Comproportionation

Combination Reactions

$$A + B \longrightarrow C$$

$$C\ (s) + O_2\ (g) \longrightarrow CO_2\ (g)$$

$$CH_4\ (g) + 2O_2\ (g) \longrightarrow CO_2\ (g) + 2H_2O\ (l)$$

Decomposition Reactions

$$C \longrightarrow A + B$$

$$2\ H_2O\ (l) \longrightarrow 2H_2\ (g) + O_2\ (g)$$

Displacement Reactions

$$X + YZ \longrightarrow XZ + Y$$

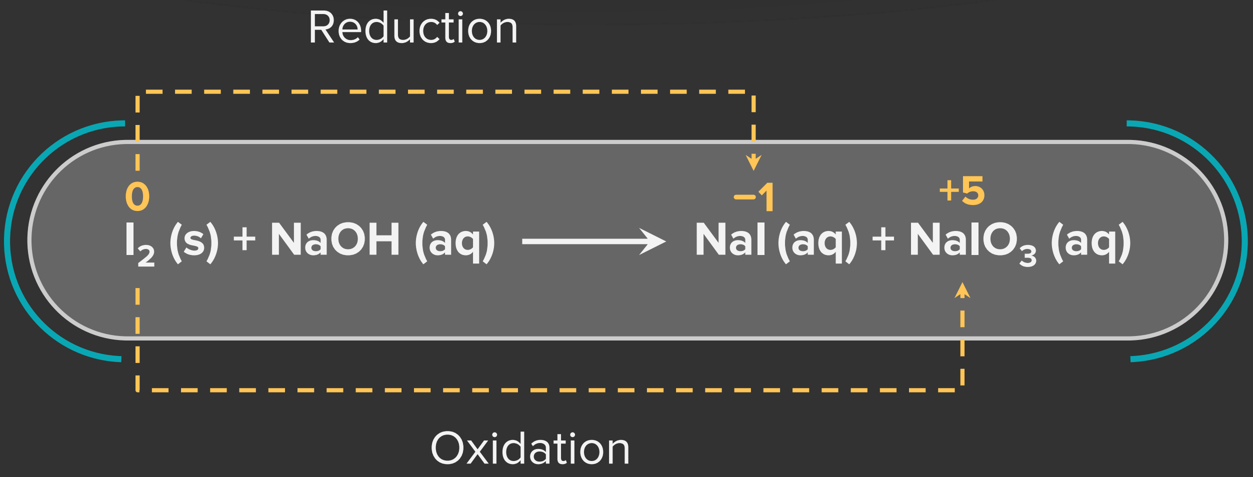
$$Cu\,(s) + 2\,AgNO_3\,(aq) \longrightarrow 2\,Ag\,(s) + Cu(NO_3)_2\,(aq)$$

$$Na\,(s) + 2\,H_2O\,(l) \longrightarrow 2\,NaOH\,(aq) + H_2\,(g)$$

Disproportionation Reactions

The redox reaction in which **an element** from the same oxidation state **changes to two different oxidation states** (one lower and other higher)

Disproportionation Reactions



Reduction

$$\overset{0}{I_2}\,(s) + NaOH\,(aq) \longrightarrow Na\overset{-1}{I}\,(aq) + Na\overset{+5}{I}O_3\,(aq)$$

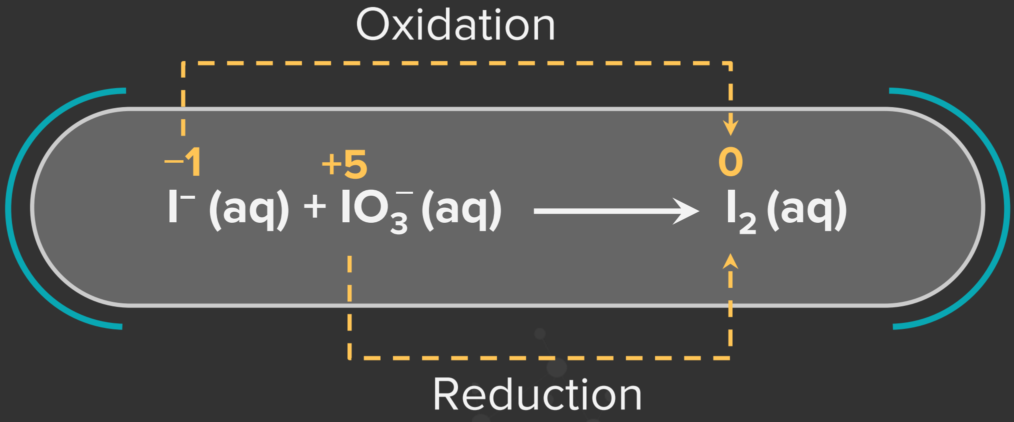
Oxidation

This reaction involves the change in oxidation state of I from **(0)** to **higher (+5)** and **lower (−1) O.S**

Comproportionation Redox Reaction

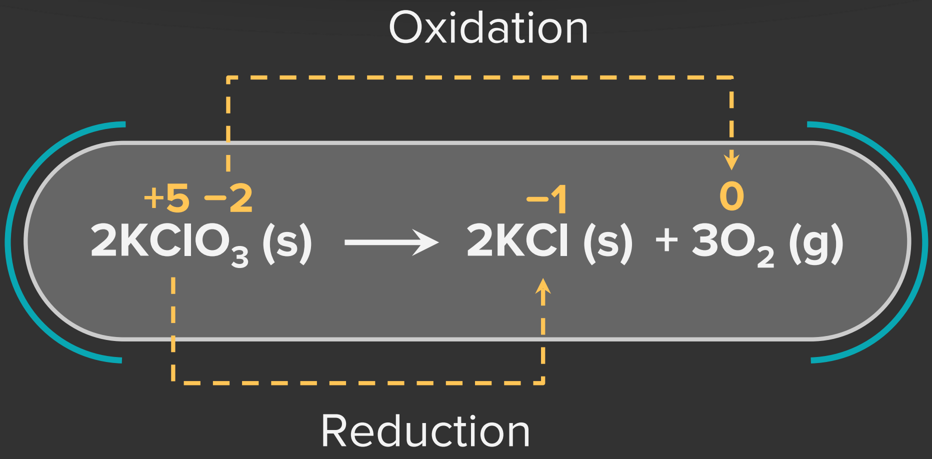
The redox reaction in which an **element from two different oxidation states** (one lower and other higher) changes to the **same oxidation state**

It is **reverse of disproportionation**.



$$\overset{-1}{I^-}(aq) + \overset{+5}{IO_3^-}(aq) \longrightarrow \overset{0}{I_2}(aq)$$

Intramolecular Redox Reaction

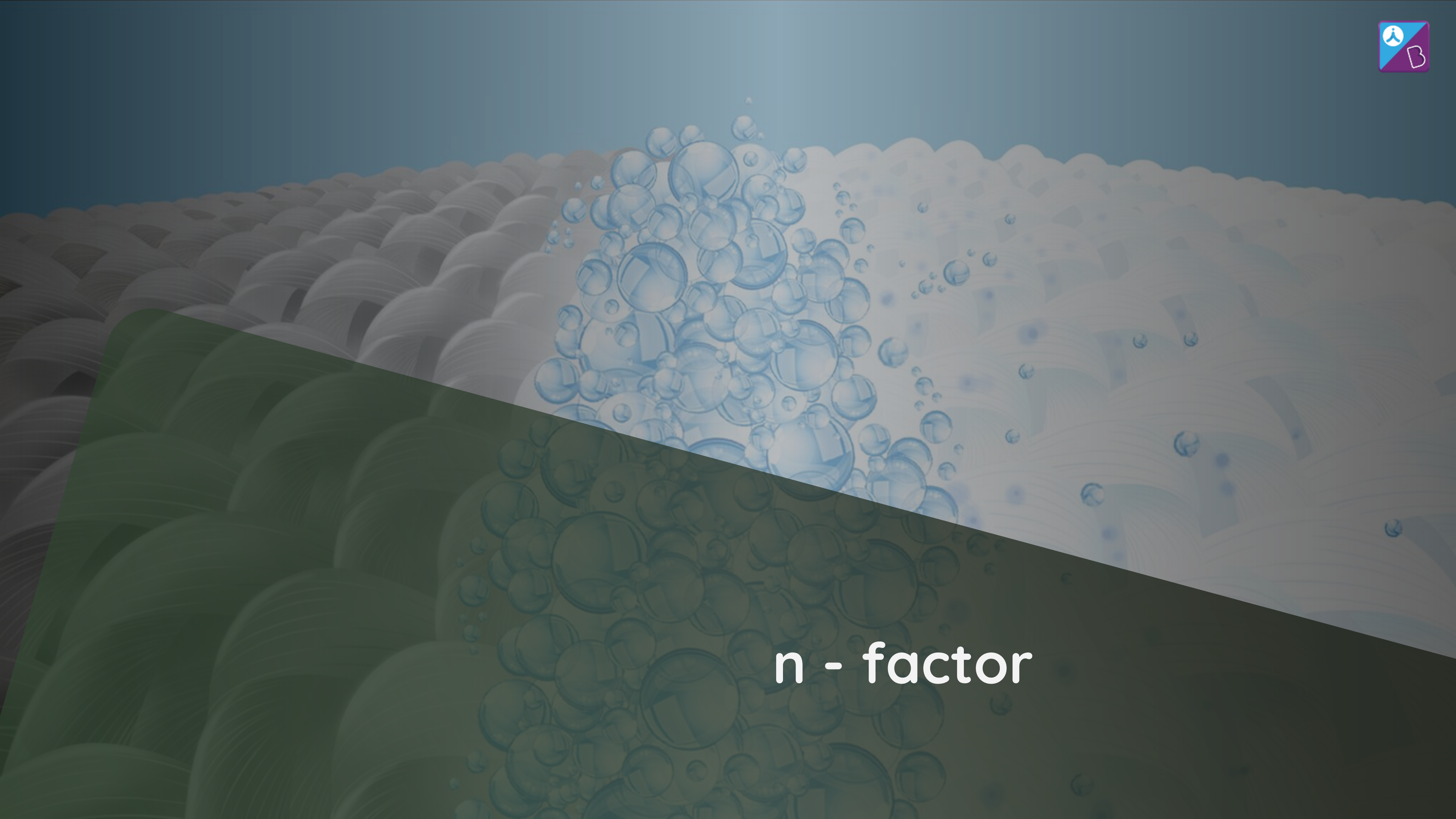


Oxidation

$$2K\overset{+5}{Cl}\overset{-2}{O_3}\,(s) \longrightarrow 2K\overset{-1}{Cl}\,(s) + 3\overset{0}{O_2}\,(g)$$

Reduction

In this case, **oxidation and reduction** takes place through a single molecule



n - factor

n-Factor

It is defined as the **change in oxidation state** per molecule. It is also known as **valence factor.**

$H_2SO_3 \longrightarrow H_2SO_4$

Step 1

● ○ ○

Find the oxidation state of the element on the **reactant and the product side** which changes its oxidation state in the reaction

$$H_2\overset{+4}{S}O_3 \longrightarrow H_2\overset{+6}{S}O_4$$

Step 2

● ● ○

Find the **difference** in oxidation states and take its **magnitude.**

$$6 - 4 = |2|$$

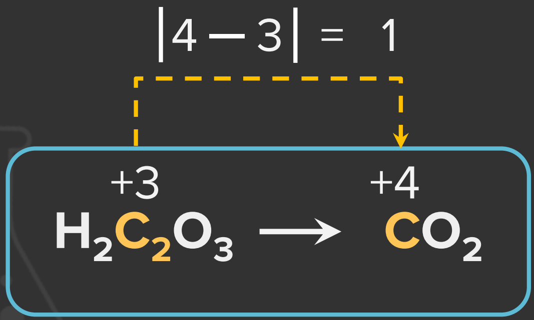
$$H_2\overset{+4}{S}O_3 \longrightarrow H_2\overset{+6}{S}O_4$$

Step 3

If the **number of atoms** of an element is **different** between the reactant and the product side, **balance them**.

Step 4

Then the balanced number should be **multiplied** with the **difference** in **oxidation state** to calculate the **n_f**.



$$|4 - 3| = 1$$

$$\overset{+3}{H_2C_2O_3} \longrightarrow \overset{+4}{CO_2}$$

n_f for $H_2C_2O_3$ ⇒ 2×1

⇒ 2

Calculation of n_f for different Species

1 For Ions

$$n_f = |\text{Charge}|$$

$Na^+ \Rightarrow n_f = 1$

$SO_4^{2-} \Rightarrow n_f = 2$

2 For Salts

$NaCl \Rightarrow n_f = 1 \Leftarrow Na^+, Cl^-$

$Al_2(SO_4)_3 \Rightarrow n_f = 6 \Leftarrow Al^{3+}, SO_4^{2-}$

Calculation of n_f for different Species

3 For Acids

n_f = Basicity

Number of H^+ ions an acid donates

Oxy Acids of Phosphorus

$H_3PO_4 \Rightarrow n_f = 3$ 3 –OH bond

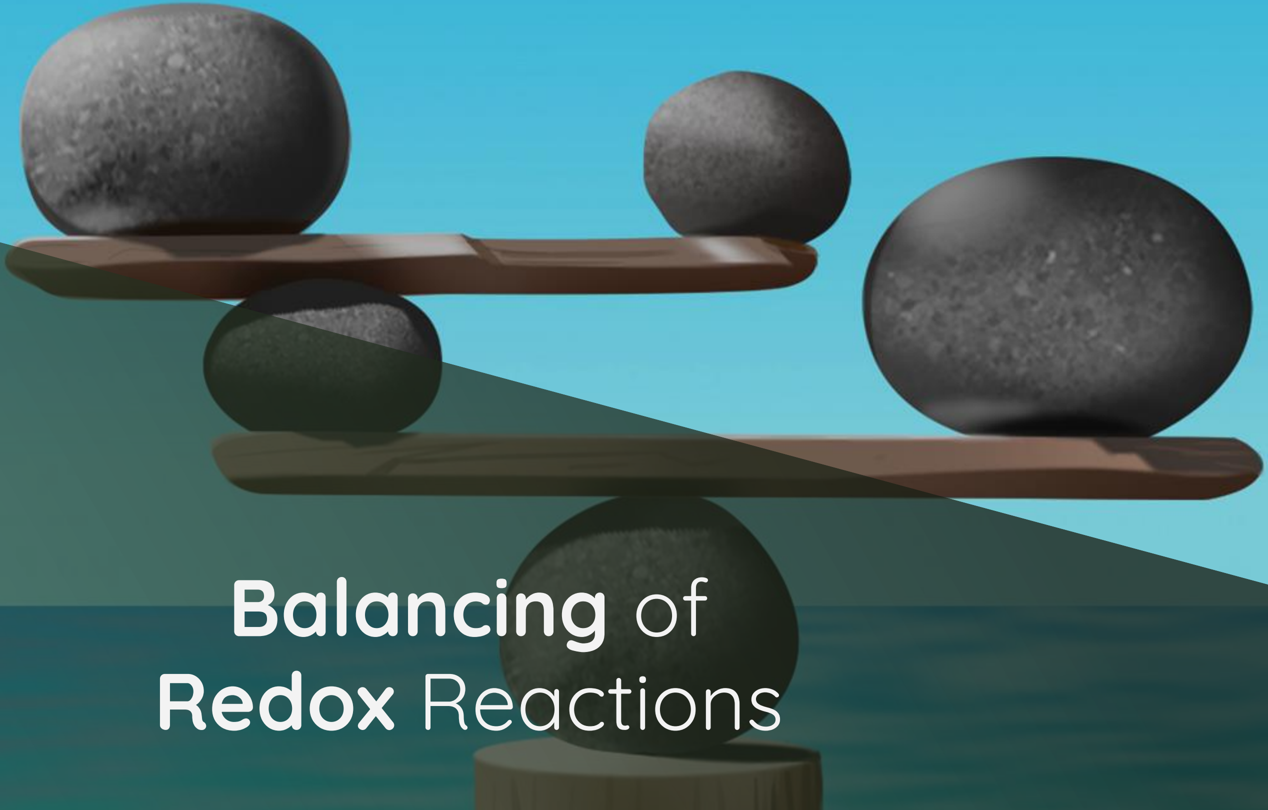
$H_3PO_3 \Rightarrow n_f = 2$ 2 –OH bond

$H_3PO_2 \Rightarrow n_f = 1$ 1 –OH bond

Remember!!!

n_f can't be **zero** or **negative**

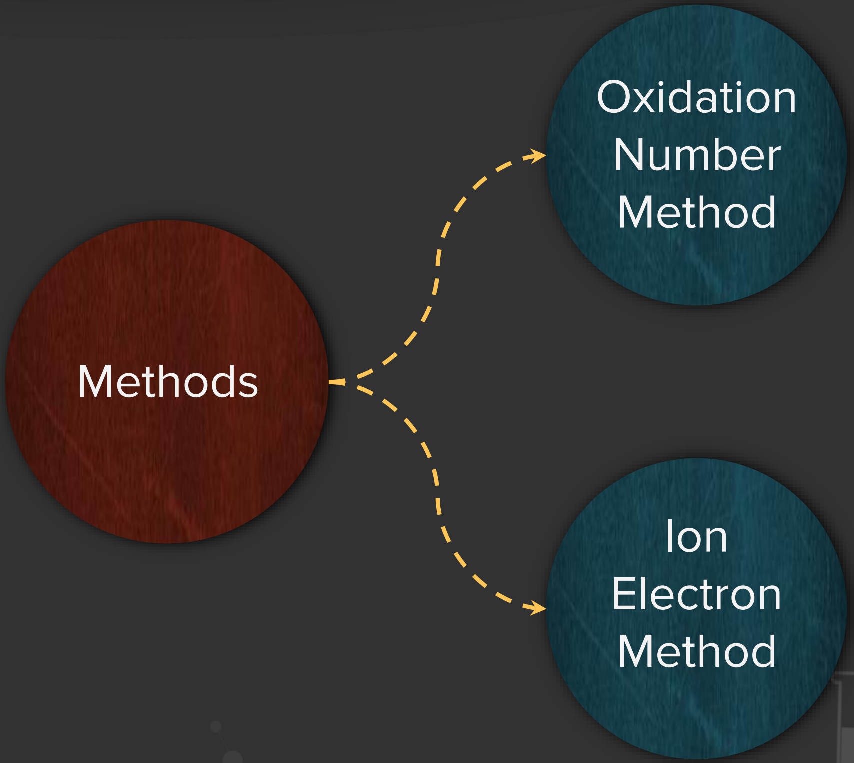
n_f can be a **fraction!**



Balancing of
Redox Reactions

Balancing of Redox Reactions

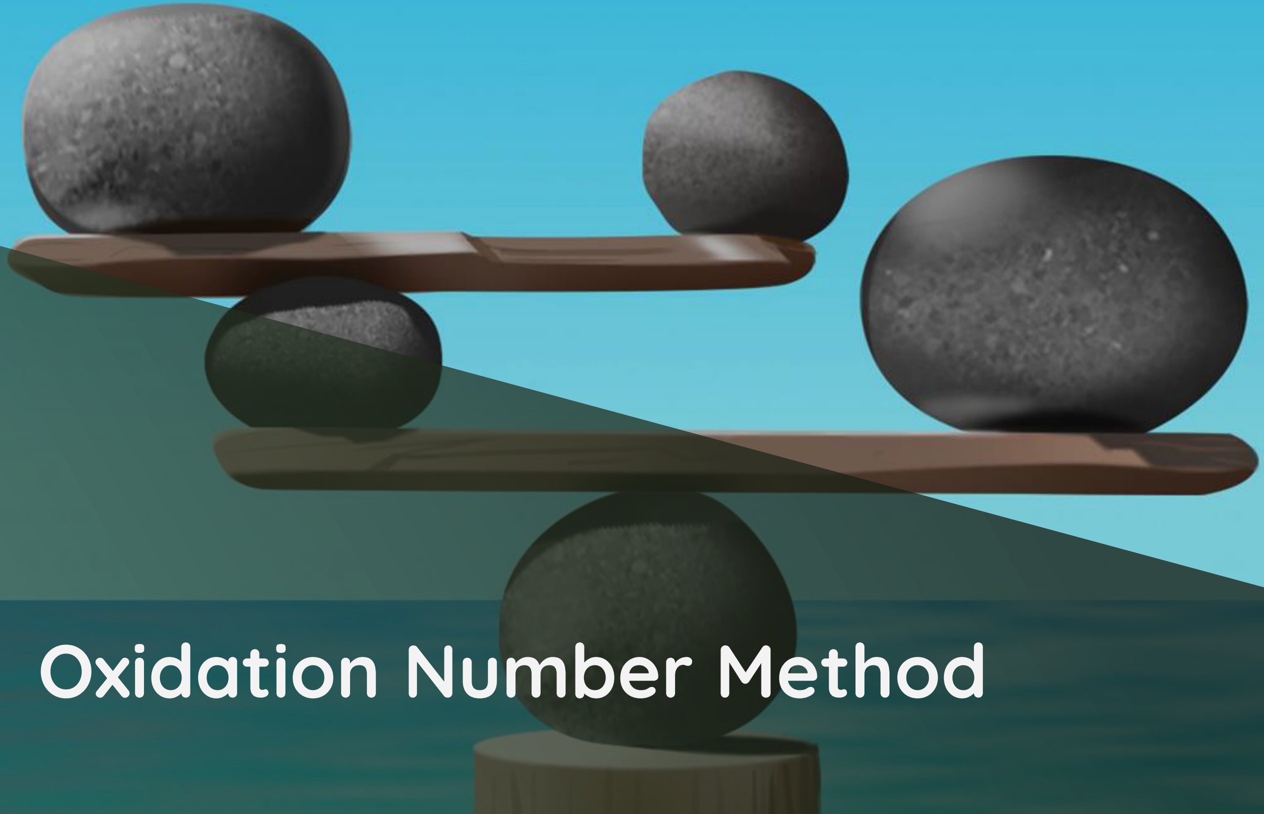
1. Atom Balance
2. Charge Balance



Methods

Oxidation Number Method

Ion Electron Method



Oxidation Number Method

Balancing of Redox Reactions

Generally balancing is carried out in 2 media

Acidic medium

(H^+/H_2O)

Basic medium

(OH^-/H_2O)

Oxidation Number Method

Example $MnO_4^- (aq) + Fe^{2+} (aq) \longrightarrow Mn^{2+} (aq) + Fe^{3+} (aq)$

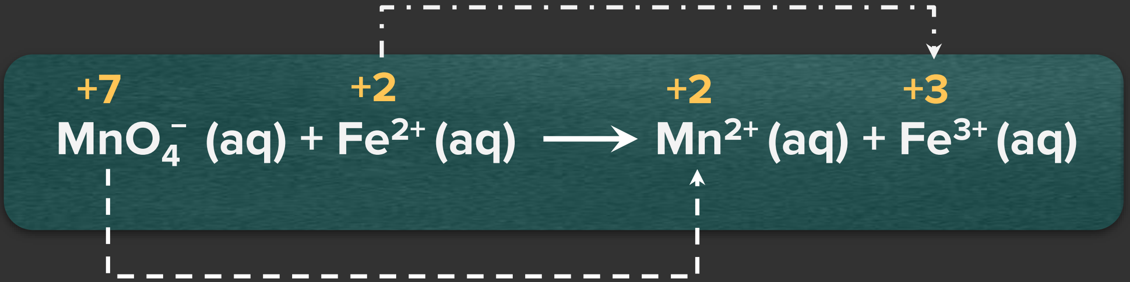
Step 1

● ○ ○ ○ ○

Identifying the oxidizing/reducing agent

Oxidation Number Method

Oxidation Number
increases by **1 unit** - - - → **Oxidation**



$$\overset{+7}{MnO_4^-}\ (aq) + \overset{+2}{Fe^{2+}}\ (aq) \longrightarrow \overset{+2}{Mn^{2+}}\ (aq) + \overset{+3}{Fe^{3+}}\ (aq)$$

Oxidation Number
decreases by **5 units** - - - → **Reduction**

MnO_4^- is the oxidising agent and
Fe^{2+} is the reducing agent

Oxidation Number Method

Step 2

○ ● ○ ○ ○

Finding the n_f

$$\overset{+7}{\mathrm{MnO_4^-}}\,(aq) + \overset{+2}{\mathrm{Fe^{2+}}}\,(aq) \longrightarrow \overset{+2}{\mathrm{Mn^{2+}}}\,(aq) + \overset{+3}{\mathrm{Fe^{3+}}}\,(aq)$$

$$n_f \text{ of } \mathrm{MnO_4^-} = \left|(7 - 2) \times 1\right| = 5$$

$$n_f \text{ of } \mathrm{Fe^{2+}} = \left|(2 - 3) \times 1\right| = 1$$

Oxidation Number Method

Step 3

○ ○ ● ○ ○

Equalising the decrease/increase in oxidation number

$$\mathbf{1}MnO_4^- (aq) + \mathbf{5}Fe^{2+} (aq) \longrightarrow Mn^{2+} (aq) + Fe^{3+} (aq)$$

Cross multiply the **Oxidising** and the **Reducing Agents** by **1** (n_f of R.A.) and **5** (n_f of O.A.) respectively on the reactant side.

Oxidation Number Method

Step 4

○ ○ ○ ● ○

Balancing the elements

Balance all the atoms **except O** and **H**, without changing the stoichiometric coefficients on the reactant side

$$MnO_4^{-}\,(aq) + 5Fe^{2+}\,(aq) \longrightarrow Mn^{2+}\,(aq) + 5Fe^{3+}\,(aq)$$

Oxidation Number Method

Step 5

○ ○ ○ ○ ●

Balancing the O atoms

Balance the O atoms by adding H_2O

$$MnO_4^{-}\,(aq) + 5Fe^{2+}\,(aq) \longrightarrow Mn^{2+}\,(aq) + 5Fe^{3+}\,(aq) + 4H_2O\,(l)$$

For an Acidic Medium

As soon as we add **H_2O**, we add twice the **H^+ ions** on the opposite side.

$$xH_2O \longrightarrow 2xH^+$$

For an Acidic Medium

$$MnO_4^- (aq) + 5Fe^{2+} (aq) + 8H^+ (aq) \longrightarrow Mn^{2+} (aq) + 5Fe^{3+} (aq) + 4H_2O (l)$$

Charge on the reactant side

$= [\ 1 \times (-1) + 5 \times (+2) + 8 \times (+1)\ ] = \mathbf{+17}$

Charge on the product side

$= [1 \times (+2) + 5 \times (+3) + 4 \times (0)] = \mathbf{+17}$

For a Basic Medium

Example

$ClO^{-}(aq) + CrO_2^{-}(aq) + OH^{-}(aq) \longrightarrow Cl^{-}(aq) + CrO_4^{2-}(aq) + H_2O(l)$

Balance the whole reaction as in an acidic medium

$3ClO^{-}(aq) + 2CrO_2^{-}(aq) + H_2O(l) \longrightarrow 3Cl^{-}(aq) + 2CrO_4^{2-}(aq) + 2H^{+}(aq)$

For a Basic Medium

Add to both sides the same number of **OH^-** as there are **H^+**

$$3ClO^- + 2CrO_2^- + H_2O\ (l) + 2OH^- \longrightarrow 3Cl^-\ (aq) + 2CrO_4^{2-} + 2H^+ + 2OH^-$$

Combine **H^+** and **OH^-** to form **H_2O**

$$3ClO^-(aq) + 2CrO_2^-(aq) + H_2O\ (l) + 2OH^-(aq) \longrightarrow 3Cl^-\ (aq) + 2CrO_4^{2-}(aq) + 2H_2O(l)$$

For a Basic Medium

Cancel any H_2O that you can

$$3ClO^{-}(aq) + 2CrO_2^{-}(aq) + 2OH^{-}(aq) \longrightarrow 3Cl^{-}(aq) + 2CrO_4^{2-}(aq) + H_2O(l)$$

Charge on reactant side = –7

Charge on product side = –7

Since the charges on both the sides are the same, this equation is **overall perfectly balanced.**

Equivalent Mass

Equivalent mass
Or
Gram Eq. mass

$$= \frac{\textbf{Molar Mass}}{\textbf{n - factor}}$$

Number of parts by mass of an element which reacts or displaces from a compound **1.008** parts by mass of **hydrogen**, **8** parts by mass of **oxygen** and **35.5** parts by mass of **chlorine**, is known as the equivalent mass of that element.

Earlier it was expressed by taking **hydrogen, oxygen, chlorine** and **silver** as the reference elements.

Number of Gram Equivalents

$$\text{No. of Gram Eq.} = \frac{\text{Given Mass}}{\text{Gram Equivalent Mass}}$$

$$= \frac{\text{Given Mass}}{\text{Molar Mass}/n_f}$$

$$= \frac{\text{Given Mass}}{\text{Molar Mass}} \times n_f$$

$$= \text{Moles} \times n_f$$

Normality

Number of **gram equivalent** of solute present in **1 litre** of the solution

$$\text{Normality} = \frac{\text{Number of gram equivalents of solute}}{\text{Volume of the solution (L)}}$$

$$= \frac{\text{Number of moles of solute}}{\text{Volume of the solution (L)}} \times n_f$$

$$= \text{Molarity} \times n_f$$

Law of Equivalence

The law states that one equivalent of an element always **combines with** one equivalent of the other.

In a chemical reaction, equivalents or milliequivalents of the reactants **react in equal amount** to **give the same number of equivalents** or milliequivalents of the products separately.

$$n_1 A + n_2 B \longrightarrow n_3 C + n_4 D$$

Eq. of A = Eq. of B = Eq. of C = Eq. of D

Recall !!!

Equivalence point is the point where:

No. of equivalent of the **analyte** = No. of equivalent of the **titrant**

- Analyte: Solution with unknown concentration
- Titrant: Solution with known concentration

In this titration, one oxidizing agent (O.A.) reacts with one reducing agent (R.A.)

O.A. + R.A. ⟶ Products

Redox Titration

At the equivalence point

Equivalence of **O.A.** = Equivalence of **R.A**

$$N_1V_1 = N_2V_2$$

N_1 and V_1= Normality and Volume of the Analyte Respectively

N_2 and V_2= Normality and Volume of the titrant Respectively

Titration using Potassium Permanganate

Strong Oxidizing Agent

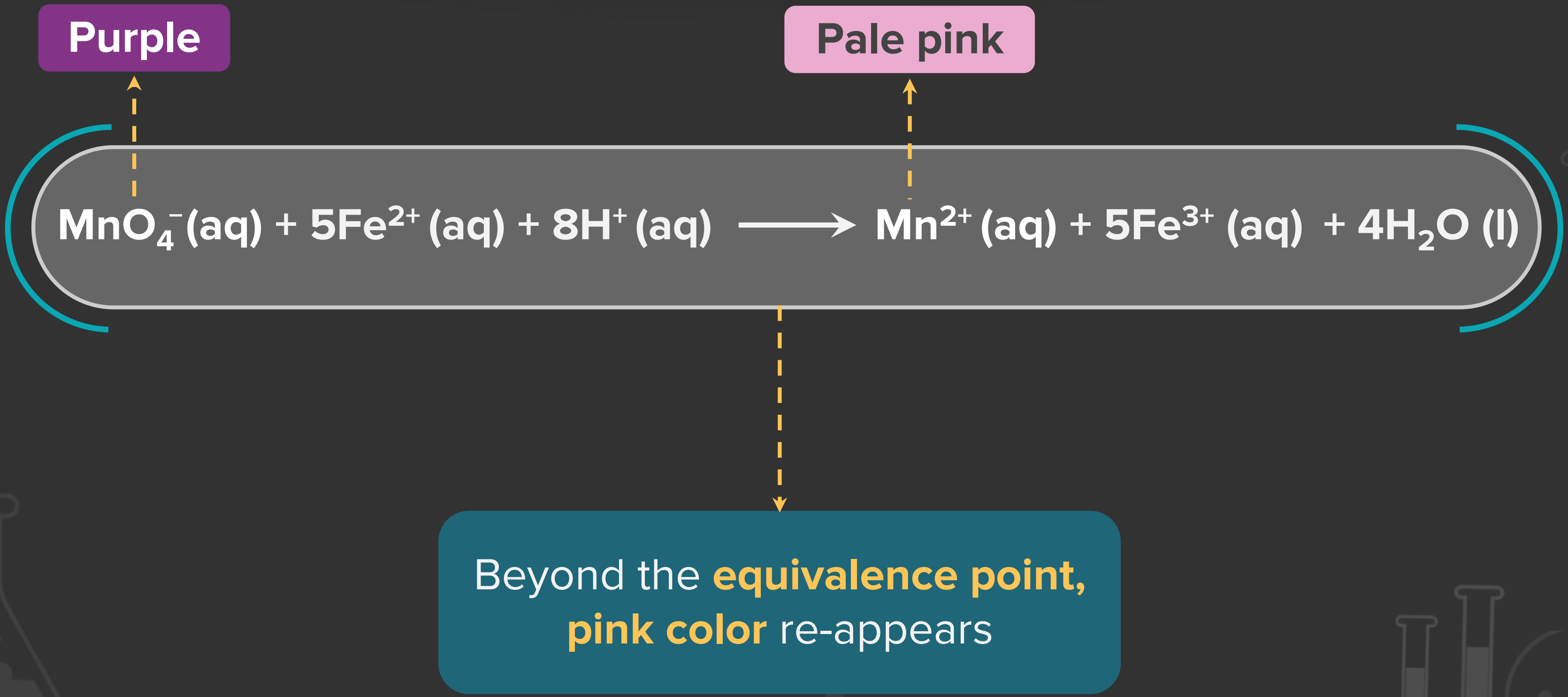
Acts in both acidic as well as basic medium

Self Indicator

For acidification, H_2SO_4 is generally used.

Use of HCl is avoided as $KMnO_4$ oxidises HCl to Cl_2 gas.

Titration using Potassium Permanganate



Purple

Pale pink

$$MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \longrightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$$

Beyond the **equivalence point, pink color** re-appears

Titration Using Potassium Dichromate

Oxidizing agent only in acidic medium

External redox indicators are used in titrations.

Example : Diphenylamine, Potassium Ferricyanide

For acidification, H_2SO_4 and HCl can be used as $K_2Cr_2O_7$ does not oxidize HCl at room temperature.

$K_2Cr_2O_7$ is less powerful oxidizing agent than $KMnO_4$.

Titration Using Potassium Dichromate

$$Cr_2O_7^{2-}\,(aq) + 14H^+\,(aq) + 6e^- \longrightarrow 2Cr^{3+}\,(aq) + 7H_2O\,(l)$$

Orange

$K_2Cr_2O_7$ **oxidises the diphenylamine indicator** just after the equivalence point giving **intense blue colour** indicating the **end point.**

Back Titration

Reaction 1

$$Z + X\ (\text{Excess}) \longrightarrow \text{Product 1}$$

Reaction 2

$$X\ (\text{Remaining}) + Y \longrightarrow \text{Product 2}$$

Back Titration

The substance or solution of **unknown concentration** (1) is made to react with **known volume and concentration** of intermediate reactant solution (2).

4 gm of contaminated chalk, $CaCO_3$ + 200 ml, 0.5N HCl

(1) **(2)**

Back Titration

The reaction goes past the equivalence point.

The amount of intermediate reactant is in excess of that required for completing reaction with analyte.

After completing the reaction with analyte, the resulting solution containing excess of intermediate reactant is titrated with known volume and concentration of titrant

Let us assume

50 ml of 0.5N NaOH

Back Titration

$N_1V_1 = N_2V_2$

$0.5 \times V_1 = 0.5 \times 50$

- N_1 and V_1 are normality and volume of intermediate reactant
- N_2 and V_2 are normality and volume of titrant

Volume of excess HCl, V_1 = 50 mL

m.eq. of excess HCl = m.eq. of titrant (NaOH)

= 0.5×50 = 25 m.eq.

Back Titration

Determination of excess volume or excess m.eq. of intermediate reactant allows us to determine the volume or m.eq. of intermediate reactant which reacted with analyte

m.eq. of Chalk = Total m.eq. of HCl − m.eq. of excess HCl

m.eq. of Chalk = (0.5 × 200) − 25

Back Titration

m.eq. of Chalk = m.eq. of HCl used for chalk = 75

$$\frac{\text{Mass of chalk}}{E} \times 1000 = \frac{\text{Mass of chalk} \times 1000}{50} = 75$$

Mass of chalk = 3.75 g

This means chalk contained **0.25 gm** of impurities in it.

Double Indicator Titration

$NaOH$

Na_2CO_3

$NaHCO_3$

Reaction 1

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

Reaction 2

$$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + H_2O$$

Reaction 3

$$NaHCO_3 + HCl \longrightarrow H_2CO_3 + H_2O$$

Double Indicator Titration

Suitable indicator is employed to identify completion of individual reaction.

The indicator is selected based on the range of pH change at equivalence volume of the titrant.

Indicator	Color Transition Range
Phenolphthalein (HPh)	8.3 – 10
Methyl Orange (MeOH)	3.2 – 4.4

Double Indicator Titration

The reaction is completed in two stages.
The first stage reaction is :

$$Na_2CO_3\,(aq) + HCl\,(aq) \longrightarrow NaCl\,(aq) + NaHCO_3\,(aq)$$

Titrant

Intermediate
Product
(Basic Salt)

It means that pH value
remains above 7.

Double Indicator Titration

The second stage reaction is :

$$NaHCO_3\,(aq) + HCl\,(aq) \longrightarrow NaCl\,(aq) + CO_2\,(g) + H_2O\,(l)$$

Acidic

pH of the solution further goes down.

Remeber !!!

Neutralization of sodium bicarbonate is detected by methyl orange - not by phenolphthalein.

Double Indicator Titration

m.eq. of HCl = m.eq. of NaOH + m.eq. of Na_2CO_3 + meq. of $NaHCO_3$

Indicator - Methyl Orange

m.eq. of HCl = **m.eq. of NaOH + m.eq. of Na_2CO_3**

Indicator - Phenolphthalein

Iodometric Titration

Iodometric titration is carried out in two steps

This titration is used to determine the strength or the concentration of an oxidising agent.

Step 1

$n_f = 2$

$$\overset{-1}{I^-}(aq) + O.A \longrightarrow \overset{0}{I_2}(g) + \text{Product}$$

unknown

Oxidising agent oxidises I^- to I_2

Eq. of oxidising agent = Eq. of I_2

The iodine liberated is then titrated with standard hypo solution ($Na_2S_2O_3$)

Step 2

$n_f = 2$

$$\overset{0}{I_2}(g) + S_2O_3^{2-}(aq) \longrightarrow \overset{-1}{I^-}(aq) + S_4O_6^{2-}(aq)$$

$$\boxed{\text{Eq. of } I_2 = \text{Eq. of } S_2O_3^{2-}}$$

In both the cases, the n-factor of I_2 is the same

$$\boxed{\text{Eq. of O.A.} = \text{Eq. of } I_2 = \text{Eq. of } S_2O_3^{2-}}$$

Iodimetric Titration

Iodimetric titration is carried out in a single step

It is used to determine the strength or the concentration of a reducing agent, which is directly titrated with I_2

Iodimetric Titration

$$\underset{\text{unknown}}{I_2\,(g) + R.A} \longrightarrow I^-\,(aq) + \text{Product}$$

Both iodometric and iodimetric titrations are carried out in an acidic medium only, as I_2 will undergo disproportion reaction in basic medium.

$$I^-\,(aq) + OH^-\,(aq) \longrightarrow I_2\,(g) + IO_3^-\,(aq)$$

H_2O_2

H_2O_2 as **reducing** agent.

Acidic Medium

$$H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$$

Basic Medium

$$H_2O_2 + 2OH^- \longrightarrow O_2 + 2H_2O + 2e^-$$

H_2O_2 as **oxidising** agent.

Acidic Medium

$$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$$

Basic Medium

$$H_2O_2 + 2e^- \longrightarrow 2OH^-$$

Volume Strength of H_2O_2

Decompostion of H_2O_2 :

$$2H_2O_2\,(aq) \longrightarrow 2H_2O\,(l) + O_2\,(g)$$

The concentration of H_2O_2 is usually represented in term of volume (vol).

If a sample of H_2O_2 is labelled as **'x V'**, it means that 1 vol of H_2O_2 solution gives **x vol** of O_2 gas at STP on complete decomposition

Volume Strength of H_2O_2

= **N × 5.6**

= **M × 11.2**

Redox Reactions in Electrochemistry

Electrochemistry

The area of chemistry concerned with the interconversion of chemical energy and electrical energy.

Let's define some basic terms in Electrochemistry like Electrode , Electrode potential etc.

Electrodes

In order to pass the current through an electrolytic solution **two rods or plates** (metallic conductors) are always needed which are **connected** with the **terminals of a battery**. These rods are known as electrodes.

Types of Electrodes

Based on the tendency to get oxidised or reduced

Anode

The electrode through which the **electron leaves** the electrolytic solution (**positive electrode**).

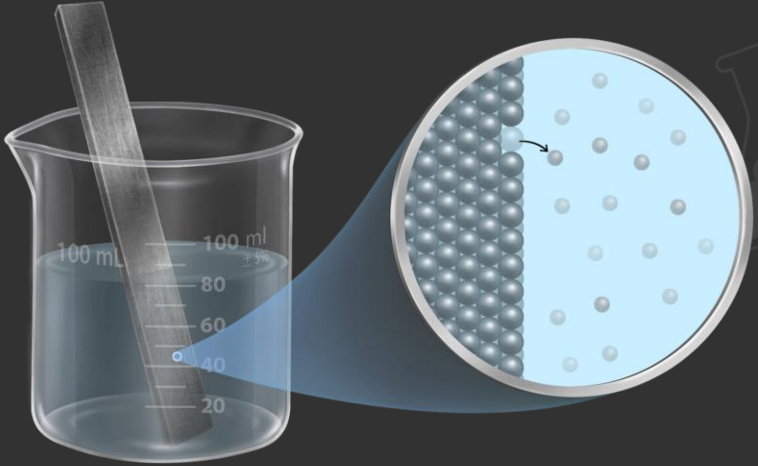
Cathode

The electrode through which the **electron enter** the electrolytic solution (**negative electrode**).

Electrolyte

The substances whose aqueous solution **allow** the passage of **electric current** and is chemically decomposed into ions, are termed **electrolytes**.

$$Zn\ (s) \rightleftharpoons Zn^{2+}\ (aq) + 2e^{-}$$



Electrode Potential

The **potential difference** developed between an **electrode** and an **electrolyte** in a solution.

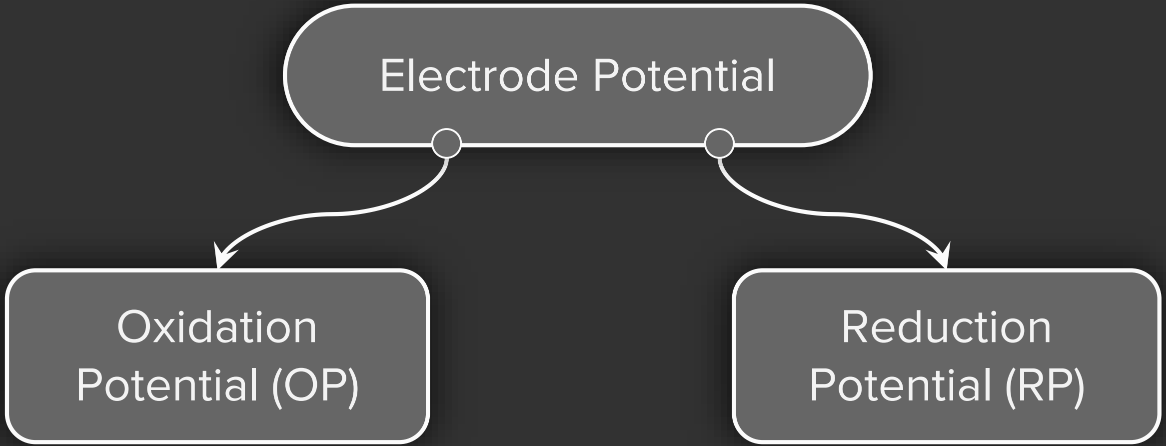
Unit: Volt

Standard Electrode Potential

Potential difference developed between **metal electrodes** and the **solution of its ions** at **1 M concentration** at **1 bar pressure** and at a particular temperature.

By convention, Standard electrode potential of hydrogen electrode = 0.00 volts

Types of Electrode Potential



Electrode Potential

Oxidation Potential (OP)

Reduction Potential (RP)

Oxidation Potential

Electrode potential for **oxidation half** reaction

$M\ (s) \longrightarrow M^{n+}\ (aq) + ne^{-}$

Termed as negative electrode

Shorthand notation

$E_{M(s)\ /\ M^{n+}(aq)}$

Under standard conditions

Indicates standard state

$E^{0}_{M(s)\ /\ M^{n+}(aq)}$

Standard Oxidation Potential (SOP)

Example of Oxidation Potential

$H_2O_2 \rightleftharpoons O_2 + 2H^+ + 2e^-$

Oxidation half

Representation

$E^{o}_{H_2O_2\,/\,O_2}$

$Cu\,(s) \rightleftharpoons Cu^{2+}\,(aq) + 2e^-$

Oxidation half

Representation

$E^{o}_{Cu(s)\,/\,Cu^{2+}(aq)} = -0.34\ V$

Example of Oxidation Potential

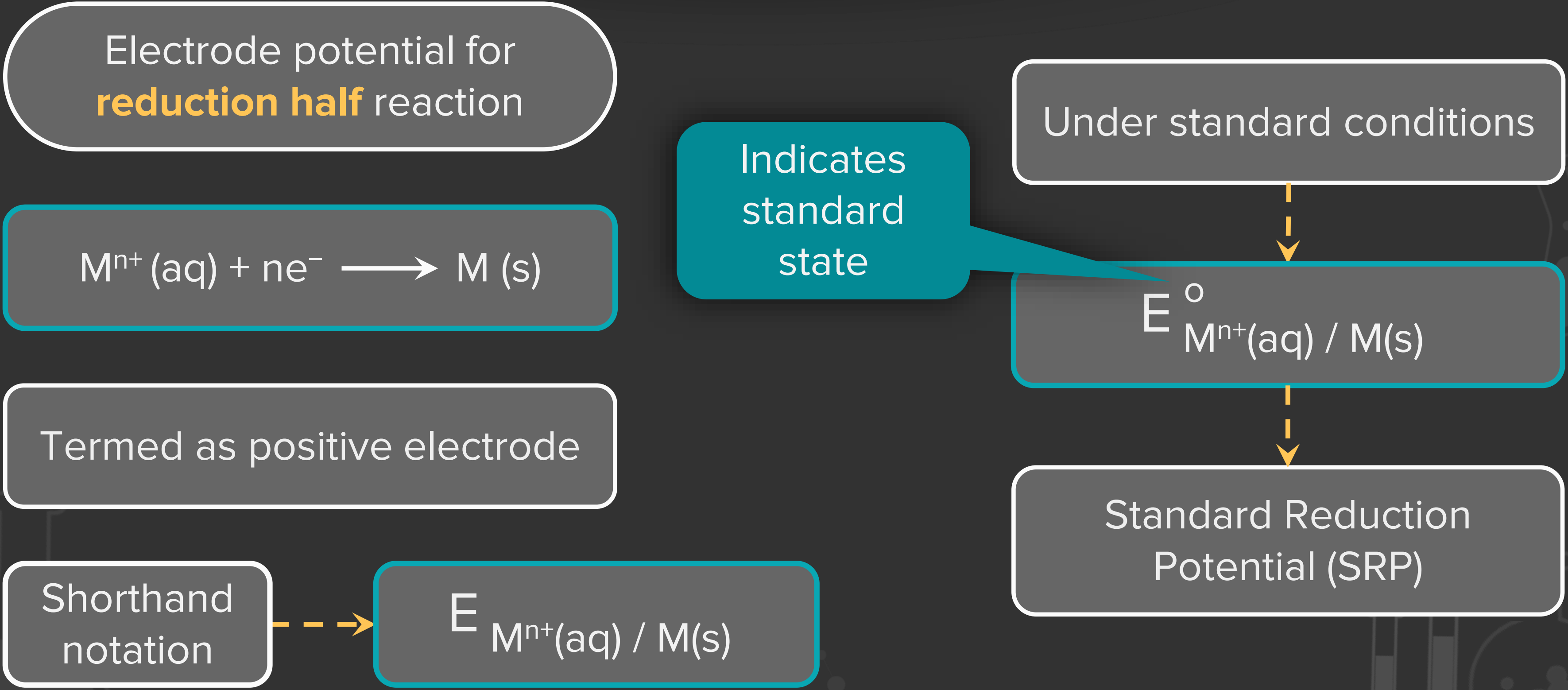
$$Zn\,(s) \rightleftharpoons Zn^{2+}\,(aq) + 2e^{-}$$

Oxidation half

Representation

$$E^{o}_{Zn(s)\,/\,Zn^{2+}(aq)} = +0.76\ V$$

Reduction Potential



Electrode potential for **reduction half** reaction

$M^{n+}(aq) + ne^{-} \longrightarrow M(s)$

Termed as positive electrode

Shorthand notation

$E_{M^{n+}(aq)\,/\,M(s)}$

Indicates standard state

Under standard conditions

$E^{o}_{M^{n+}(aq)\,/\,M(s)}$

Standard Reduction Potential (SRP)

Example of Reduction Potential

$Cu^{2+}(aq) + 2e^{-} \rightleftharpoons Cu(s)$

Reduction half

Representation

$E^{o}_{Cu^{2+}(aq)\,/\,Cu(s)} = 0.34\ V$

$Zn^{2+}(aq) + 2e^{-} \rightleftharpoons Zn(s)$

Reduction half

Representation

$E^{o}_{Zn^{2+}(aq)\,/\,Zn(s)} = -0.76\ V$

Example of Reduction Potential

$$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$$

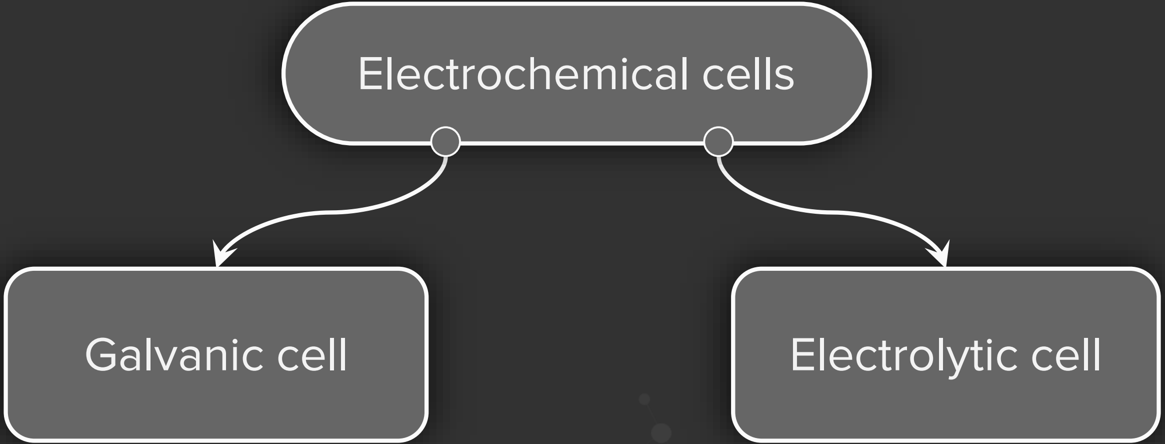
Reduction half

Representation

$$E^{o}_{H_2O_2\,/\,H_2O}$$

Electrochemical Cell

It is a device for the **interconversion** of **chemical energy** & **electrical energy**.



Electrochemical cells

Galvanic cell

Electrolytic cell

Galvanic Cell

A galvanic cell is an **electrochemical cell** that produces **electricity** as a result of the **spontaneous reaction** occurring inside it.

$\Delta_r G$ < 0

Example **Daniel cell**

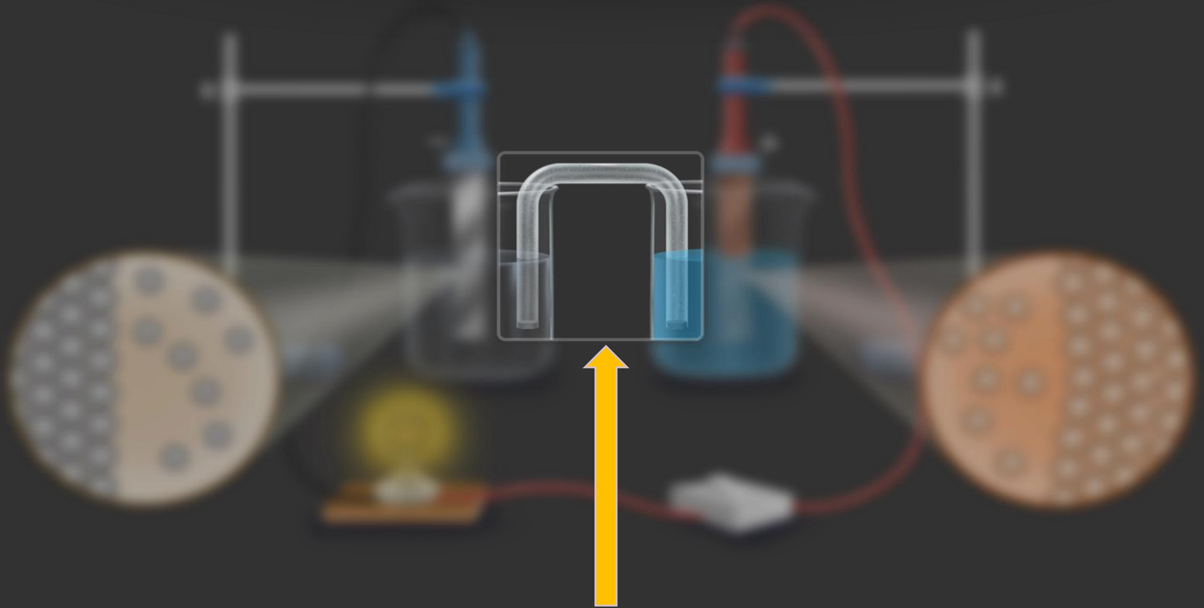
Chemical energy is converted into **electrical energy**.

Electrolytic Cell

Electrical energy is being used to carry out chemical reactions **(chemical energy).**

An electric current drives a **non-spontaneous reaction.**

Salt Bridge



U-shaped tube containing a solution of **KCl or NH_4NO_3** usually solidified by boiling with **agar agar** and later cooled to form a **jelly like substance**.

Functions of Salt Bridge

01

Completes the circuit.

02

Maintains **electrical neutrality** in the solution of both half cells.

03

Provides **anions** to the **oxidation half cell** and **cations** to the **reduction half cell**.

Redox Couple

Redox couple is the combination of **oxidized** and **reduced** forms of the same substance taking part in **oxidation** or **reduction half reaction**.

Represented as M^{a+}/M

Eg: Zn^{2+}/Zn and Cu^{2+}/Cu

Electrochemical Series

A list of oxidizing agents arranged in the decreasing order of their **standard reduction potential**

Increasing strength of oxidizing agent

Reaction (Oxidized form + ne^- $\longrightarrow$ Reduced form)	E^o / V
$F_2(g) + 2e^- \rightarrow 2F^-$	**2.87**
$O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23
$Cu^{2+} + 2e^- \rightarrow Cu(s)$	**0.34**
$2H^+ + 2e^- \rightarrow H_2(g)$	0.00
$Fe^{2+} + 2e^- \rightarrow Fe(s)$	**-0.44**
$Zn^{2+} + 2e^- \rightarrow Zn(s)$	-0.76
$Li^+ + e^- \rightarrow Li(s)$	**-3.05**

Increasing strength of reducing agent

Zn Rod in $CuSO_4$ Solution

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

This reaction is **spontaneous** as

↓

Reduction potential of Cu^{2+} is **more** than Zn^{2+}

Applications of Electrochemical Series

01

Predicting the **feasibility** of the redox reaction.

02

Calculation of **EMF** of the **cells.**

03

Comparison of **strength** of **oxidising** and **reducing agent.**