CHEMISTRY

REDOX REACTIONS

OXIDATION NUMBER AND OXIDATION STATE

NOTES

What you will learn

- Redox reactions
- Oxidation and reduction
- Oxidation number and oxidation state
- Rules for finding oxidation number
- Range of the oxidation number

BOARDS MAIN

Redox Reactions

The chemical reactions in which both oxidation and reduction take place simultaneously are known as redox reactions.

Oxidation

The term **oxidation** is defined as the addition of oxygen or an electronegative element to a substance or the removal of hydrogen or an electropositive element from a substance. In terms of electron transfer, oxidation is considered as the **loss of electrons** (OIL).

Reduction

The term **reduction** is defined as the removal of oxygen or an electronegative element from a substance or the addition of hydrogen or an electropositive element to a substance. In terms of electron transfer, reduction is considered as the **gain of electrons** (RIG).

Oxidation Number and Oxidation State

- **Oxidation number:** It provides an insight about the number of electrons lost/gain by an element, and thereby, describes the extent of oxidation/reduction of the atom in any chemical compound.
- **Oxidation state:** It is a hypothetical or imaginary charge developed over the atom of an element when it goes from its elemental free state to its combined state in a compound.

Oxidation number

The oxidation number is a **game of electronegativity** (ability to attract a shared pair of electrons towards it). It can be positive, negative, or even fractional.

(a) In A–B molecule, consider the electronegativity of A > B. It results in A^- and B^+ on breaking A – B bond hypothetically.

(b) In a BF_3 molecule, fluorine is more electronegative than boron. So, hypothetically the bond is broken between B and F each and results in −1 charge on fluorine and +3 charge on boron.

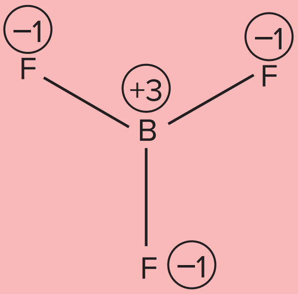


Fig. 1: Oxidation number of boron and fluorine in BF_3

(c) In $H_4P_2O_7$, oxygen gets −2 charge, H gets +1 charge, and P gets +5 charge on breaking the bonds hypothetically.

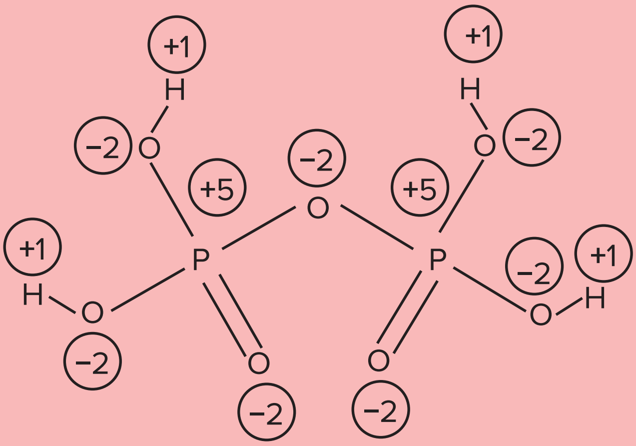
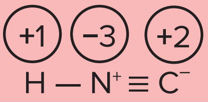


Fig. 2: Oxidation number of phosphorus in $H_4P_2O_7$

- **Contribution of coordinate bond**

A coordinate bond is drawn as a simple covalent bond with positive charge on the donor atom and negative charge on acceptor atom. **For example** H–N≡C can be represented as $H{-}N^+{\equiv}C^-$. Now, covalent bonds are broken by giving −1 charge to more electronegative atom and +1 charge to less electronegative atom. The total charge on each atom will be the oxidation state of that atom. Oxidation state of H = +1, N = −1 −3 + 1 = −3 and C = −1 + 3 = +2



$$\overset{+1}{H} — \overset{-3}{N^+} \equiv \overset{+2}{C^-}$$

Fig. 3: Oxidation number of nitrogen and carbon in HNC

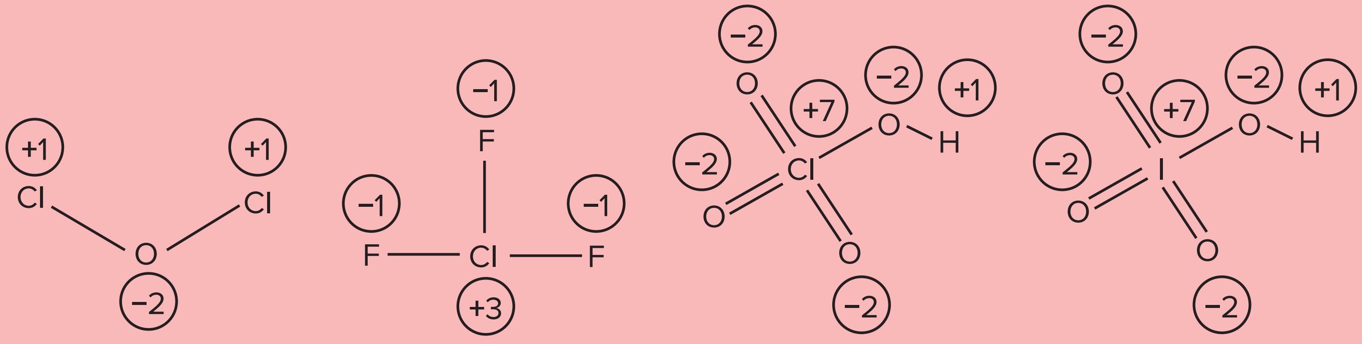
- **Rules for finding oxidation number**

(a) For single monatomic ions, the oxidation number is equal to the charge on the ion.

(i) $Na^+ = +1$
(ii) $Ca^{2+} = +2$
(iii) $H^+ = +1$
(iv) $Cl^- = -1$

(b) In general, the oxidation number of halogens (F, Cl, Br, I) is −1.

(c) If any halogen atom is attached to a more electronegative atom, then it will have a positive oxidation number. For example, **Cl_2O, ClF_3, HIO_4, $HClO_4$.**



Cl_2O **ClF_3** **$HClO_4$** **HIO_4**

Fig. 5: Examples of molecules having halogen attached to more electronegative atom

(d) Fluorine is the most electronegative atom (known). It always has an oxidation number equal to −1 in all of its compounds.

(e) Generally, the oxidation number of hydrogen is +1 i.e. in **HCl, H_2S, and H_2O.**

(f) In metal hydrides (metals are more electropositive than hydrogen), the oxidation number of H is −1. For example, **LiH, NaH, and CaH_2.**

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

Example 1: In NaCl, the oxidation number of Na is +1 and Cl is −1. The sum of oxidation numbers is zero.

Example 2: In $H_4P_2O_7$, the oxidation number of O is −2, H is +1, and P is +5. Thus, the sum of oxidation numbers of all the atoms is zero.

(h) In complex ions or polyatomic ions, the sum of oxidation numbers of all the atoms is equal to the net charge on the ion.
In OH^- ion, the oxidation number of H is +1 and that of oxygen is −2.

(i) For elements in an elementary state, the oxidation number is zero.
Examples: **H_2, Cl_2, N_2, O_2, Br_2, Cu, Fe, Zn, etc.**
All the given elements are in their elementary form. So, the oxidation number is zero.

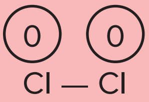


Fig. 6: Oxidation number of chlorine in its elementary form

(j) Generally, the oxidation number of oxygen is –2 in most of its compounds, i.e., oxides.
Examples: In **H_2O, CO_2, SO_2,** and other oxides, the oxidation number of oxygen is –2.

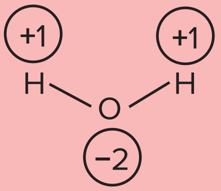


Fig. 7: Oxidation number of oxygen in H_2O

(k) The oxidation number of oxygen is –1 in peroxides, O_2^{2-}.
Examples: In **H_2O_2, Na_2O_2, BaO_2, and other peroxides,** the oxidation number of oxygen is –1.

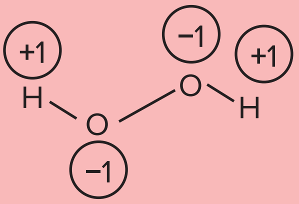
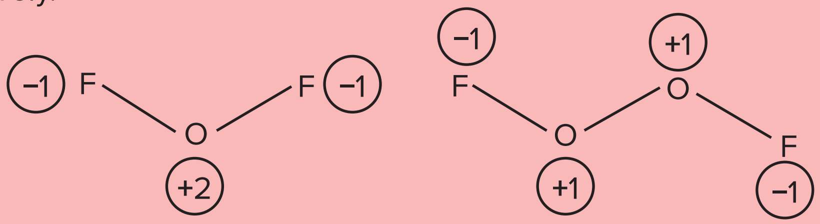


Fig. 8: Oxidation number of oxygen in H_2O_2

(l) The oxidation number of oxygen is $-\left(\frac{1}{2}\right)$ in superoxides, O_2^-.

Examples: In **KO_2, RbO_2, CsO_2, and other superoxides,** the oxidation number of oxygen is $-\left(\frac{1}{2}\right)$.

(m) The oxidation number of oxygen is +1 or +2 in oxy-fluorides depending upon the bonding state. Fluorine being more electronegative than oxygen, results in a positive oxidation number of oxygen. Examples: In **OF_2 and O_2F_2**, the oxidation number of oxygen is +2 and +1, respectively.



OF_2 **O_2F_2**

Fig. 9: Oxidation number of oxygen in OF_2 and O_2F_2

(n) The oxidation number of alkali metals is +1 and the oxidation number of alkaline earth metals is +2 in their compounds.
Alkali metals (group 1, i.e., Li, Na, K, Rb, Cs, Fr) always have oxidation number +1.
Alkaline earth metals (group 2, i.e., Be, Mg, Ca, Sr, Ba) always have oxidation number +2.

Alkali metals (group 1)	Alkaline earth metals (group 2)
Lithium (Li)	Beryllium (Be)
Sodium (Na)	Magnesium (Mg)
Potassium (K)	Calcium (Ca)
Rubidium (Rb)	Strontium (Sr)
Caesium (Cs)	Barium (Ba)

Table 1: Elements present in the first and second group

(o) Aluminium usually has oxidation number +3 in all of its compounds.
Example: The oxidation state of **Al is +3 in Al_2O_3, $AlCl_3$, and $Al(OH)_3$.**

Name of the radical	Representation
Ammonium	NH_4^+
Nitrate	NO_3^-
Nitrite	NO_2^-
Bisulphate	HSO_4^-
Bicarbonate	HCO_3^-
Hydroxide	OH^-
Cyanide	CN^-
Sulphide	S^{2-}
Sulphate	SO_4^{2-}
Carbonate	CO_3^{2-}
Dichromate	$Cr_2O_7^{2-}$
Phosphate	PO_4^{3-}
Bromide	Br^-
Chloride	Cl^-
Iodide	I^-
Sulphite	SO_3^{2-}
Acetate	CH_3COO^-
Thiosulphate	$S_2O_3^{2-}$
Tetrathionate	$S_4O_6^{2-}$
Oxalate	$C_2O_4^{2-}$

Table 2: Important radicals and their representation

Based on finding the oxidation number

Calculate the oxidation number of the underlined atoms in the following molecules:

1. $H\underline{\mathbf{N}}O_3$
2. $\underline{\mathbf{Cr}}O_4^{2-}$
3. $H_2\underline{\mathbf{C}_2}O_4$
4. $K_2\underline{\mathbf{Mn}}O_4$
5. $K_2\underline{\mathbf{Cr}_2}O_7$
6. $Na_2\underline{\mathbf{S}_2}O_3$
7. $\underline{\mathbf{Fe}}S$
8. $K_4[\underline{\mathbf{Fe}}(CN)_6]$
9. $[\underline{\mathbf{Ag}}(S_2O_3)_2]^{3-}$

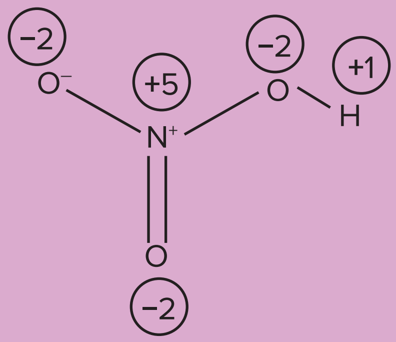
Solution

1. $H\underline{\mathbf{N}}O_3$

Let the oxidation number of nitrogen (N) be x.

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

Then x = +5

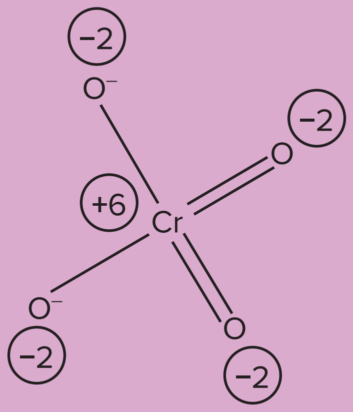


2. $\underline{\mathbf{Cr}}O_4^{2-}$

Let the oxidation number of chromium (Cr) be x.

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

Then x = +6

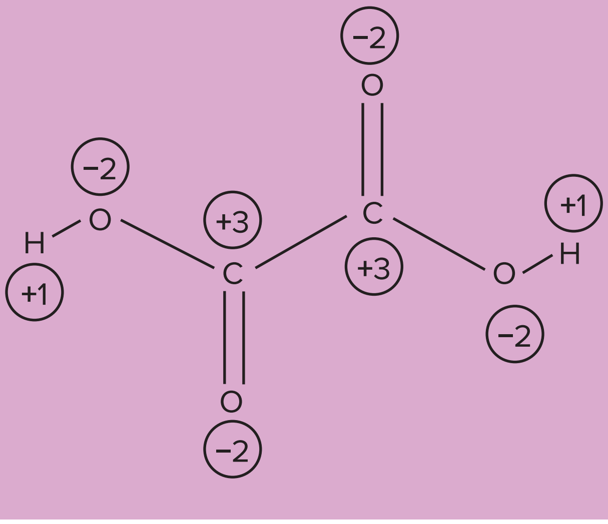


3. $H_2\underline{\mathbf{C}_2}O_4$

Let the oxidation number of carbon (C) be x.

If $+1(2) + 2x + (-2)4 = 0$,

Then x = +3

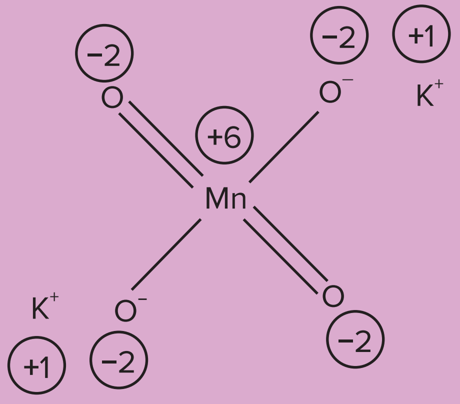


4. $\mathrm{K_2\underline{\mathbf{Mn}}O_4}$

Let the oxidation number of manganese (Mn) be x.

If $+1(2) + x + (-2)4 = 0$,

Then x = +6

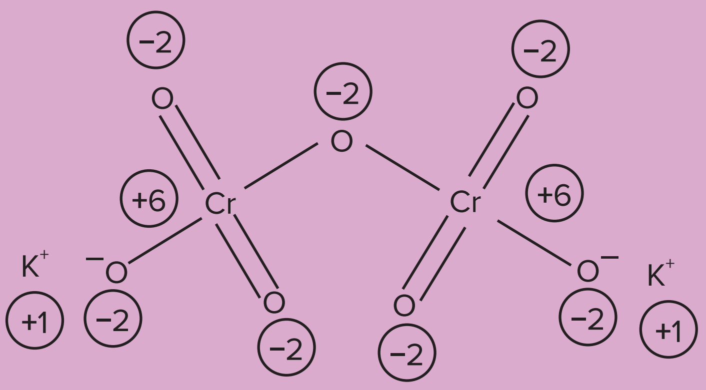


5. $\mathrm{K_2\underline{\mathbf{Cr}}_2O_7}$

Let the oxidation number of chromium (Cr) be x.

If $+1(2) + 2x + (-2)7 = 0$,

Then x = +6

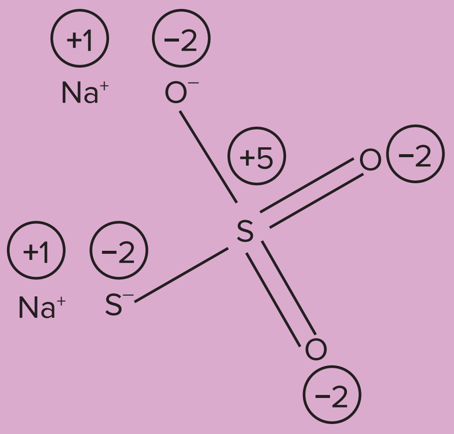


6. $\mathrm{Na_2\underline{\mathbf{S}}_2O_3}$

Let the oxidation number of sulphur (S) be x.

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

Then x = +2



7. $\mathrm{\underline{\mathbf{Fe}}S}$

Let the oxidation number of iron (Fe) be x.

If $x + (-2) = 0$,

Then x = +2

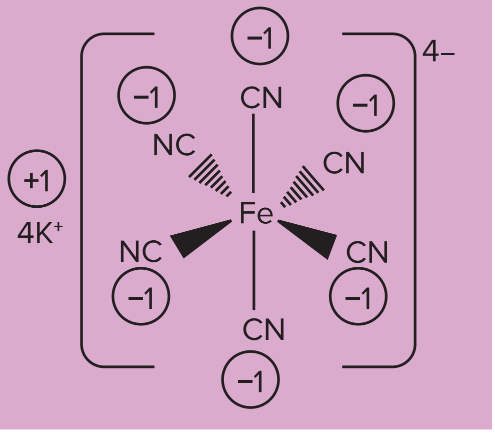
8. $\mathrm{K_4[\underline{\mathbf{Fe}}(CN)_6]}$

Let the oxidation number of iron (Fe) be x.

The coordination compound can be written as a sum of two parts, i.e., Complex ions $\mathrm{[Fe(CN)_6]^{4-}}$ + Counter ions ($\mathrm{4K^+}$ ions). In complex compounds, the overall charge on the ligand (i.e., $\mathrm{CN^-}$) is considered as whole instead of considering the charge on the individual atoms.

If $+1(4) + x + (-1)6 = 0$,

Then x = +2



9. $[\underline{\textbf{Ag}}(S_2O_3)_2]^{3-}$

Let the oxidation number of silver (Ag) be x.

In complex compounds, the overall charge on the ligand (i.e., $S_2O_3^{2-}$) is considered as whole instead of considering the charge on the individual atoms.

If x + (−2)2 = −3,

Then x = +1

BOARDS NEET

Range of Oxidation Numbers

Oxidation number

- Maximum O.N. = Electrons in the valence shell
- Minimum O.N. = Electrons in the valence shell − 8

Example: Oxidation number of Cl in $HClO_4$ (Perchloric acid) and HCl (Hydrochloric acid)

Let the oxidation number of Cl be x in $\mathbf{HClO_4}$.

If (+1) + x + (−2)4 = 0,

Then x = +7

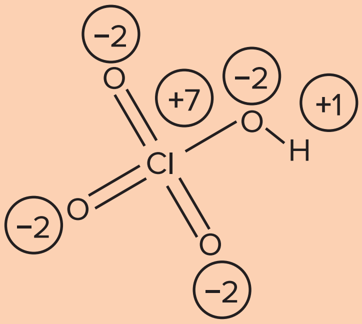


Fig. 10: Oxidation number of Chlorine in perchloric acid ($HClO_4$)

Let the oxidation number of Cl be x in **HCl.**

If (+1) + x = 0,

Then x = −1

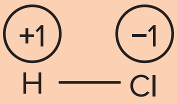
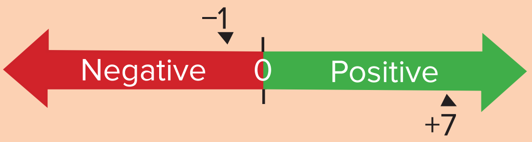


Fig. 11: Oxidation number of chlorine in HCl

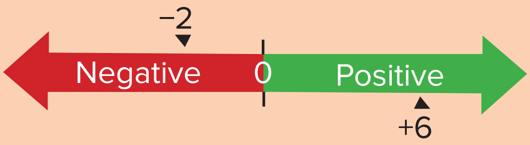
Group 17 halogens

For halogens, the oxidation number ranges from −1 to +7. However, this is not applicable to F (F can have an oxidation number of either −1 or zero).



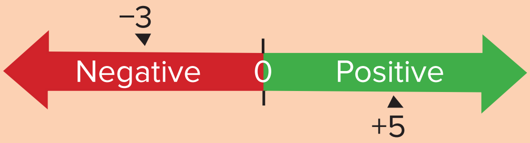
Group 16 elements

For group 16 elements, the oxidation number ranges from −2 to +6, except oxygen.



Group 15 elements

For group 15 elements, the oxidation number ranges from −3 to +5.



Oxidation State of Some Oxygen Containing Compounds

Case 1: Calculated oxidation state > Maximum oxidation state

Oxidation state of some oxygen containing compounds.

(a) $H_2\underline{\mathbf{S}}O_5$ (Peroxymonosulfuric acid)

For the calculated oxidation state of sulphur,
Let the oxidation state of sulphur be x
If (+1)2 + x + (−2)5 = 0,
Then x = +8

Here, all the oxygens are considered with −2 oxidation states. However, there is one peroxy linkage (single bond between two oxygens). Hence, it results in −2 charge on three oxygen atoms and −1 charge on two oxygen atoms with peroxy linkage.

If (+1)2 + x + (−2)3 + (−1)2 = 0, Then x = +6

Thus, the maximum oxidation state of S is +6.

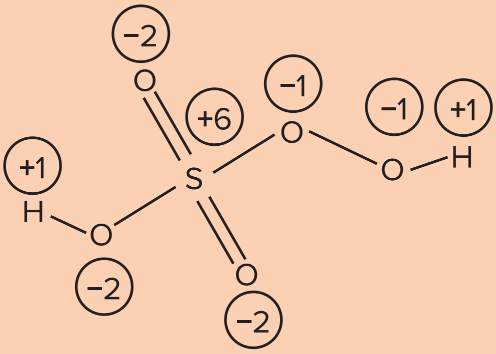


Fig. 12: Oxidation state of sulphur in H_2SO_5

(b) $\underline{\mathbf{Cr}}O_5$

For the calculated oxidation state of Cr,
Let the oxidation state of Cr be x.
If x + (−2)5 = 0,
Then x = +10

Here, the state of all the oxygens is considered as −2 charge but there are two peroxy linkages (single bond between two oxygens).

If x + (−2)1 + (−1)4 = 0,
Then x = +6

Thus, the maximum oxidation state of Cr is +6.

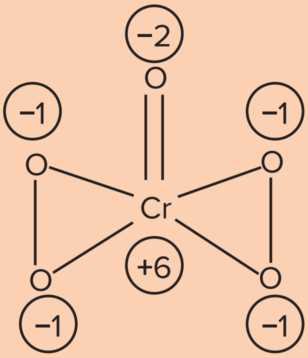


Fig. 13: Oxidation state of chromium in CrO_5

Case 2: Calculated oxidation state = Maximum oxidation state

$H_2\underline{S}_2O_7$

Calculated oxidation state of S is +6.

If $(+1)2 + 2x + (-2)7 = 0$,

Then $x = +6$

Thus, the maximum oxidation state of S is +6.

Hence,

Calculated oxidation state = Maximum oxidation state

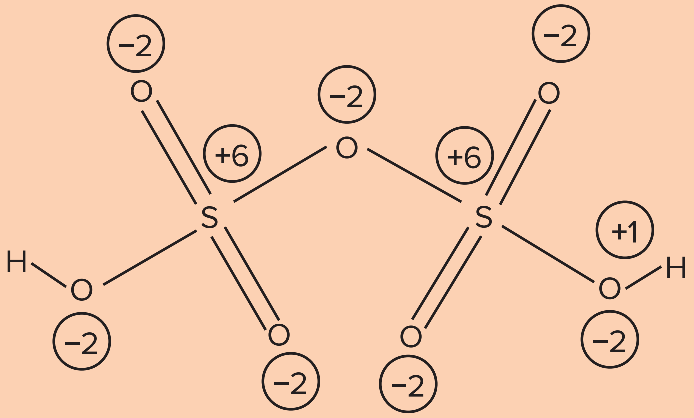


Fig. 14: Oxidation state of sulphur in $H_2S_2O_7$

Case 3: Calculated oxidation state < Maximum oxidation state

$H_2\underline{S}_2O_6$

The calculated oxidation state of sulphur is +5.

Let the oxidation state of sulphur be x.

If $(+1)2 + 2x + (-2)6 = 0$,

Then $x = +5$

Since S–S bond is non polar, it does not contribute to the oxidation state.

Thus, the maximum oxidation state of sulphur is +6.

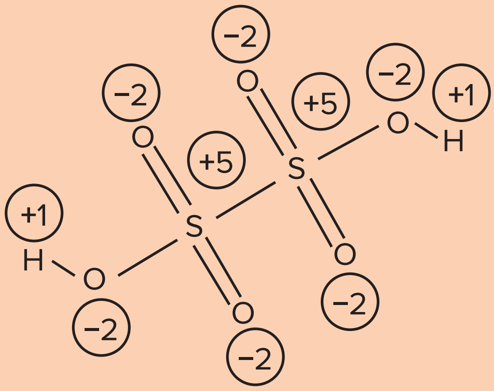


Fig. 15: Oxidation state of sulphur in $H_2S_2O_6$

Paradox of fractional oxidation states

$(\underline{S}_4O_6)^{2-}$

Assume that the oxidation state of sulphur is 'x'.

The average oxidation state of sulphur is,

$4x + 6(-2) = -2$

$x = 2.5$

There are a total of four sulphur atoms. The oxidation state of two sulphur atoms is zero, and the oxidation state for the other two sulphur atoms is +5. In general, the **four sulphur atoms share +10 charge,** resulting in the **average oxidation state of +2.5.**

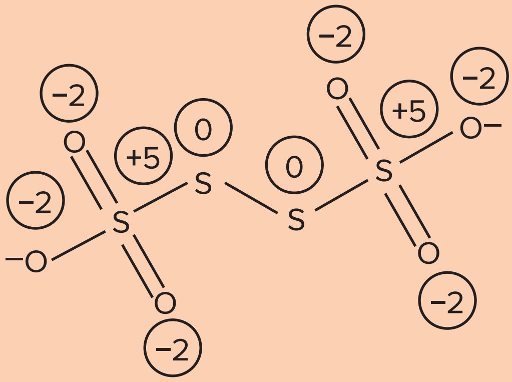


Fig. 16: Oxidation state of sulphur in $S_4O_6^{2-}$

CHEMISTRY

REDOX REACTIONS

OXIDATION AND REDUCTION

NOTES

What you already know

- Redox reaction
- Oxidation and reduction
- Oxidation number and oxidation state
- Rules for finding oxidation number
- Range of the oxidation number

What you will learn

- Classical concept of reduction and oxidation
- Redox vs non-redox reactions
- Types of redox reactions
- n-factor

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Classical Concept of Oxidation

(a) Addition of oxygen

(b) Addition of an electronegative element

(c) Removal of hydrogen

(d) Removal of an electropositive element

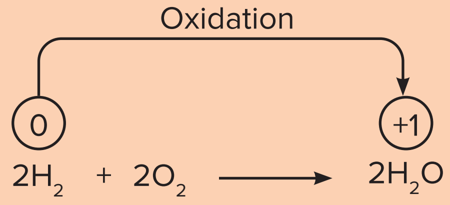
Concept of oxidation

It is the process in which there is an increase in the oxidation number of the element from the reactants to the products in a chemical reaction.

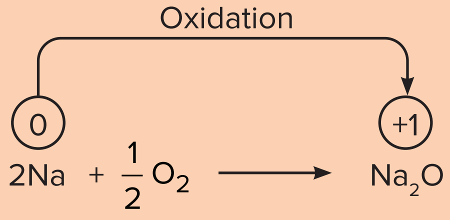
Example:

Increase in oxidation number

The oxidation number of hydrogen (H) in H_2 is 0, but in H_2O, it is +1.
The oxidation number of hydrogen increases from 0 to +1.
Thus, hydrogen undergoes oxidation.



The oxidation number of Na is 0, but in Na_2O, it is +1.
The oxidation number of sodium increases from 0 to +1.
Thus, sodium is oxidised



Electronic concept of oxidation

Removal or loss of electrons

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

From the given reaction, a loss of two electrons takes place from Zn(s) to form $Zn^{2+}(aq)$.

BOARDS MAIN

Classical Concept of Reduction

(a) Addition of hydrogen
(b) Removal of oxygen
(c) Addition of an electropositive element
(d) Removal of an electronegative element

Concept of reduction

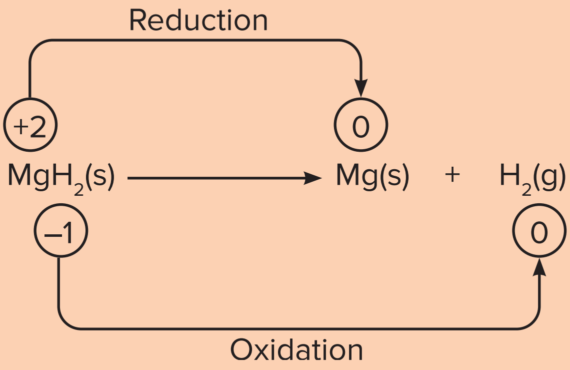
Reduction is the process in which there is a decrease in the oxidation number of the element from the reactants to the product in a chemical reaction.

Example:

Decrease in oxidation number

The oxidation number of Mg is +2 in $MgH_2(s)$and 0 in Mg(s).
The oxidation number of magnesium decreases from +2 to 0. Thus, Mg is reduced.
The oxidation number of hydrogen is −1 in $MgH_2(s)$ and 0 in $H_2(g)$.

So, in any reaction, if oxidation is taking place, simultaneously reduction must take place.



Electronic concept of reduction

Addition/gain of electrons

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

Cu^{2+} gains two electrons to form Cu.

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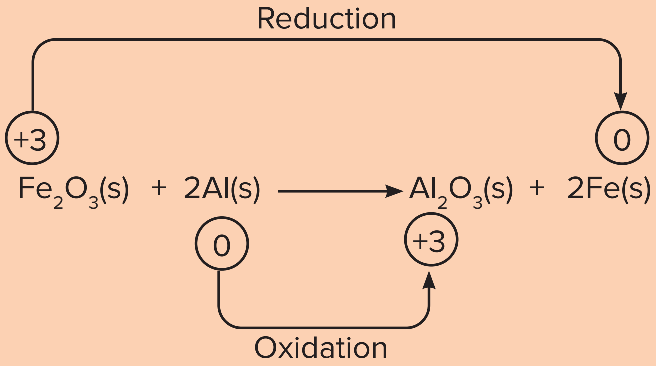
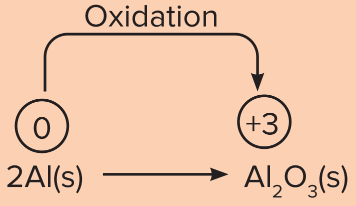
Redox Reaction

Redox reactions are oxidation-reduction chemical reactions in which the reactants undergo a change in their oxidation states. The term ‘redox’ is a short form of reduction-oxidation. All the redox reactions can be broken down into two different processes, a reduction process and an oxidation process. Combustion is a redox reaction.

An example of a redox reaction

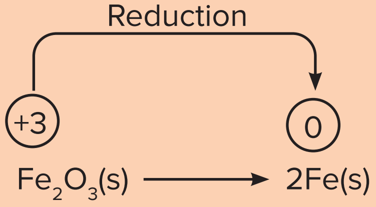


(i) Oxidation



The oxidation number of aluminium (Al) increases from 0 to +3.

(ii) Reduction



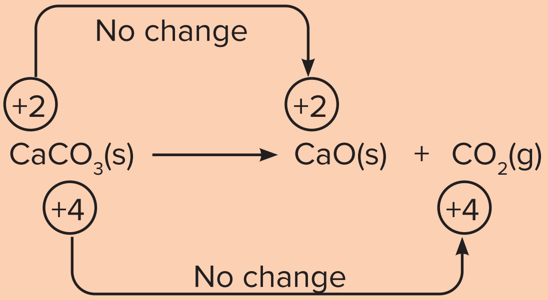
The oxidation number of iron (Fe) decreases from +3 to 0 , so iron(Fe) is reduced in the process.

Fe_2O_3 is an oxidising agent. Al is a reducing agent. In a complete redox reaction, both oxidation and reduction reactions take place simultaneously.

Non-Redox Reaction

In $CaCO_3$, the oxidation number of Ca is +2, C is +4, and O is −2.
In CaO, the oxidation number of Ca is +2 and O is −2.
In CO_2, the oxidation number of C is +4 and O is −2.

There is no change in the oxidation number of any of the elements in the non-redox reaction.



Oxidising agent/Oxidant

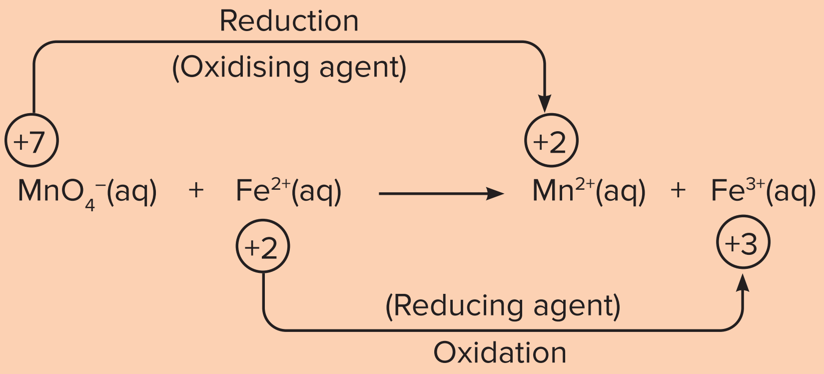
A substance that oxidises others and itself gets reduced is known as an oxidising agent.
Examples: $KMnO_4$, H_2O_2, $K_2Cr_2O_7$

Reducing agent/Reductant

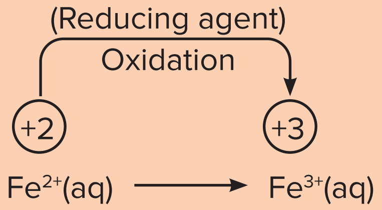
A substance that reduces others and gets itself oxidised is known as a reducing agent.
Examples: $Na_2S_2O_3$, H_2O_2

- H_2O_2 acts as both oxidising and reducing agent because the oxidation number of O in H_2O_2 is −1, which is neither maximum nor minimum.
- H_2SO_4 can behave only as an oxidant. It can never reduce any substance because the oxidation number of sulphur is +6, which is the maximum for sulphur, and the range of oxidation numbers of S is from −2 to +6.

Finding the oxidising and the reducing agent

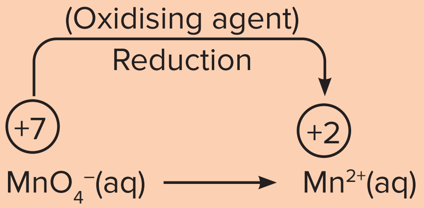


(i) Oxidation



The oxidation state of Fe increases from +2 to +3.

(ii) Reduction



The oxidation state of Mn decreases from +7 to +2.

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

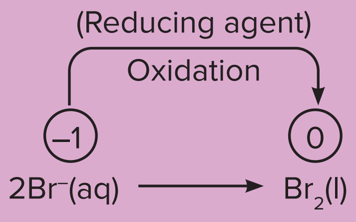
Based on finding the oxidant and reductant

Identify the oxidant and the reductant in the following reaction.

$$Cl_2(g) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(l)$$

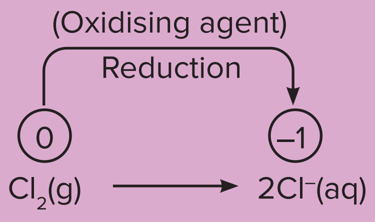
Solution

(i) Oxidation



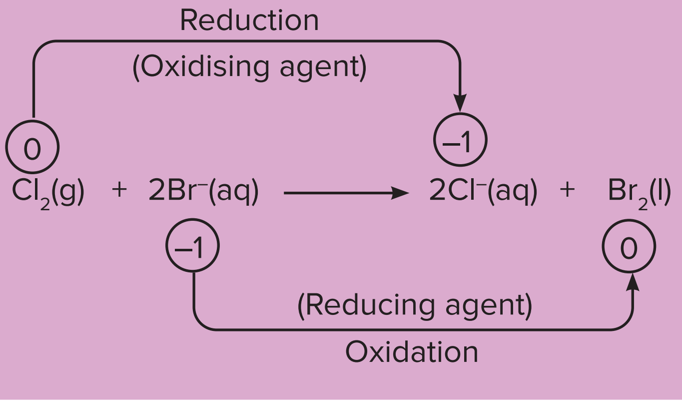
The oxidation number of bromine increases from –1 to 0.

(ii) Reduction



The oxidation number of chlorine decreases 0 to –1.

Thus, Cl_2 is the oxidising agent and Br^- is the reducing agent.



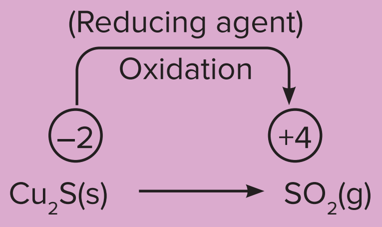
Based on the redox reaction

The following reaction is a redox reaction. Justify.

$$\mathbf{2Cu_2O(s) + Cu_2S(s) \rightarrow 6Cu(s) + SO_2(g)}$$

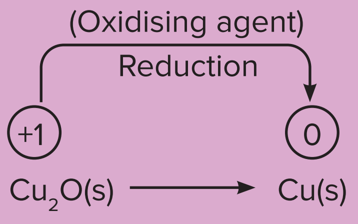
Solution

(i) Oxidation



The oxidation number of sulfur (S) increases from −2 (Cu_2S) to +4 (SO_2).

(ii) Reduction



The oxidation number of copper (Cu) decreases from +1 to 0.

Since reduction and oxidation both are involved in the reaction, hence the given reaction is redox reaction.

BOARDS MAIN ADVANCED

Types of Redox Reactions

1. Combination reactions
2. Decomposition reactions
3. Displacement reactions
4. Disproportionation reactions
5. Comproportionation reactions
6. Intramolecular reactions

Combination reactions

In combination reactions, one or more than one reactants must be in an elementary standard state that results in one or two products.

Combination reaction is generally given as:

$$\mathbf{A + B \rightarrow C}$$

Where, **A** and **B** are the reactants in their elementary state and **C** is the product formed.

Examples:

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

It is a combustion reaction, where C is oxidised and O is reduced.

Some more examples are:

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

$3Mg(s) + N_2(g) \rightarrow Mg_3N_2(s)$

Decomposition reactions

In decomposition reactions, one or more than one product must be in an elementary state. Decomposition reaction is generally given as:

$$\mathbf{C \rightarrow A + B}$$

Where, **C** is the reactant, and **A** and **B** are the products of the decomposition reaction.

Example:

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

Displacement reactions

In displacement reactions, a part of one reactant is displaced by another reactant.

$$\mathbf{X + YZ \rightarrow XZ + Y}$$

Metals or nonmetals can be displaced in a displacement reaction.

Examples of displacement reactions:

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

The metal, Ag, is displaced by Cu in the given reaction.

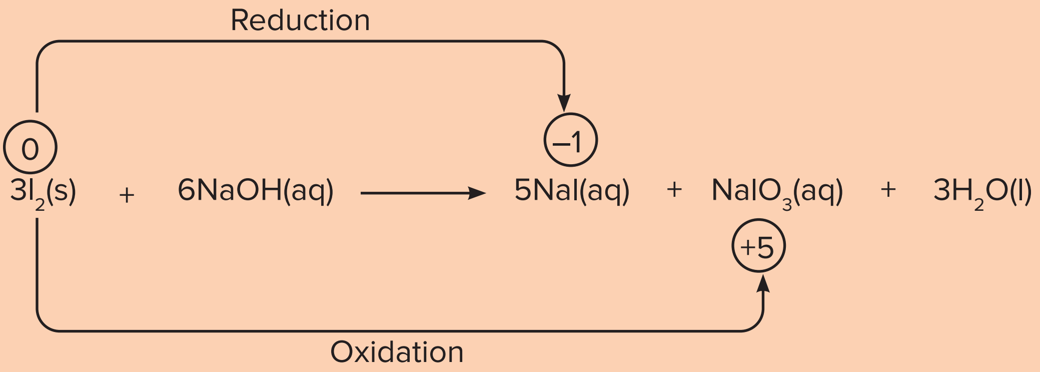
$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$

Hydrogen is displaced by Na in the given reaction.

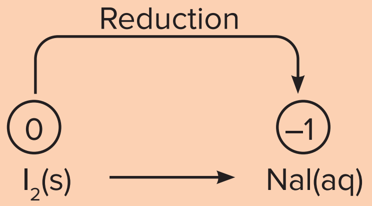
Disproportionation reactions

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

Disproportionation redox reaction

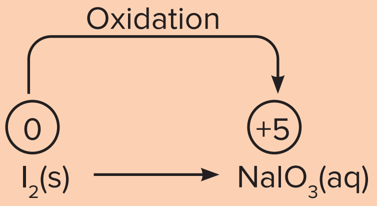


(i) Reduction



The oxidation state of I decreases from 0 to −1.

(ii) Oxidation



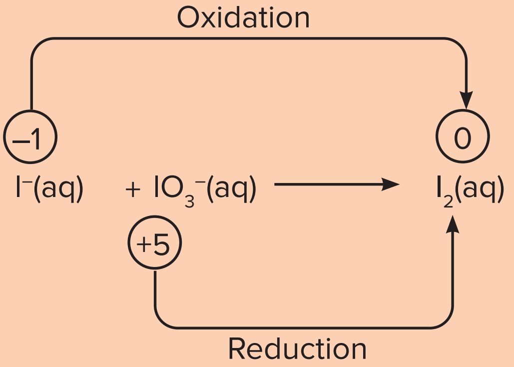
The oxidation state of I increases from 0 to +5.

This reaction involves the change in the oxidation state of iodine (I) from 0 to higher oxidation state, i.e., +5 and lower oxidation state, i.e., −1.

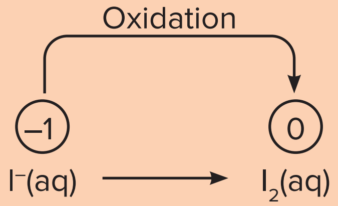
Comproportionation reactions

The redox reaction in which an element from two different oxidation states (one lower and other higher) changes to the same oxidation state is known as the comproportionation reaction. It is reverse of the disproportionation reaction.

Comproportionation reaction

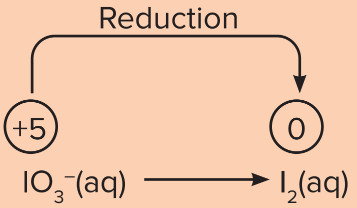


(i) Oxidation



The oxidation number of Iodine increases from −1 to 0.

(ii) Reduction

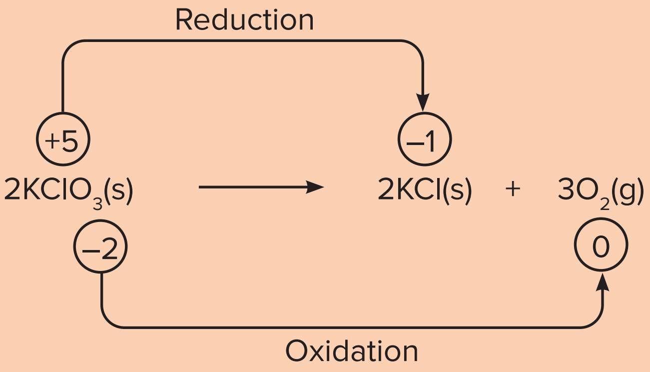


The oxidation number of iodine decreases from +5 to 0.

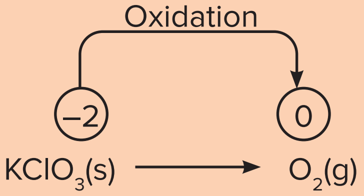
Intramolecular redox reaction

Intramolecular redox reactions are the reactions in which a single compound undergoes reduction-oxidation by the process of decomposition. It is a reaction between two or more atoms in the same reactant molecule.

Example:

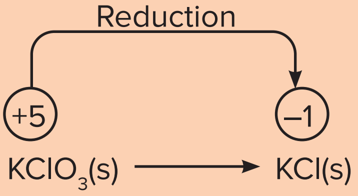


(i) Oxidation



The oxidation number of oxygen increases from −2 to 0.

(ii) Reduction



The oxidation number of chlorine decreases from +5 to –1.

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

n-Factor

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

Finding n-factor: $H_2\underline{\mathbf{S}}O_3 \rightarrow H_2\underline{\mathbf{S}}O_4$

Step 1: Find the oxidation state of the element on the reactant and the product side whose oxidation state is changing.

$H_2\underline{\mathbf{S}}O_3 \rightarrow H_2\underline{\mathbf{S}}O_4$

The oxidation number of **S** is +4 in $H_2\underline{\mathbf{S}}O_3$ and +6 in $H_2\underline{\mathbf{S}}O_4$.

Step 2: Find the difference in the oxidation states and take its magnitude.

$6 - 4 = |2|$

$H_2\underline{\mathbf{S}}O_3 \rightarrow H_2\underline{\mathbf{S}}O_4$; n-factor must always be positive.

Step 3: To find n_f multiply the difference in the oxidation states with the number of elements/atoms present whose oxidation state is changing.

n_f of S = 2 × 1 = 2

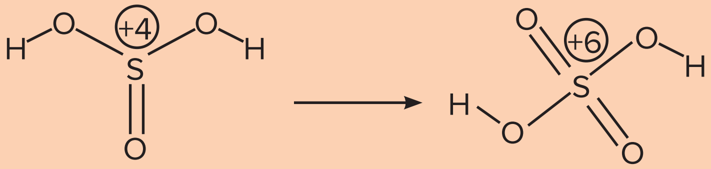


Fig. 1: Change in oxidation number of S in H_2SO_3 and H_2SO_4

n_f = Number of elements whose oxidation state is changing × Difference in oxidation states

$H_2\underline{C}_2O_4 \rightarrow \underline{C}O_2$

The oxidation number of **C** is +3 in $H_2\underline{C}_2O_4$ and +4 in $\underline{C}O_2$.

Change in oxidation number = (4 − 3) = 1

$n_f = 1 \times 2 = 2$

Calculation of n_f for different species

i) **For ions**

$n_f = |\text{Charge}|$

$Na^+ \Rightarrow n_f = 1$

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

ii) **For salts**

n_f = total positive or negative charge

NaCl, $n_f = 1$ (Na^+, Cl^-)

$Al_2(SO_4)_3$,

$n_f = 6$ ($2Al^{3+}$, $3SO_4^{2-}$)

iii) **For acids**

n_f = Basicity

Number of H^+ ions an acid donates

H_2SO_4, Basicity = 2, $n_f = 2$

iv) **For bases**

n_f = Acidity

Number of OH^- ions a base donates

NaOH, Acidity = 1, $n_f = 1$

Some Special Cases of Acids

The n_f of any acid depends on the type of the reaction.

$H_2SO_4(aq) + NaOH(aq) \rightarrow NaHSO_4(aq) + H_2O(l)$

The n-factor (n_f) of H_2SO_4 is 1.

In the given reaction, only one hydrogen ion is replaceable per 1 mole of H_2SO_4.

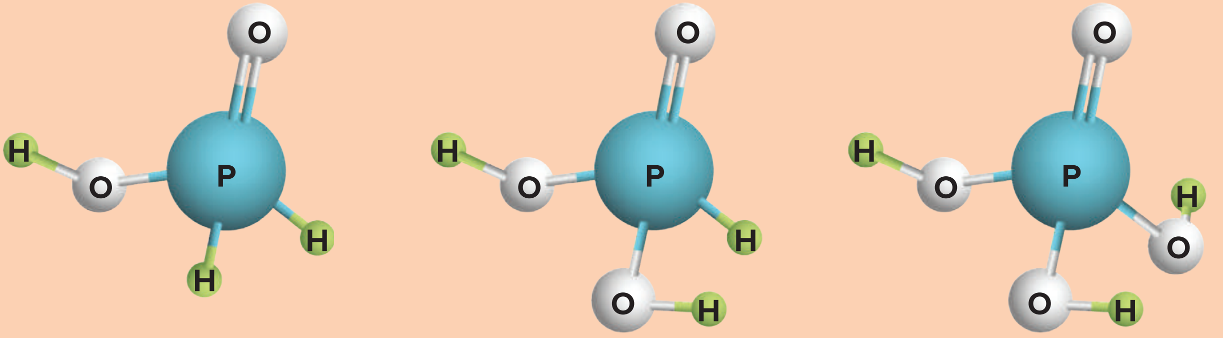
$H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$

The n-factor (n_f) of H_2SO_4 is 2 here.

Oxyacids of phosphorus

Number of replaceable hydrogens = Number of OH groups present in oxyacids

$H_3PO_4 \Rightarrow n_f = 3$	**3 – OH bond**
$H_3PO_3 \Rightarrow n_f = 2$	**2 – OH bond**
$H_3PO_2 \Rightarrow n_f = 1$	**1 – OH bond**



One acidic H in H_3PO_2 Two acidic H in H_3PO_3 Three acidic H in H_3PO_4

Fig. 2: Oxyacids of phosphorus

$B(OH)_3(s) + H_2O(l) \rightarrow B(OH)_4^-(aq) + H^+(aq)$

In H_3BO_3,

$n_f = 1$

Here, H_3BO_3 behaves as a Lewis acid. It is accepting electrons from H_2O and giving one mole of H^+ per mole of the acid.

Notes

- The value of n_f cannot be zero or negative.
- The value of n_f can be a fraction.

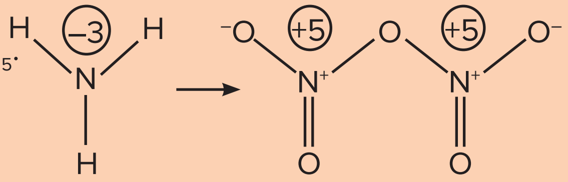
a) Find n_f for NH_3 to N_2O_5

The oxidation number of N is −3 in NH_3 and +5 in N_2O_5.

Change in oxidation number = 5 − (−3) = 8

For NH_3, n-factor = 8 × 1 = 8

For N_2O_5, n-factor = 8 × 2 = 16



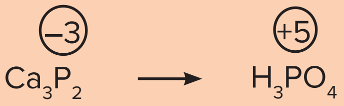
b) Find n_f for Ca_3P_2 to H_3PO_4

The oxidation number of P is −3 in Ca_3P_2 and +5 in H_3PO_4.

Change in oxidation number = 5 − (−3) = 8

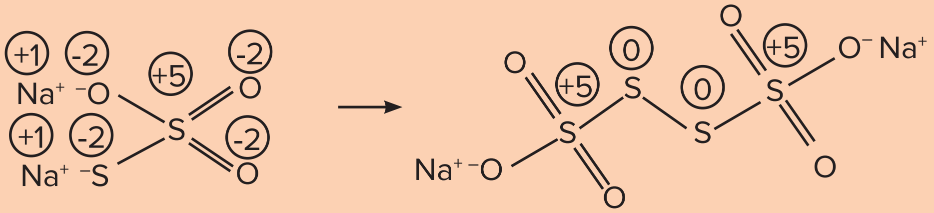
For H_3PO_4, n–factor = 8 × 1 = 8

For Ca_3P_2, n–factor = 8 × 2 = 16



$$\overset{(-3)}{Ca_3P_2} \longrightarrow \overset{(+5)}{H_3PO_4}$$

c) Find n_f for $Na_2S_2O_3$ to $Na_2S_4O_6$



The average oxidation number of S is +2 in $Na_2S_2O_3$ and +2.5 in $Na_2S_4O_6$.

Change in oxidation number = 2.5 − 2 = 0.5

For $Na_2S_2O_3$, n-factor = 0.5 × 2 = 1

For $Na_2S_4O_6$, n-factor = 0.5 × 4 = 2

CHEMISTRY

REDOX REACTIONS

TOOLS OF TITRATIONS

What you already know

- Balancing redox reactions
- Unusual n-factor calculation cases

What you will learn

- Calculation of n-factor in different types of reactions
- Equivalent mass
- Number of equivalents
- Law of equivalence
- Normality
- Redox titrations

Finding the n-factor

Find the n-factor of the compound $Fe_{0.9}O$ in the following reaction. $Fe_{0.9}O \xrightarrow{n_f = ?} Fe_2O_3$

Solution

First method

Step 1: To balance Fe on both the sides, multiply L.H.S by 2 and R.H.S by 0.9

$2 \times Fe_{0.9}O \longrightarrow 0.9 \times Fe_2O_3$

Now, on both the sides, we have 1.8 Fe

Step 2: To balance oxygen on both the sides, add 0.7 H_2O on L.H.S and 1.4 H^+ on R.H.S

$2Fe_{0.9}O + 0.7H_2O \longrightarrow 0.9Fe_2O_3 + 1.4H^+$

Step 3: To balance the charge on both the sides, add 1.4 e^- on R.H.S

$2Fe_{0.9}O + 0.7H_2O \longrightarrow 0.9Fe_2O_3 + 1.4H^+ + 1.4e^-$

1.4 moles of e^- are released from 2 moles of $Fe_{0.9}O$

Therefore, the number of moles of electrons released by 1 mole of $Fe_{0.9}O = (\frac{1.4}{2}) = 0.7\ mol$

Therefore, the n-factor of compound $Fe_{0.9}O$ in the reaction $Fe_{0.9}O \longrightarrow Fe_2O_3$ is 0.7.

Second method

In Fe_2O_3, 100% Fe exists in +3 oxidation state, and in FeO, 100% Fe exists in +2 oxidation state.
However, in $Fe_{0.9}O$, (Fe) exists in both +2 and +3 oxidation states.
The total negative charge on oxygen (O) in $Fe_{0.9}O = -2$
And as per the law of charge conservation, the total positive charge on iron (Fe) must be +2.

Now, Let x moles of Fe have a charge of +2 in $Fe_{0.9}O$ and (0.9 – x) moles of Fe have a charge of +3. Therefore,

$(+2)x + (+3)(0.9 - x) = 2$

$2x + 2.7 - 3x = 2 \Rightarrow x = 0.7$

- Number of moles of Fe^{2+} = 0.7 *mol*
- Number of moles of Fe^{3+} = 0.2 *mol*

On the product side, Fe is present in +3 oxidation state. So, in $Fe_{0.9}O$, only Fe^{2+} is oxidised to Fe^{3+}.

1 mole of $Fe_{0.9}O$ has 0.7 moles of Fe^{2+} and 0.2 moles of Fe^{3+}.

Therefore, the n-factor of the compound $Fe_{0.9}O$ in the reaction $Fe_{0.9}O \longrightarrow Fe_2O_3$ is 0.7.

Finding the n-factor

Find the n-factor of the compound $Fe_{0.9}O$ in the following reaction. $Fe_{0.9}O \xrightarrow{n_f = ?} FeO$

Solution

Step 1: To balance Fe on both the sides, multiply R.H.S by 0.9

$Fe_{0.9}O \longrightarrow 0.9FeO$

Step 2: To balance oxygen on both the sides, add 0.1 H_2O on R.H.S and 0.2 H^+ on L.H.S

$Fe_{0.9}O + 0.2H^+ \longrightarrow 0.9FeO + 0.1H_2O$

Step 3: To balance the charges on both the sides, add $0.2e^-$ on L.H.S

$Fe_{0.9}O + 0.2H^+ + 0.2e^- \longrightarrow 0.9FeO + 0.1H_2O$

0.2 moles of e^- are gained by 1 mole of $Fe_{0.9}O$

Hence, the n-factor is 0.2.

Therefore, the n-factor of the compound $Fe_{0.9}O$ in the reaction $Fe_{0.9}O \longrightarrow FeO$ is 0.2.

Equivalent Mass

$$\textbf{Equivalent mass or Gram equivalent mass} = \frac{\textbf{Molar mass}}{\textbf{n-factor}}$$

Example:

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

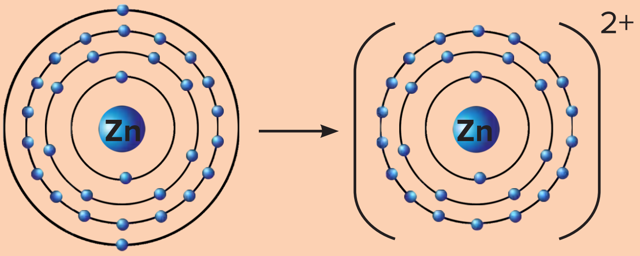


Fig. 1: Illustration of Zn becoming Zn^{2+} by releasing two electrons

From the **Fig. 1,** we can see that 1 mole of Zn releases 2 moles of electrons and converts into Zn^{2+}. Therefore, as per the definition of n-factor, the n-factor for conversion of $Zn \longrightarrow Zn^{2+}$ is 2. Molar mass of Zn = 65 *g mol⁻¹*

Therefore, gram equivalent mass of Zn = $\frac{65}{2} = 32.5\ g\ eqv^{-1}$

Finding the equivalent mass

Calculate the equivalent mass of $K_2Cr_2O_7$ in the following reaction.

$$\mathbf{K_2Cr_2O_7(aq) + K_2S_2O_3(aq) \longrightarrow Cr^{3+}(aq) + SO_4^{2-}(aq)}$$

Given molar mass of Cr = 52 $g\ mol^{-1}$

Solution

Here, the oxidation state of Cr changes from +6 in $K_2Cr_2O_7$(aq) to +3 in Cr^{3+}(aq).

The change in the oxidation state of Cr = $|(6-3)| = 3$

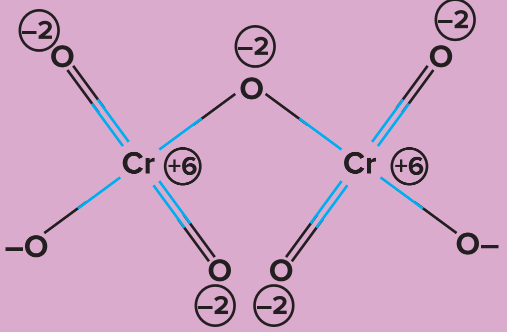
For 2 Cr-atoms (as two Cr-atoms are present in 1 molecule of $K_2Cr_2O_7$, the net change in oxidation state = $(3 \times 2) = 6$

Therefore, the n-factor is 6.

Now, molar mass of $K_2Cr_2O_7 = (39\times2) + (52\times2) + (16\times7)$

$= 294\ g\ mol^{-1}$

Equivalent mass of Cr = $\frac{\text{Molar mass}}{\text{n-factor}} = \frac{294}{6} = 49\ g\ eqv^{-1}$

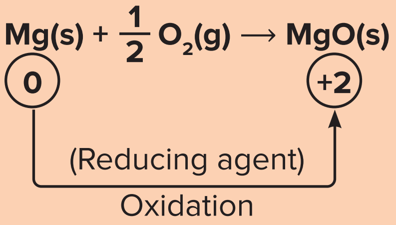


$K_2Cr_2O_7$

Equivalent mass: The number of parts by mass of an element that reacts or displaces from a compound having 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.

The equivalent mass of an element may change with the type of reaction.

Example 1:

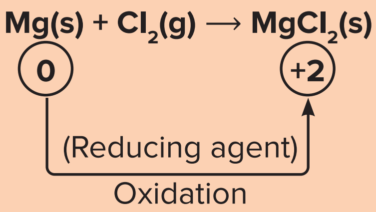


$$\mathbf{Mg(s) + \frac{1}{2}O_2(g) \longrightarrow MgO(s)}$$

- Here, 1 *mol* of Mg reacts with $\frac{1}{2}$ *mol* of O_2.
- In terms of mass, 24 *g* of Mg reacts with 16 *g* of O_2. Therefore, 12 *g* of Mg will react with 8 *g* of O_2. Thus, we can say that 12 parts by weight of Mg is displacing 8 parts by weight of oxygen. So, the equivalent mass of Mg in this reaction is equal to 12 $g\ eqv^{-1}$. Alternatively, equivalent mass can also be calculated as:
- The oxidation state of Mg changes from 0 to +2. So, the n-factor of Mg is 2.

- Therefore, equivalent mass of Mg = $\frac{24}{2}$ = 12 *g eqv*$^{-1}$

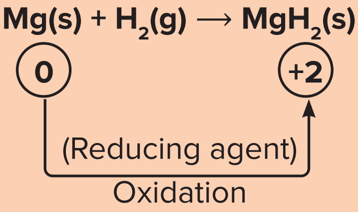
Example 2:



$$\mathrm{Mg(s) + Cl_2(g) \longrightarrow MgCl_2(s)}$$

- 1 *mol* of Mg reacts with 1 *mol* of Cl_2.
- In terms of mass, 24 *g* of Mg reacts with 71 *g* of Cl_2. Therefore, 12 *g* of Mg reacts with 35.5 *g* of Cl_2. Thus, we can say that 12 parts by weight of Mg is displacing 35.5 parts by weight of Cl. So, the equivalent mass of Mg in this reaction is equal to 12 *g eqv*$^{-1}$. Alternatively, equivalent mass can also be calculated as:
- The oxidation state of Mg changes from 0 to +2. So, the n-factor of Mg is 2.
- Therefore, equivalent mass of Mg = $\frac{24}{2}$ = 12 *g eqv*$^{-1}$

Example 3:



$$\mathrm{Mg(s) + H_2(g) \longrightarrow MgH_2(s)}$$

- 1 *mol* of Mg reacts with 1 *mol* of H_2.
- In terms of mass, 24 *g* of Mg reacts with 2 *g* of H_2. Therefore, 12 *g* of Mg will react with 1 *g* of H_2 Thus, we can say that 12 parts by weight of Mg is displacing 1 part by weight of H. So, the equivalent mass of Mg in this reaction is equal to 12 *g eqv*^{1}. Alternatively, equivalent mass can also be calculated as:
- The oxidation state of Mg changes from 0 to +2. So, the n-factor of Mg is 2.
- Therefore, equivalent mass of Mg = $\frac{24}{2}$ = 12 *g eqv*$^{-1}$

Number of Equivalents

Number of equivalents or Number of gram equivalents $= \dfrac{\textbf{Given mass}}{\textbf{Equivalent mass}}$

Number of equivalents or Number of gram equivalents $= \dfrac{\textbf{Given mass}}{\left(\dfrac{\textbf{Molar mass}}{\textbf{n-factor}}\right)}$

Number of equivalents or Number of gram equivalents $= (\textbf{Number of moles}) \times (\textbf{n-factor})$

Note

Equivalent weight in case of redox change can also be understood as the weight of a substance that is responsible for release or gain of 1 mole of electrons.

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Law of Equivalence

It states that one equivalent of a substance always combines with one equivalent of the other.

Or

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

Thus according to the law of equivalence, for the reaction given below:

$$n_1A + n_2B \longrightarrow n_3C + n_4D$$

Where, n_1, n_2, n_3 and n_4 are the stoichiometric coefficients.

Equivalents of A reacted = Equivalents of B reacted = Equivalents of C formed = Equivalents of D formed

Let us understand this with the help of an example.

Example: In the reaction, $3A + 2B \longrightarrow A_3B_2$

We know that,

$$\frac{\text{Number of moles of A}}{\text{Stoichiometric coefficient}} = \frac{\text{Number of moles of B}}{\text{Stoichiometric coefficient}} = \frac{\text{Number of moles of } A_3B_2}{\text{Stoichiometric coefficient}}$$

$$\text{i.e., } \frac{n_A}{3} = \frac{n_B}{2} = \frac{n_{A_3B_2}}{1}$$

Where, n_A, n_B, and $n_{A_3B_2}$ are the moles of A, B and A_3B_2, respectively.

Let 6 *mol* of A and 4 *mol* of B react to give 2 *mol* of A_3B_2.

Thus we can write,

$$\frac{6}{3} = \frac{4}{2} = \frac{2}{1}$$

Therefore, the n-factor of A is 2 (The change in oxidation state is from 0 to +2).

The n-factor of B is 3 (The change in oxidation state is from 0 to –3).

The n-factor of A_3B_2 is 6 (The magnitude of the total charge on cation or anion is equal to 6.)

Since in $\mathbf{A_3B_2 \longrightarrow 3A^{2+} + 2B^{3-}}$

Magnitude of total charge = 3(+2) or 2(–3) = 6

From the above, we can conclude that

$\mathbf{A \longrightarrow A^{2+} + 2e^-}$ **;** 6 *mol* of A releases 12 *mol* of e^-.

$\mathbf{B + 3e^- \longrightarrow B^{3-}}$ **;** 4 *mol* of B accepts 12 *mol* of e^-.

$\mathbf{3A + 2B \longrightarrow A_3B_2}$ **;** For formation of 2 *mol* of A_3B_2, a total of 12 *mol* of e^- are transacted.

Since, Number of equivalent = n_f × Moles

Therefore,

Equivalents of A = 2 × 6 = 12

Equivalents of B = 3 × 4 = 12

Equivalents of A_3B_2 = 6 × 2 = 12

Hence, we can say that Equivalents of A = Equivalents of B = Equivalents of A_3B_2

Calculating the number of equivalents

How many equivalents of hydrogen gas reacts with 56 *g* of nitrogen gas to form ammonia? Also calculate the mass of hydrogen gas reacted.

$N_2(g) \longrightarrow 3H_2(g) + 2NH_3(g)$

Solution

Step 1: Finding n_f of N_2 and H_2

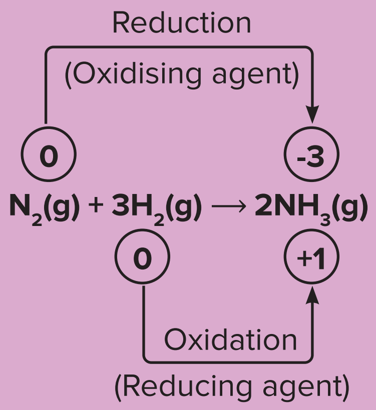
The oxidation state of nitrogen in N_2 is zero, and in NH_3, it is –3.

n-factor = |Oxidation state of the products − Oxidation state of the reactants| × Number of atoms per molecule

Therefore, n-factor of $N_2 = |-3 - 0| \times 2 = 6$

The oxidation state of hydrogen in H_2 is zero, and in NH_3, it is +1.

Therefore, n-factor of $H_2 = |1 - 0| \times 2 = 2$



Step 2: Finding the number of equivalents of N_2 and H_2 and the mass of H_2 required to carry out the reaction

$$\text{Number of moles} = \frac{\text{Given mass}}{\text{Molar mass}}$$

$$\text{Number of moles of } N_2 = \frac{56}{28} = 2\ mol$$

Number of equivalents of N_2 reacted = Number of moles × n_f

Therefore, number of equivalents of N_2 reacted = 2 × 6 = 12

Now, as per the law of equivalence,

Number of equivalents of N_2 reacted = Number of equivalents of H_2 reacted

Therefore, number of equivalents of H_2 reacted = 12

Number of equivalents of H_2 reacted = Number of moles × n_f = n_f × 2 = 12

Thus number of moles of H_2 required = 6 *mol*

Mass of H_2 required = Number of moles × Molar mass of hydrogen

Mass of H_2 = 6 × 2 = 12 *g*

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Normality

It is the number of gram equivalents of solute present in 1 litre of the solution.

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

Relation between Normality and Molarity

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

$$\text{Normality} = \frac{\text{Number of moles of the solute}}{\text{Volume of the solution}(L)} \times \text{n-factor}$$

Thus, **Normality = (Molarity × n-factor)**

Finding the number of equivalents

Calculate the number of milliequivalents in 100 mL of 0.3 N aqueous NaOH solution.

Solution

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

Given volume of the solution = 100 mL = 0.1 L

Given value of normality = 0.3 N

Putting values,

$$0.3 = \frac{\text{Number of equivalents of the solute}}{0.1\ L}$$

Number of equivalents = 0.03

Therefore, the number of milliequivalents of the solute = 0.03 × 1000 = 30

Finding the normality of the solution

Calculate the normality of the solution if 2.65 g of solid Na_2CO_3 is added in 100 mL of the solution.

Solution

Molar mass of Na_2CO_3 = 106 g

$$\mathbf{Na_2CO_3 \longrightarrow 2Na^+ + CO_3^{2-}}$$

Total charge (magnitude) on cation or anion is 2. Therefore, n-factor = 2

Number of equivalents of the solute = (Number of moles of the solute) × n-factor

$$\text{Number of moles} = \frac{\text{Given mass}}{\text{Molar mass}}$$

$$\text{Number of moles} = \frac{2.65}{106} = 0.025\ mol$$

$$\text{Number of equivalents of the solute} = 0.025 \times 2 = 0.05$$

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

$$\text{Normality} = \frac{0.05}{0.1} = 0.5\ N$$

Therefore, the normality of the solution is 0.5 *N*.

Normality of Dilution

Let us assume that the initial solution has normality N_1 and volume V_1 and is diluted to the final solution of volume V_2 and normality N_2.
For dilution,

$$\mathbf{N_1V_1 = N_2V_2}$$

Finding the normality of the final solution

Calculate the normality of the resultant solution formed by adding 1 *L* of 0.1 *N* H_2SO_4 to 2 *L* of water.

Solution

Given data:

- $N_1 = 0.1\ N$
- $V_1 = 1\ L$
- $V_2 = (1\ L + 2\ L) = 3\ L$

We know that, $\mathbf{N_1V_1 = N_2V_2}$

$0.1\ N \times 1\ L = N_2 \times 3\ L$

$N_2 = 0.033\ N$

Therefore, the normality of the resultant solution is 0.033 *N*.

Normality of Mixing

For mixing of two non-reacting solutions of same nature:

$$\mathbf{N_1V_1 + N_2V_2 = N_{Mixing}(V_1 + V_2)}$$

Where,

N_1 = Normality of solution 1, N_2 = Normality of solution 2, V_1 = Volume of solution 1

V_2 = Volume of solution 2 , $V_1 + V_2$ = Volume of the final solution after mixing

N_{Mixing} = Normality of the final solution on mixing solutions 1 and 2

Finding the normality of the final solution

200 *mL* of 0.2 *N* HCl and 200 *mL* of 0.4 *N* HCl are mixed. Calculate the normality of the resultant solution.

Solution

Given data:

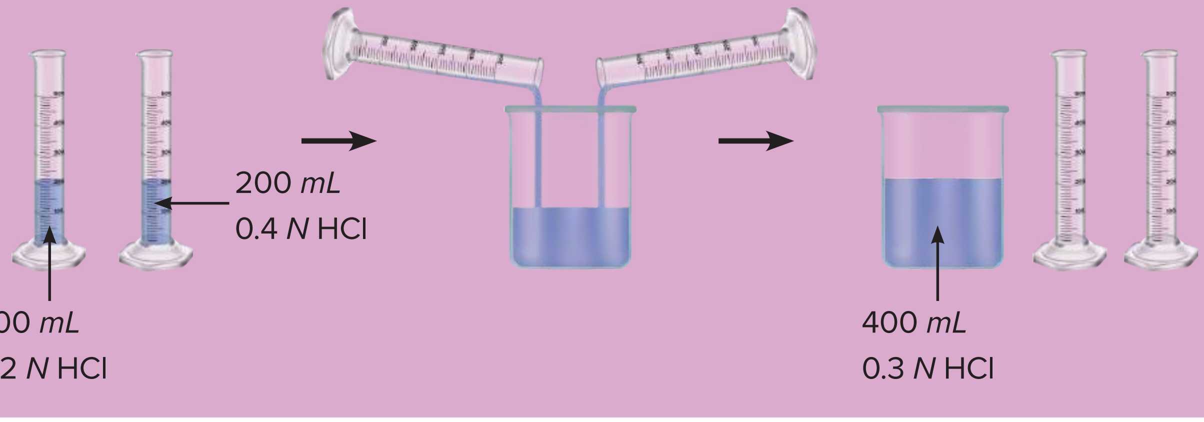
- $N_1 = 0.2\ N$
- $N_2 = 0.4\ N$
- $V_1 = 200\ mL$
- $V_2 = 200\ mL$
- $V_1 + V_2 = 400\ mL$

We know that,

$$N_{mixing} = \frac{N_1V_1 + N_2V_2}{V_1 + V_2}$$

$$N_{mixing} = \frac{0.2 \times 200 + 0.4 \times 200}{400} = 0.3\ N$$

Therefore, the normality of the resultant solution is 0.3 *N*.



Finding the normality of the final solution

Calculate the normality of H^+ in the resultant solution made by mixing 200 *mL* of 0.2 *N* HCl and 500 *mL* of 0.1 *N* H_2SO_4 .

Solution

Given data:

- Normality of HCl solution (N_1) = Normality of H^+ from HCl = 0.2 *N*
- Normality of H_2SO_4 solution (N_2) = Normality of H^+ from H_2SO_4 = 0.1 *N*

- Volume of HCl solution (V_1) = 200 *mL*
- Volume of H_2SO_4 solution (V_2) = 500 *mL*
- Volume of the final solution = $V_1 + V_2$ = 200 *mL* + 500 *mL* = 700 *mL*

Using the formula,

$$\mathbf{N_{mixing} = \frac{N_1V_1 + N_2V_2}{V_1 + V_2}}$$

$$N_{mixing} = \frac{0.2 \times 200 + 0.1 \times 500}{700} = 0.128\ N$$

Therefore, the normality of H^+ in the resulting solution is 0.128 *N*.

Finding the normality of the final solution

Calculate the normality of H^+ or OH^- in the resultant solution having 500 *mL* of 0.1 *N* H_2SO_4 and 250 *mL* of 0.1 *N* NaOH.

Solution

Given data:

Milliequivalents of H^+ = Normality × Volume (*mL*)

Milliequivalents of H^+ = 0.1 × 500 = 50

Milliequivalents of OH^- = Normality × Volume (*mL*)

Milliequivalents of OH^- = 0.1 × 250 = 25

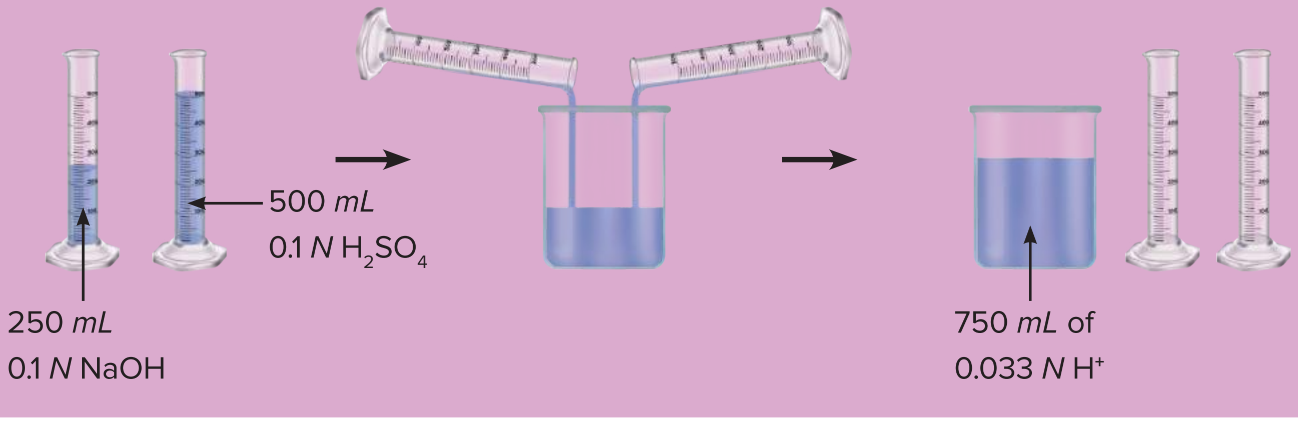
Total volume = $V_1 + V_2$ = 500 + 250 = 750 *mL*

Here, H^+ is in excess amount. Therefore, the solution will be acidic in nature.

$$\mathbf{N_{mixing} = \frac{|N_1V_1 - N_2V_2|}{V_1 + V_2}}$$

$$N_{mixing} = \frac{|50 - 25|}{750} = 0.033\ N$$

Therefore, the normality of H^+ in the resulting solution is 0.033 *N*.



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Redox Titrations

Titration is the slow addition of a solution of a known concentration called as the titrant, to a known volume of the another solution of unknown concentration called as the analyte, until the reaction reaches the endpoint, which is often indicated by a change of colour.

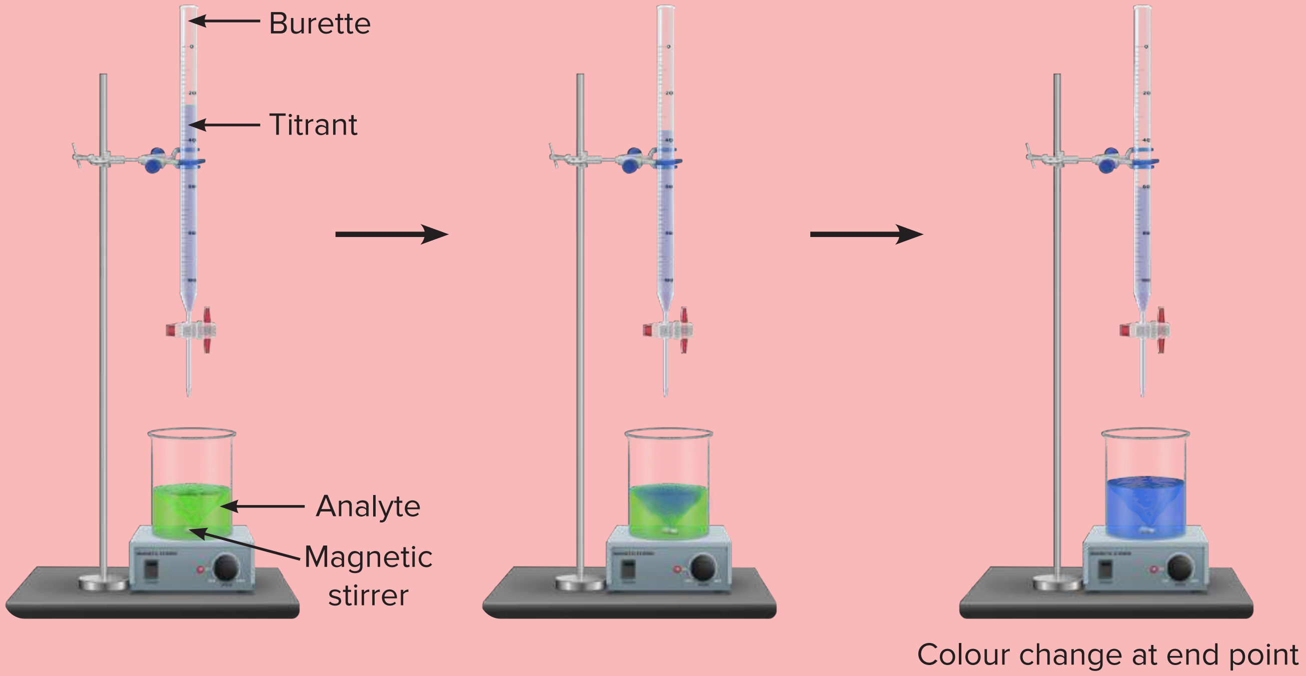


Fig. 2: Illustration of titration process

Types of titrations:

1. Acid-base titration
2. Redox titration

Equivalence point

It is a point at which the number of equivalents of the analyte = number of equivalents of the titrant

Analyte: It is the solution with unknown concentration.

Titrant: It is the solution with known concentration.

In redox titration, an oxidising agent (O.A.) reacts with a reducing agent (R.A.).

$$\textbf{O.A. + R.A.} \longrightarrow \textbf{Products}$$

At the equivalence point,

Gram equivalents of the oxidising agent (O.A.) = Gram equivalents of reducing agent (R.A.)

Important list of half reactions	
$Cr_2O_7^{2-} \longrightarrow Cr^{3+}$ (Acidic medium)	$NO_3^- \longrightarrow NO$
$MnO_4^- \longrightarrow Mn^{2+}$ (Acidic medium)	$NO_3^- \longrightarrow N_2O$

$MnO_4^- \longrightarrow MnO_2$ (Faintly alkaline/Neutral medium)	$NO_3^- \longrightarrow NH_4^+$
$MnO_4^- \longrightarrow MnO_4^{2-}$ (Highly basic medium)	$Na^+ \longrightarrow Na$
$IO_3^- \longrightarrow I^-$	$Fe^{2+} \longrightarrow Fe^{3+}$
$MnO_2 \longrightarrow Mn^{2+}$ (Acidic)	$Sn^{2+} \longrightarrow Sn^{4+}$
$I_2 \longrightarrow I^-$	$S_2O_3^{2-} \longrightarrow S_4O_6^{2-}$
$ClO^- \longrightarrow Cl^-$	$S^{2-} \longrightarrow S$
$H_2O_2 \longrightarrow H_2O$	$NO_2^- \longrightarrow NO_3^-$
$NO_3^- \longrightarrow NO_2^-$	$H_2O_2 \longrightarrow O_2$
$NO_3^- \longrightarrow NO_2$	$C_2O_4^{2-} \longrightarrow CO_2$
$NO_3^- \longrightarrow NO$	$Zn \longrightarrow ZnO_2$ (Basic medium)
$NO_3^- \longrightarrow NO_2^-$	$H_2O_2 \longrightarrow O_2$

Table 1: List of important half reactions

CHEMISTRY

REDOX REACTIONS

REDOX TITRATIONS

NOTES

What you already know

- Calculation of n-factor in reactions
- Equivalent mass
- Number of equivalents
- Law of equivalence
- Normality
- Redox titrations

What you will learn

- Redox titrations
- Back titrations
- Double indicator titrations
- Iodometric titrations and Iodimetric titrations

Based on redox titration

A solution of 10 *mL* of 0.1 *M* $FeSO_4$ was titrated with $KMnO_4$ solution in an acidic medium. What is the amount of $KMnO_4$ used?

(a) 5 *mL* of 0.1 *M*

(b) 10 *mL* of 0.1 *M*

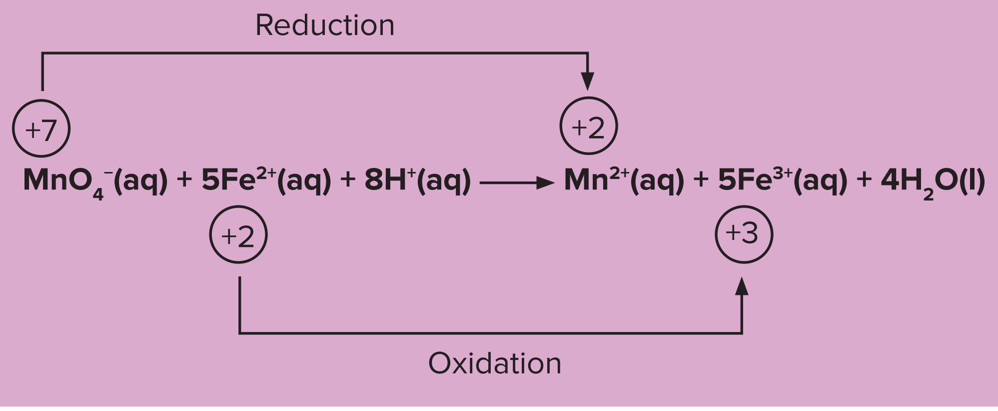
(c) 10 *mL* of 0.5 *M*

(d) 10 *mL* of 0.02 *M*

Solution

The reaction for the given titration is as follows:

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



During titration, Fe^{2+} changes to Fe^{3+}. Therefore, n-factor (n_f) = 3 − 2 = 1
For MnO_4^-, the oxidation state of Mn is calculated as follows:
Take the oxidation state of Mn as 'x'.
$x + (-2)4 = -1 \Rightarrow x = -1 + 8 \Rightarrow x = +7$
MnO_4^- changes to Mn^{2+}. Therefore, n-factor (n_f) = 7 − 2 = 5

By the law of equivalence, $N_1V_1 = N_2V_2$ ... (1)
Where, $\mathbf{N_1}$ = Normality of $KMnO_4$
$\mathbf{V_1}$ = Volume of $KMnO_4$
$\mathbf{N_2}$ = Normality of $FeSO_4$
$\mathbf{V_2}$ = Volume of $FeSO_4$

Equation 1 can be written as $(n_f)_1M_1\,V_1 = (n_f)_2M_2\,V_2$ ... (2)
Where, $\mathbf{(n_f)_1}$ = n-factor of $KMnO_4$
$\mathbf{(n_f)_2}$ = n-factor of $FeSO_4$
$\mathbf{M_1}$ = Molarity of $KMnO_4$
$\mathbf{M_2}$ = Molarity of $FeSO_4$

Given: $(n_f)_1 = 5$
$(n_f)_2 = 1$
$M_2 = 0.1\ M$
$V_2 = 10\ mL$
Substituting the values in equation 2,
$5 \times M_1 \times V_1 = 1 \times 0.1 \times 10$
$M_1 \times V_1 = 0.2$

As molarity and volume are given in the options, we can find the product of each of them.

(a) $M_1 \times V_1 = 5 \times 0.1 = 0.5$
(b) $M_1 \times V_1 = 10 \times 0.1 = 1$
(c) $M_1 \times V_1 = 10 \times 0.5 = 5$
(d) $M_1 \times V_1 = 10 \times 0.02 = 0.2$
As option (d) has the same $M_1 \times V_1$, 10 *mL* of 0.02 *M* $KMnO_4$ has been used for the titration.
Hence, option (d) is the correct answer.

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Redox Titrations

Titrations involving potassium permanganate ($KMnO_4$)

Potassium permanganate ($KMnO_4$) is a strong oxidising agent. It is used in the estimation of many reducing agents such as Fe^{2+} ions, oxalate ions, etc. Consider the following reaction for the titration of MnO_4^- against Fe^{2+} ions.

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$
$$[Fe^{2+} \rightarrow Fe^{3+} + e^-] \times 5$$
$$\mathbf{MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O}$$

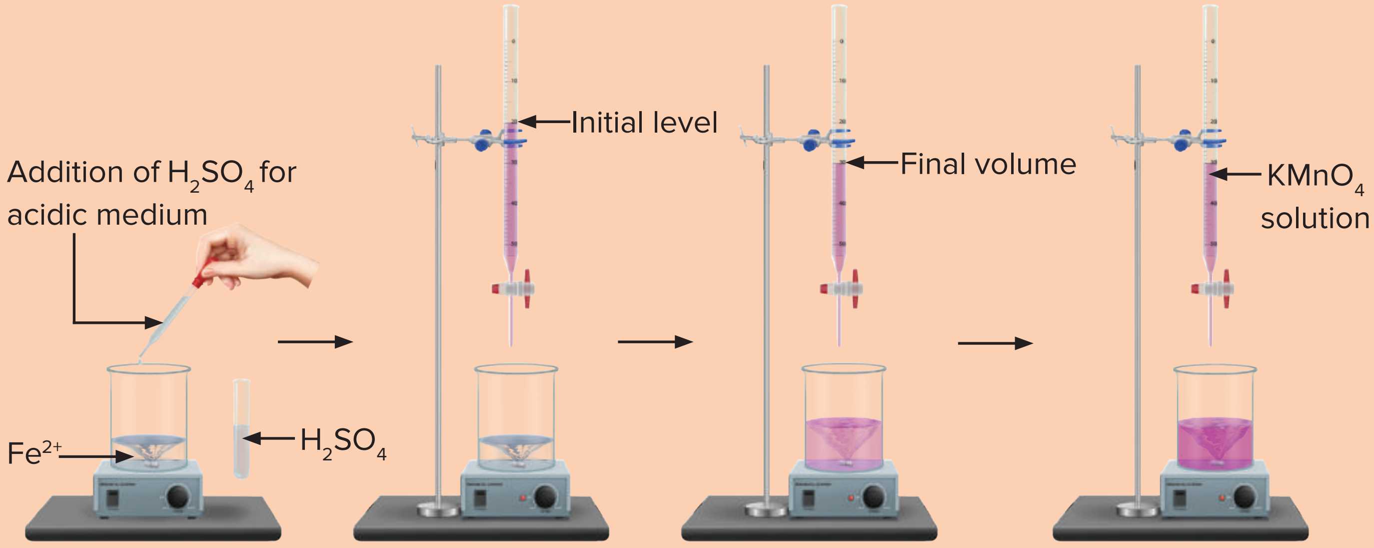
From the given reaction, it is clearly understood that 1 *mol* of MnO_4^- can oxidise 5 *mol* of Fe^{2+} into 5 *mol* of Fe^{3+}. This proves that $KMnO_4$ is a strong oxidising agent. It acts as an oxidising agent in **both acidic and basic media.**

In these titrations, no indicator is used because $KMnO_4$ itself is deeply coloured. So, $KMnO_4$ acts as a **self indicator** and when it is titrated against a reducing agent, its colour disappears. As soon as the reducing agent is used up, the additional single drop of potassium permanganate gives a tinge of pink colour to the solution.

When $KMnO_4$ is titrated against Fe^{2+} in an acidic medium, the purple colour of $KMnO_4$ vanishes completely as all the ions are used up for the reduction of Fe^{2+} to Fe^{3+} primarily. Further addition of a drop of $KMnO_4$ gives pink colour to the solution due to the presence of slight extra $KMnO_4$. Therefore, without adding an external indicator, the endpoint can be determined using $KMnO_4$. The reaction for the titration is as follows:

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

Generally, H_2SO_4 is used for acidification. The usage of HCl is avoided as $KMnO_4$ oxidises HCl to Cl_2 gas i.e. the oxidation number of Cl changes from −1 to 0. However, in H_2SO_4, the oxidation state of S is +6, which is the maximum valency of sulphur as it is a group 16 element. Therefore, it cannot be oxidised further.



Persistent pink colour indicates the end point

Dark pink colour indicates the addition of extra $KMnO_4$ added

Fig. 1: Titration of Fe^{2+} with $KMnO_4$ in acidic medium

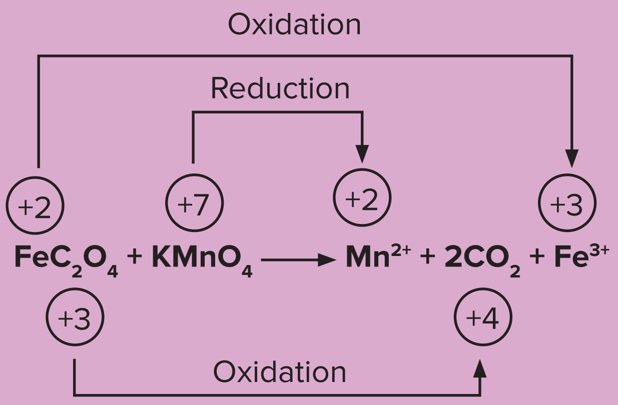
Based on redox titration

Calculate the number of moles of $KMnO_4$ required in an acidic medium to completely oxidise 5 moles of ferrous oxalate.

Solution

Here, ferrous oxalate (FeC_2O_4) is acting as a reducing agent and $KMnO_4$ as an oxidising agent. The reaction for the given titration is as follows:

$$\mathbf{FeC_2O_4 + KMnO_4 \longrightarrow Fe^{3+} + 2CO_2 + Mn^{2+}}$$



During titration, Fe^{2+} changes to Fe^{3+}. Therefore, n-factor (n_f) = 3 − 2 = 1

$C_2O_4^{2-}$ changes to $2CO_2$. Therefore, the n-factor is determined as follows: We need to find the oxidation states of carbon in both $C_2O_4^{2-}$ and $2CO_2$.

$C_2O_4^{2-}$

Take the oxidation state of carbon as “x”.

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

$2x = -2 + 8$

$x = +3$

The oxidation state of carbon in $C_2O_4^{2-}$ is +3.

CO_2

Take the oxidation state of carbon as ‘x’.

Thus,

$x - 4 = 0$

$x = +4$

The oxidation state of carbon in CO_2 is +4.

As $C_2O_4^{2-}$ changes to $2CO_2$, n-factor = $(4 - 3)2 = 2$

(We are multiplying it by 2 due to the presence of two carbons)

The overall n-factor for FeC_2O_4 is the sum of two n-factors $(n_f)_1 = 1 + 2 = 3$

MnO_4^- changes to Mn^{2+}. Therefore, n-factor $(n_f)_2 = |2 - 7| = 5$

By the law of equivalence, Number of equivalence of FeC_2O_4 = Number of equivalence of $KMnO_4$

$(n_f)_1$ × Number of moles of FeC_2O_4 = $(n_f)_2$ × Number of moles of $KMnO_4$ ... (3)

Given number of moles of FeC_2O_4 = 5

Substituting the values in equation (3),

3 × 5 = 5 × Number of moles of $KMnO_4$

Thus, the number of moles of $KMnO_4$ = 3

Hence, 3 *mol* of $KMnO_4$ are required in an acidic medium to completely oxidise 5 *mol* of ferrous oxalate.

Based on redox titration

Find the number of moles of $KMnO_4$ needed to oxidise 1 *mol* of Cu_2S in an acidic medium.

$$\mathbf{KMnO_4(aq) + Cu_2S(aq) \longrightarrow Mn^{2+}(aq) + Cu^{2+}(aq) + SO_2(g)}$$

Solution

In the given reaction, Cu_2S changes to Cu^{2+} and SO_2.

For Cu, as the oxidation state changes from +1 to +2, the n-factor is $(2 - 1)2 = 2$

For S, as the oxidation state changes from −2 to +4, the n-factor is $4 - (-2) = 6$

$$\mathbf{KMnO_4(aq) + Cu_2S(aq) \longrightarrow Mn^{2+}(aq) + Cu^{2+}(aq) + SO_2(g)}$$

Therefore, the total n-factor of Cu_2S, $(n_f)_1 = 2 + 6 = 8$

Also, the n-factor of $KMnO_4$ $(n_f)_2 = 5$

By the law of equivalence, Number of equivalence of Cu_2S = Number of equivalence of $KMnO_4$

$(n_f)_1 \times$ Number of moles of Cu_2S = $(n_f)_2 \times$ Number of moles of $KMnO_4$ … (4)

Given number of moles of Cu_2S = 1

Substituting the values in equation (4),

$8 \times 1 = 5 \times$ Number of moles of $KMnO_4$

Thus, the number of moles of $KMnO_4 = \frac{8}{5} = 1.6$

Hence, 1.6 moles of $KMnO_4$ are needed to oxidise 1 *mol* of Cu_2S in an acidic medium.

Titrations involving potassium dichromate ($K_2Cr_2O_7$)

$K_2Cr_2O_7$ is used as an oxidising agent in an acidic medium for redox titrations. It is relatively a weaker oxidising agent when compared to $KMnO_4$. Unlike $KMnO_4$, it **does not act as a self indicator** because no dramatic auto-colour change occurs in its titrations. Therefore, external indicators such as **diphenylamine** are commonly used.

For example, $K_2Cr_2O_7$ oxidises the diphenylamine indicator just after the equivalence point, giving an intense blue colour indicating the endpoint. The chemical equation showing $Cr_2O_7^{2-}$ as an oxidising agent is as follows:

$$\mathbf{\overset{\substack{\text{(Orange)}\\ \uparrow}}{Cr_2O_7^{2-}}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)}$$

For acidification, H_2SO_4 and HCl can be used since $K_2Cr_2O_7$ does not oxidise HCl at room temperature. When $K_2Cr_2O_7$ is titrated against Fe^{2+} in an acidic medium, the orange colour of $K_2Cr_2O_7$ vanishes completely as all the ions have been used up primarily for the oxidation of Fe^{2+} to Fe^{3+}. Further addition of a drop of $K_2Cr_2O_7$ gives an intense blue colour to the solution due to the oxidation of diphenylamine indicator. The reaction for the titration is as follows:

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

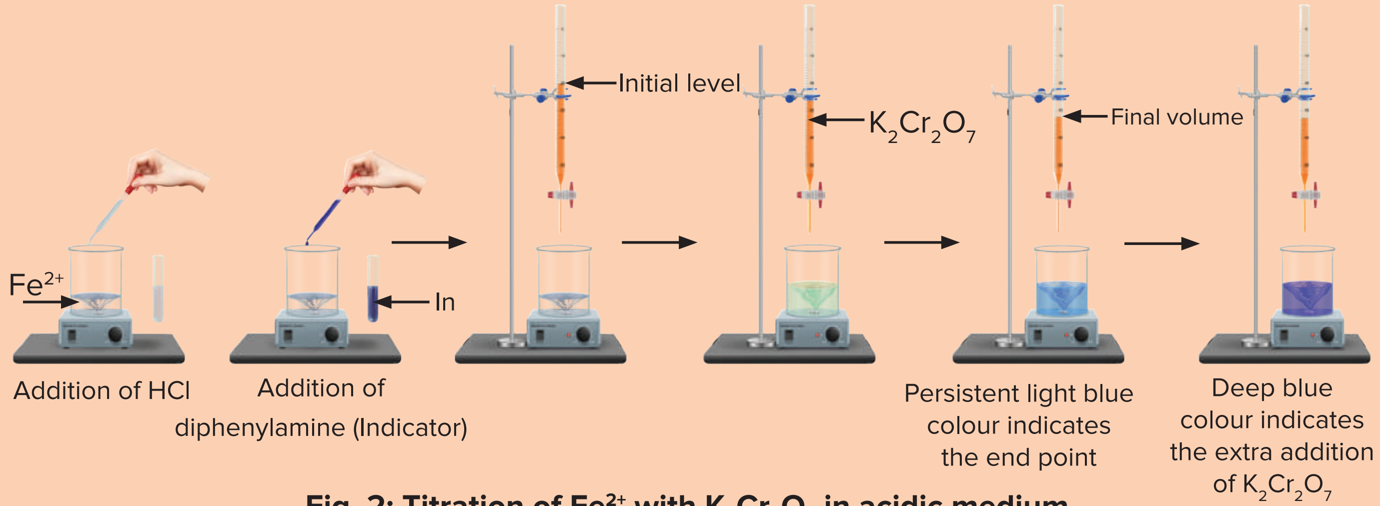


Fig. 2: Titration of Fe^{2+} with $K_2Cr_2O_7$ in acidic medium

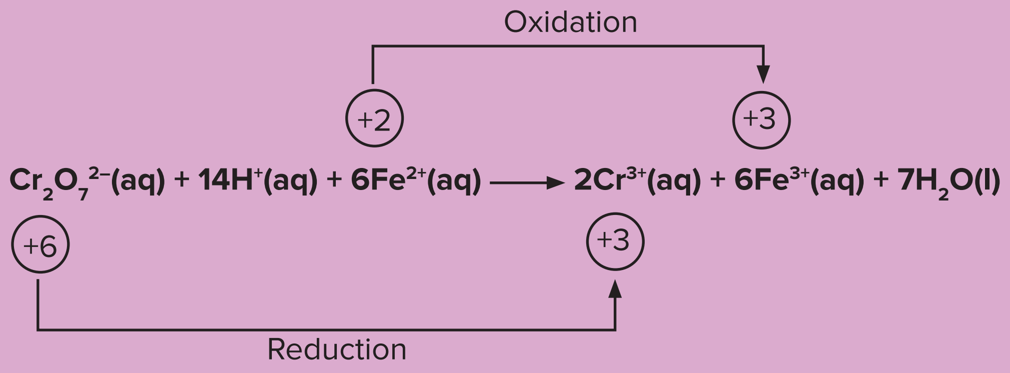
Calculating the volume

Calculate the volume of 0.1 *M* $K_2Cr_2O_7$ required to oxidise 35 *mL* of 0.5 *M* $FeSO_4$ solution.

Solution

The reaction for the given titration is as follows:

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



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

In $K_2Cr_2O_7$, the oxidation state of Cr changes from +6 to +3.
As there are 2 chromium atoms, the n-factor of $K_2Cr_2O_7 = |3 - 6| \times 2 = 6$
In $FeSO_4$, the oxidation state of Fe changes from +2 to +3.
Therefore, the n-factor of $FeSO_4 = 3 - 2 = 1$

By the law of equivalence, $N_1V_1 = N_2V_2$ ... (5)
Where, $\mathbf{N_1}$ = Normality of $K_2Cr_2O_7$
$\mathbf{V_1}$ = Volume of $K_2Cr_2O_7$
$\mathbf{N_2}$ = Normality of $FeSO_4$
$\mathbf{V_2}$ = Volume of $FeSO_4$

Equation 5 can be written as, $(n_f)_1M_1V_1 = (n_f)_2M_2V_2$ ... (6)
Where, $\mathbf{(n_f)_1}$ = n-factor of $K_2Cr_2O_7$
$\mathbf{(n_f)_2}$ = n-factor of $FeSO_4$
$\mathbf{M_1}$ = Molarity of $K_2Cr_2O_7$

M_2 = Molarity of $FeSO_4$

Given, $(n_f)_1 = 6$; $(n_f)_2 = 1$
$M_1 = 0.1$; $M_2 = 0.5$;
$V_2 = 35\ mL$

Substituting the values in equation 6,

$$6 \times 0.1 \times V_1 = 1 \times 0.5 \times 35$$

$$V_1 = \frac{1 \times 0.5 \times 35}{6 \times 0.1}$$

$$V_1 = 29.166\ mL$$

The volume of 0.1 *M* $K_2Cr_2O_7$ required to oxidise 35 *mL* of 0.5 *M* $FeSO_4$ solution is 29.166 *mL*.

BOARDS MAIN

Back Titrations

A back titration is a titration method where the **concentration of an analyte is determined by reacting it with a known amount of excess reagent,** whereas a direct titration directly measures the concentration of the unknown compound.

Let a 10 *g* impure sample of Z only have 7.65 *g* of Z and the remaining 2.35 *g* is impurity. To determine the exact quantity of impurity, the impure sample 'Z' is made to react with compound 'X', which is taken in excess to form product 1 along with some quantities of X.

Reaction 1: Z + X (Excess) → Product 1

(Even though Z contains impurities, X reacts only with pure Z)

Then the remaining quantity of X after the reaction is allowed to react with the known amount of Y to form product 2.

Reaction 2: X (Remaining) + Y (Known) → Product 2

We can determine the quantity of X reacted with Z from the quantity of Y added and the total amount of X is known. Using the quantity of X reacted, it is possible to find the amount of Z reacted, thereby the amount of impurity.

Steps involved

(1) The substance or solution of an unknown concentration is made to react with a known volume and concentration of an intermediate reactant solution.
Example: 4 *g* of contaminated chalk, $CaCO_3$ (unknown concentration) + 200 *mL*, 0.5 *N* HCl (known volume and concentration)
Here, the chalk is the analyte.

(2) The reaction goes past the equivalence point.

(3) The amount of intermediate reactant is in excess of that required for completing the reaction with an analyte.

(4) After completing the reaction with an analyte, the resultant solution containing an excess of intermediate reactants is titrated with a known volume and concentration of a titrant.

(a) Let us assume the titrant as 50 *mL* of 0.5 *N* NaOH.
By the law of equivalence, $N_1V_1 = N_2V_2$ ... (7)
Where, N_1 = Normality of HCl
V_1 = Volume of HCl
N_2 = Normality of NaOH
V_2 = Volume of NaOH
Given, $N_1 = 0.5$
$V_2 = 50\ mL$
$N_2 = 0.5$
Substituting the values in equation 7,
$0.5 \times V_1 = 0.5 \times 50$
$V_1 = 50\ mL$
Thus, the volume of excess HCl = 50 *mL*
We know that,

(b) *mEq*. of excess HCl = *mEq.* of titrant (NaOH); where, *mEq.* = Milliequivalent
= 0.5 × 50
= 25 *mEq.*

(c) The determination of excess volume or excess *mEq.* of an intermediate reactant allows us to determine the volume or *mEq.* of the intermediate reactant that is reacted with an analyte.
mEq. of chalk = Total *mEq.* of HCl – *mEq.* of excess HCl
mEq. of chalk = (0.5 × 200) − 25
mEq. of chalk = *mEq.* of HCl used for chalk = 75 ... (8)

(d) n-factor × number of millimoles of chalk = 75
(n-factor of chalk = 2)
$$\text{Number of millimole of chalk} = \frac{75}{2} = 37.5$$

$$\text{Number of millimoles of chalk} = \frac{\text{Mass of chalk}}{\text{Molecular weight of chalk}} \times 1000$$

$$\text{Therefore, mass of chalk} = \frac{\text{Number of millimoles of chalk} \times \text{Molecular weight of chalk}}{1000}$$

$$\text{Mass of chalk} = \frac{37.5 \times 100}{1000} = 3.75\ g$$

As there are 4 *g* of contaminated chalk, the **chalk contains 0.25 *g* of impurities in it.**

Based on back titrations

A 60 *g* sample of $Ca(OH)_2$(aq) is dissolved in 100 *mL* of 0.5 *N* HCl(aq) solution. The excess of HCl(aq) is titrated with 20 *mL* of 0.3 *N* NaOH(aq). Calculate the % purity of $Ca(OH)_2$(aq) sample.

Solution

mEq. of NaOH = 0.3 × 20 = 6 (*mEq*. = Volume (*mL*) × Normality)

mEq. of NaOH = *mEq*. of excess HCl = 6

Total *mEq*. of HCl = (0.5 × 100) = 50

mEq. of HCl reacted with $Ca(OH)_2$ = 50 – 6 = 44

mEq. of HCl reacted with $Ca(OH)_2$ = *mEq*. of $Ca(OH)_2$ = 44 ... (9)

n-factor × Number of millimoles of $Ca(OH)_2$ = 44

(n-factor of $Ca(OH)_2$ = 2)

Number of millimoles of $Ca(OH)_2 = \frac{44}{2} = 22$

$$\text{Number of millimoles of } Ca(OH)_2 = \frac{\text{Mass of } Ca(OH)_2}{\text{Molar mass of } Ca(OH)_2} \times 1000$$

$$\text{Therefore, mass of } Ca(OH)_2 = \frac{\text{Number of millimoles of } Ca(OH)_2 \times \text{Molar mass of } Ca(OH)_2}{1000}$$

$$= \frac{22 \times 74}{1000} = 1.628\ g$$

$$\text{Hence, \% purity of } Ca(OH)_2 \text{ sample} = \frac{1.628}{60} \times 100$$

$$= 2.71\%$$

Hence, % purity of $Ca(OH)_2(aq)$ sample is 2.71%.

BOARDS MAIN

Double Indicator Titrations

In the **titration** of an alkali mixture, e.g., NaOH + Na_2CO_3 or (KOH + Na_2CO_3) and (Na_2CO_3 + $NaHCO_3$) with a strong acid, the two **indicators**, phenolphthalein (HPh) and methyl orange (MeOH), are used. The **indicator** HPh is a weak organic acid and gives an endpoint between pH 8.3 to 13, while MeOH is a weak base that gives an endpoint between 3.2 and 4.4. Consider NaOH, Na_2CO_3 and $NaHCO_3$ solutions in a beaker. When we add HCl to it, the following reactions occur.

Reaction 1: $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$
Reaction 2: $Na_2CO_3(aq) + HCl(aq) \rightarrow NaCl(aq) + NaHCO_3(aq)$
Reaction 3: $NaHCO_3(aq) + HCl(aq) \rightarrow NaCl(aq) + CO_2(g) + H_2O(l)$

As NaOH is a strong base among all, the extent of the reaction will be high for the first reaction, followed by the second and the third reaction. A suitable indicator is employed to identify the completion of individual reactions. The indicator selected is based on the product formed.

Reaction 1: $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$

As the product NaCl is a salt, we can get the endpoint using any of the two indicators.

Reaction 2: $Na_2CO_3(aq) + HCl(aq) \rightarrow NaCl(aq) + NaHCO_3(aq)$

As the intermediate product, $NaHCO_3$ is a basic salt, the pH value remains above 7. The phenolphthalein indicator is used because the colour transition range is between 8.2 and 13.

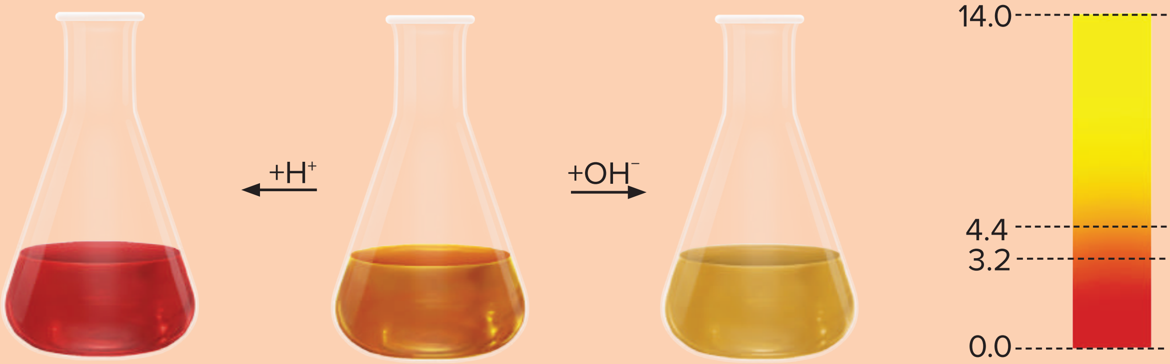
Phenolphthalein in pH range of 0 - 8.2 and 13 - 14

Phenolphthalein in pH range of 8.2 - 13

Fig. 3: Illustration of colour transition range of phenolphthalein indicator

Reaction 3: $NaHCO_3(aq) + HCl(aq) \rightarrow NaCl(aq) + CO_2(g) + H_2O(l)$

$CO_2(g) + H_2O$ is acidic. Therefore, the pH of the solution further decreases. Hence, the suitable indicator is methyl orange (MeOH), because the colour transition range is between 3.2 and 4.4.



Methyl orange in pH range of 0 - 3.2

Methyl orange in pH range of 3.2 - 4.4

Methyl orange in pH range of 4.4 - 14

Fig. 4: Illustration of colour transition range of methyl orange indicator

The neutralisation of sodium bicarbonate is detected by methyl orange, not by phenolphthalein.

Indicator: Phenolphthalein

mEq. of HCl = *mEq*. of NaOH + *mEq*. of Na_2CO_3

Note

Here, the n-factor of Na_2CO_3 is 1, as only 1 Na^+ ion is replaced by the acid.

Indicator: Methyl orange

mEq. of HCl = *mEq*. of NaOH + *mEq*. of Na_2CO_3 + *mEq*. of $NaHCO_3$

Note

Here, the n-factor of Na_2CO_3 is 2, as 2 Na^+ ions are replaced by the acid.

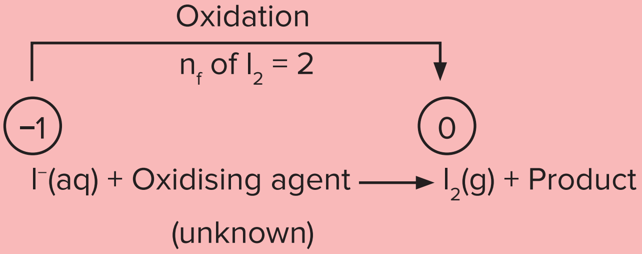
BOARDS MAIN ADVANCED

Iodometric Titration and Iodimetric Titration

Iodometric titration

Iodometric titration is used to **determine the strength or the concentration of an oxidising agent.** The titration is carried out in two steps.

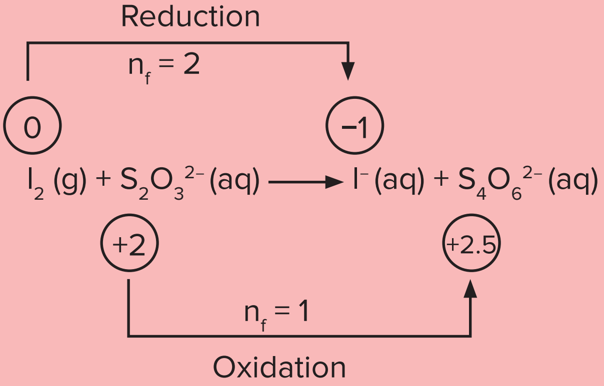
Step 1: The unknown oxidising agent is made to react with I^-. Thus, the following reaction occurs.



$$I^-(aq) + \text{Oxidising agent} \longrightarrow I_2(g) + \text{Product}$$

The unknown oxidising agent oxidises I^- to I_2.
From the equation, Equivalence of oxidising agent = Equivalence of I_2
Also, the n-factor of I_2 in $2I^-(aq) \rightarrow I_2(g) = |0 - (-1)| \times 2 = 2$

Step 2: The iodine liberated is then titrated with a standard hypo solution ($Na_2S_2O_3$). The reaction for the same is as follows:



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

Equivalence of I_2 = Equivalence of $S_2O_3^{2-}$

The oxidation state of S in $S_2O_3^{2-}$
Take the oxidation state of S as ‘x’.
$2x + 3(-2) = -2$
$2x = -2 + 6$
$2x = 4 \Rightarrow x = 2$
Oxidation state of S in $S_2O_3^{2-} = +2$

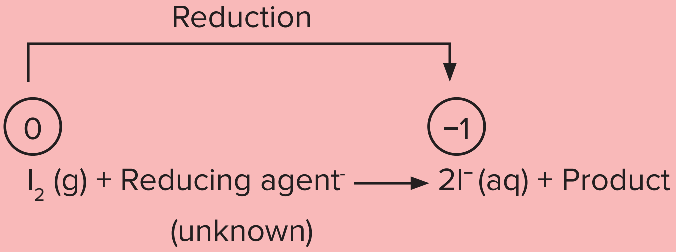
The oxidation state of S in $S_4O_6^{2-}$
Take the oxidation state of S as ‘x’.
$4x + 6(-2) = -2$
$4x = -2 + 12$
$4x = 10 \Rightarrow x = 2.5$
Oxidation state of S in $S_4O_6^{2-} = +2.5$

The n-factor of $S_2O_3^{2-}(aq) = (2.5 - 2)2 = 1$
The n-factor of $I_2(g) = |0 - (-1)| \times 2 = 2$
In both cases, the n-factor of I_2 is the same.
By combining both the steps, we can write it as follows:

Equivalence of oxidising agent = Equivalence of I_2 = Equivalence of $S_2O_3^{2-}$

Iodimetric titration

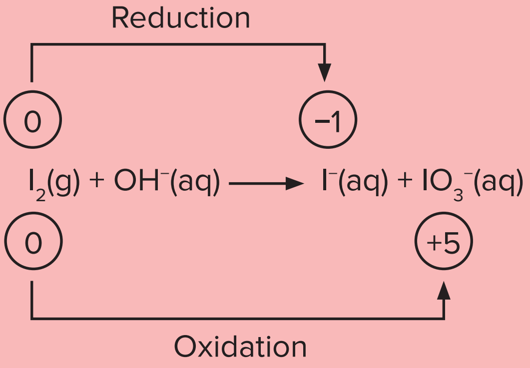
It is used to **determine the strength or the concentration of a reducing agent** which is directly titrated with I_2. Iodimetric titration is carried out in a single step. The unknown reducing agent is directly titrated with I_2. The reaction is given as follows:



$$\overset{0}{I_2}(g) + \underset{\text{(unknown)}}{\text{Reducing agent}} \longrightarrow 2\overset{-1}{I^-}(aq) + \text{Product}$$

Both iodometric and iodimetric titrations are carried out in an acidic medium only as I_2 undergoes a disproportionation reaction in the basic medium as follows:

$$\mathbf{I_2(g) + OH^-(aq) \longrightarrow I^-(aq) + IO_3^-(aq)}$$



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

CHEMISTRY

REDOX REACTIONS

SPECIAL CASES

NOTES

What you already know

- Redox titrations
- Back titrations
- Double indicator titrations
- Iodometric titrations and iodimetric titrations

What you will learn

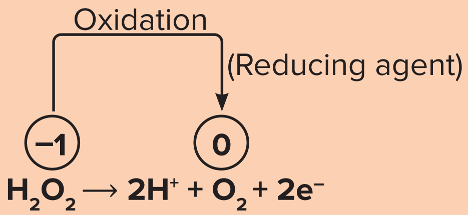
- Volume strength of H_2O_2
- Strength of oleum
- Concept of available chlorine
- Hardness of water
- Degree of hardness

BOARDS **MAIN** **ADVANCED**

Volume Strength of H_2O_2

The oxidation state of oxygen in oxide is −2 and that in peroxide is −1.

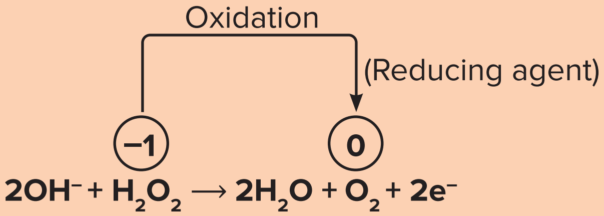
H_2O_2 as a reducing agent in acidic medium



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

The oxidation state of oxygen is changing from −1 in H_2O_2 to 0 in O_2.
Hence, H_2O_2 will act as a reducing agent.
n-factor = $|$Oxidation state of product − Oxidation state of reactant$|$ × Number of atoms
n-factor of $H_2O_2 = |0 - (-1)| \times 2 = 2$
Hence, the n-factor of H_2O_2 as a reducing agent in an acidic medium is 2.

H_2O_2 as a reducing agent in basic medium



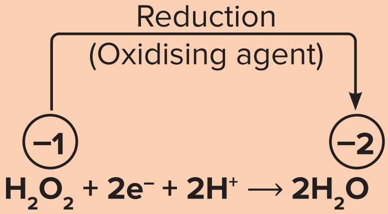
$$2OH^- + H_2O_2 \longrightarrow 2H_2O + O_2 + 2e^-$$

The oxidation state of oxygen is changing from −1 in H_2O_2 to 0 in O_2
Hence, H_2O_2 will act as a reducing agent.

n-factor = |Oxidation state of product − Oxidation state of reactant| × Number of atoms

n-factor of H_2O_2 = $|0 - (-1)| \times 2 = 2$

H_2O_2 as an oxidising agent in acidic medium



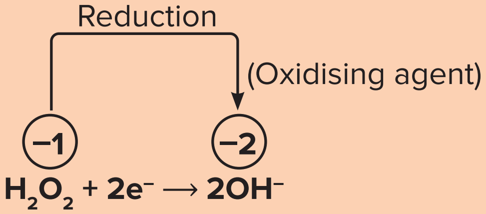
$$H_2O_2 + 2e^- + 2H^+ \longrightarrow 2H_2O$$

The oxidation state of oxygen is changing from −1 in H_2O_2 to −2 in H_2O.

n-factor = |Oxidation state of product − Oxidation state of reactant| × Number of atoms

n-factor of H_2O_2 = $|-2 - (-1)| \times 2 = 2$

H_2O_2 as an oxidising agent in basic medium



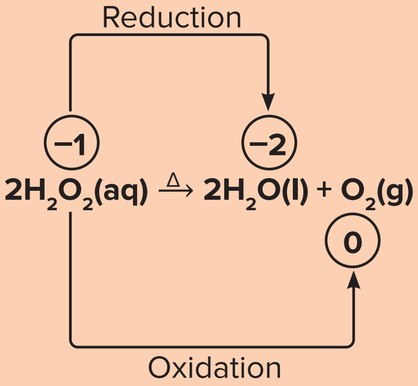
$$H_2O_2 + 2e^- \longrightarrow 2OH^-$$

The oxidation state of oxygen is changing from −1 in H_2O_2 to −2 in OH^-.

n-factor = |Oxidation state of product - Oxidation state of reactant| × Number of atoms

n-factor of H_2O_2 = $|-2 - (-1)| \times 2 = 2$

Decomposition of H_2O_2



$$2H_2O_2(aq) \xrightarrow{\Delta} 2H_2O(l) + O_2(g)$$

Disproportionation redox reaction: The reaction in which same element undergoes oxidation and reduction simultaneously.

Volume strength of H_2O_2

The **concentration of H_2O_2** is usually represented in terms of volume (vol). If a sample of H_2O_2 is labelled as **x V,** it means that **1 *L*** of H_2O_2 solution gives **x *L*** of **O_2** gas at STP on complete decomposition.

We know that H_2O_2 decomposes as,

$$2H_2O_2(aq) \xrightarrow{\Delta} 2H_2O(l) + O_2(g)$$

2 moles of H_2O_2 gives 22.4 *L* of O_2 at STP.

1 moles of H_2O_2 gives 0.5 moles of O_2.

1 moles of H_2O_2 gives 11.2 *L* of O_2 at STP.

1 *L* of 1 *M* H_2O_2 gives 11.2 *L* of O_2 at STP, then the volume strength is 11.2 V.

1 *L* of 2 *M* H_2O_2 gives 22.4 *L* of O_2 at STP, then the volume strength is 22.4 V.

2 *L* of 1 *M* H_2O_2 gives 22.4 *L* of O_2at STP, then the volume strength is 11.2 V.

Volume strength in terms of normality

Volume strength of H_2O_2 = **N × 5.6**

$$\boxed{N = n_f \times M}$$

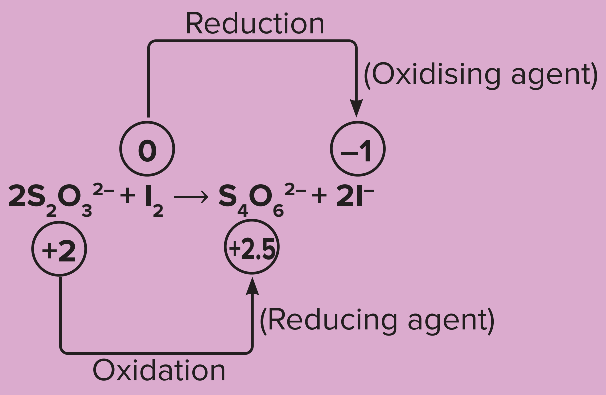
Where,
N = Normality
n_f = n-factor
M = Molarity
For H_2O_2, $n_f = 2$
So, volume strength of H_2O_2 = **M × 11.2**

Based on calculating the volume strength of H_2O_2

500 *mL* of H_2O_2 solution is added to an excess of acidified KI solution. The I_2 liberated requires 25 *mL* of 0.1 *N* hypo solution for titration. Calculate the volume strength of H_2O_2.

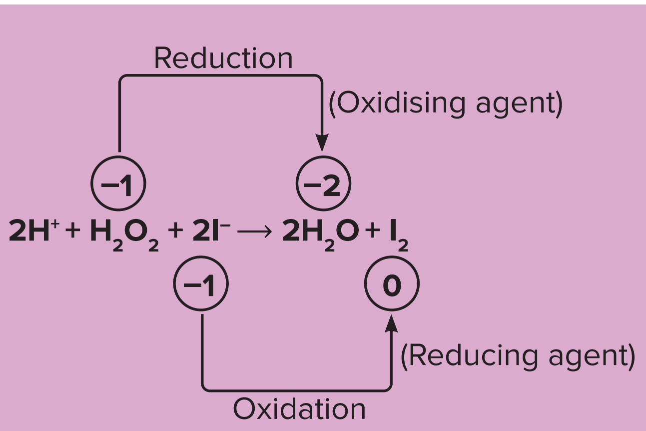
Solution

The reaction for the given titration is as follows:



$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$$

Number of equivalents of $S_2O_3^{2-}$ = Number of equivalents of I_2



$$2H^+ + H_2O_2 + 2I^- \longrightarrow 2H_2O + I_2$$

Number of equivalents of H_2O_2 = Number of equivalents of I_2

So, number of equivalents of $S_2O_3^{2-}$ = Number of equivalents of H_2O_2

In terms of milliequivalents,

Volume of $S_2O_3^{2-}$ (hypo) solution = 25 *mL*

Normality of $S_2O_3^{2-}$ (hypo) solution = 0.1 *N*

Volume of H_2O_2 used = 500 *mL*

Number of milliequivalents of $S_2O_3^{2-}$ = Number of milliequivalents of H_2O_2

$$25 \times 0.1 = 500 \times N$$

$$N = \frac{0.1}{20} = 0.005\ N$$

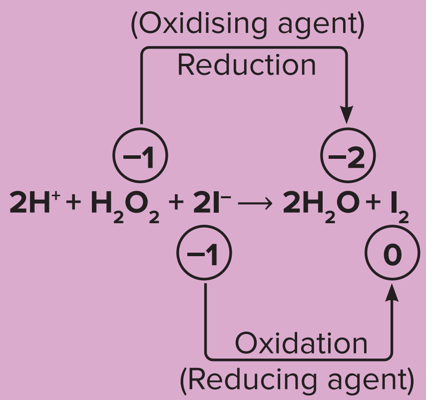
Volume strength of H_2O_2 = $N \times 5.6$

Volume strength of H_2O_2 = 0.005 × 5.6 = **0.028 V**

If the n-factor of I_2 is the same in both the reactions, then,

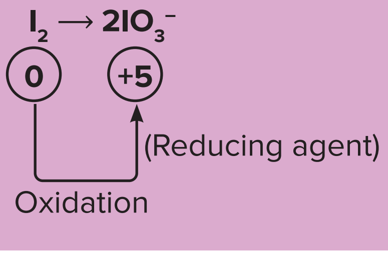
Equivalents of $S_2O_3^{2-}$ = Equivalents of H_2O_2

But suppose if the reactions are:



$$2H^+ + H_2O_2 + 2I^- \longrightarrow 2H_2O + I_2$$

The oxidation number of I in iodide ion is −1, and that in I_2 is 0, so the n_f of I_2 is 1 × 2 = 2 And the other reaction is,



$$I_2 \longrightarrow 2IO_3^-$$

The oxidation number of iodine is 0 in I_2 and +5 in IO_3^-, so the n_f of I_2 is 5 × 2 = 10

So, if the n-factors are not the same, then the equivalents of I_2 in both the reactions will not be the same.

BOARDS MAIN ADVANCED

Strength of Oleum

Percentage labelling of oleum

Oleum is a mixture of H_2SO_4 and SO_3 that is, $H_2S_2O_7$.

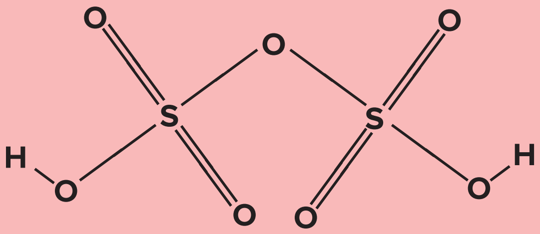


Fig. 1: Structure of oleum

This is obtained by passing SO_3 in the H_2SO_4 solution.

$SO_3(g) + H_2SO_4(aq) \longrightarrow H_2S_2O_7(aq)$

To dissolve free SO_3, water is added to it. Dilution is continued till the entire SO_3 gets converted into H_2SO_4.

$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(aq)$

$H_2SO_4(aq) + SO_3(g) + H_2O(l) \longrightarrow 2H_2SO_4(aq)$

Free SO_3 reacts with H_2O to form H_2SO_4 and the mass of the solution increases.

Let us take 100 *g* oleum having 80 *g* SO_3 and 20 *g* H_2SO_4 in composition.

The molar mass of SO_3 is 80 $g\ mol^{-1}$.

$80\ g\ SO_3 + 18\ g\ H_2O \longrightarrow 98\ g\ H_2SO_4$

We know that 1 *mol* of SO_3 reacts with 1 *mol* of H_2O to form 1 *mol* of H_2SO_4.

$100\ g \text{ oleum} + 18\ g\ H_2O \longrightarrow 118\ g\ H_2SO_4$

98 *g* H_2SO_4 is formed from SO_3, and 20 g H_2SO_4 is already present.

So, 100 *g* oleum upon addition of water gives 118 *g* of H_2SO_4.

Hence, % labelling of oleum is 118% in this case.

Percentage labelling in oleum

When a 100 *g* sample of oleum is diluted with the desired weight of H_2O (in *g*), then the total mass of H_2SO_4 obtained after dilution is known as the % labelling in oleum.

So, The % oleum is always more than 100.

Let weight of (100 *g* oleum + Weight of H_2O added) be 'y'

Or if % labelling in oleum = y

Then the percentage of free SO_3 in oleum sample is given as :

$$\%\ \text{Free } SO_3 = \frac{(y-100)}{18} \times 80\%$$

Based on calculating the composition of oleum

Calculate the composition of 109% oleum.

Solution

Given,

109% oleum means 9 *g* of water is required, i.e.,

100 *g* oleum + 9 *g* H_2O = 109 *g* H_2SO_4

9 *g* H_2O means 0.5 *mol* of H_2O

We know that 0.5 *mol* SO_3 reacts with 0.5 *mol* H_2O to form 0.5 *mol* H_2SO_4. That is,

40 *g* SO_3 + 9 *g* $H_2O \longrightarrow$ 49 *g* H_2SO_4

The percentage composition of 109% oleum is 40% SO_3 and 60% H_2SO_4.

Based on labelling the sample of oleum

The percent free SO_3 in a sample of oleum is 20%. Label the sample in terms of percent H_2SO_4.

Solution

Let weight of (100 *g* oleum + Weight of H_2O added) be y

The percent free SO_3 in oleum is given as: $\frac{(y-100)}{18} \times 80\%$

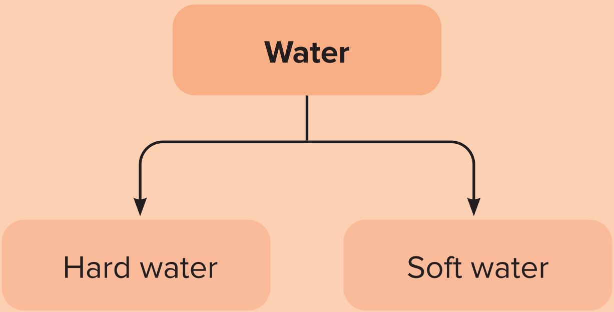
$$\frac{(y-100)}{18} \times 80 = 20$$

y = 104.5%

So, the % labelling in oleum is 104.5%

BOARDS **MAIN** **ADVANCED**

Hardness of Water



Hard water: It does not generate lather with soap.

Soft water: It generates lather with soap.

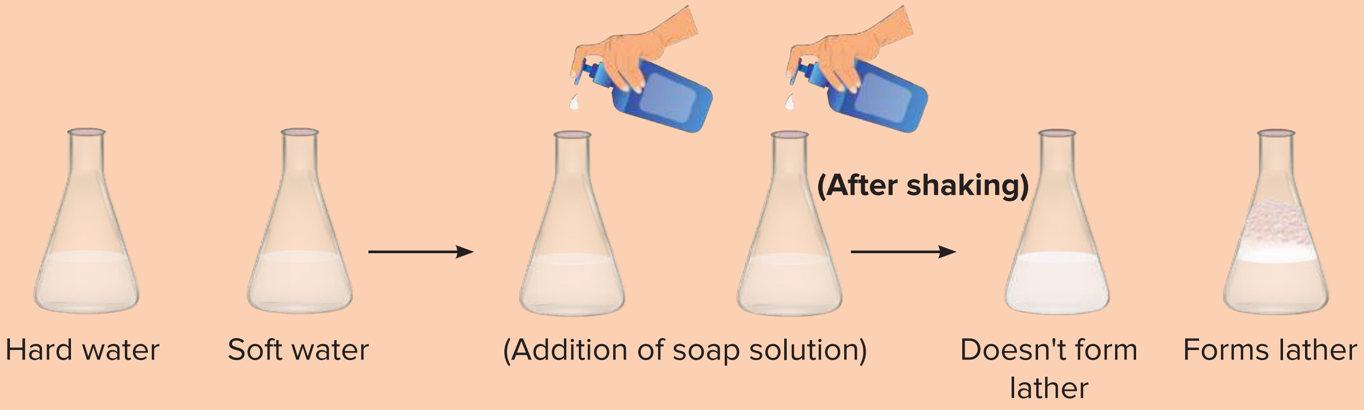
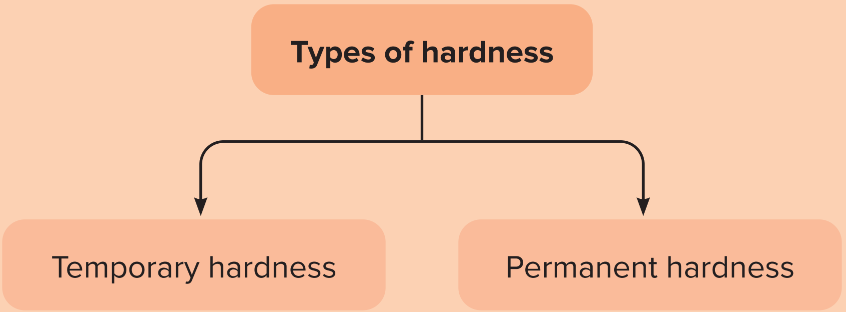


Fig. 2: Illustration of hard and soft water



Temporary hardness

Temporary hardness is due to the presence of soluble bicarbonates of Ca and Mg.

Examples: $Ca(HCO_3)_2$and $Mg(HCO_3)_2$

Removal of temporary hardness

By boiling:

$$Ca(HCO_3)_2(aq) \longrightarrow CaCO_3(s) + CO_2(g) + H_2O(l)$$

$$Mg(HCO_3)_2(aq) \longrightarrow MgCO_3(s) + CO_2(g) + H_2O(l)$$

Bicarbonates of Ca and Mg are water soluble, but carbonates of Ca and Mg are insoluble. So, carbonates of Ca and Mg can be separated by filtration.

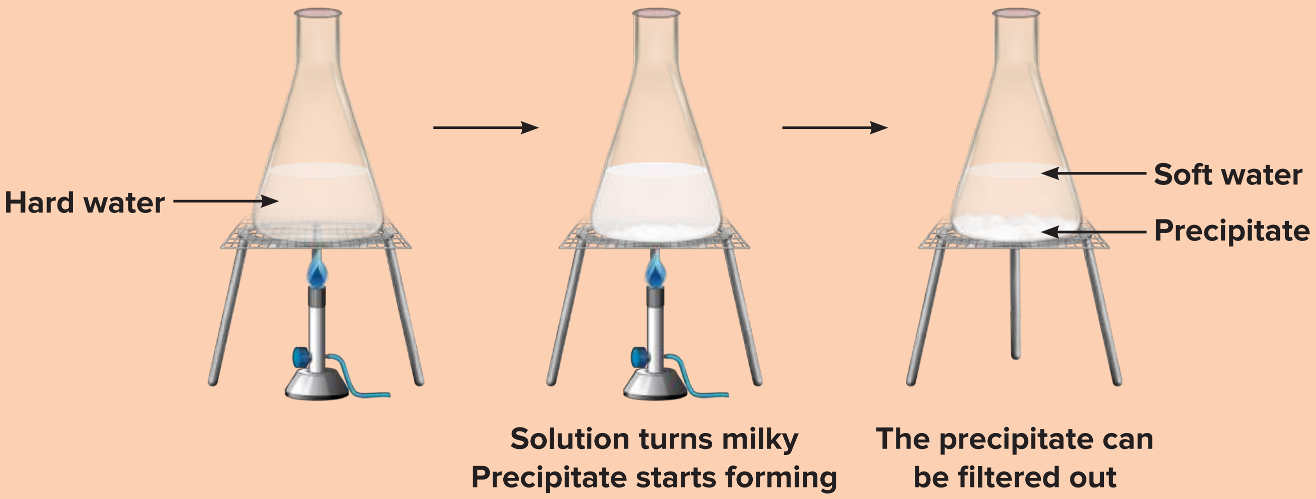


Fig. 3: Removal of temporary hardness through boiling

Permanent hardness

Permanent hardness is due to the presence of soluble chlorides and sulphates of Mg and Ca.

Examples: $CaCl_2$, $CaSO_4$, $MgCl_2$, $MgSO_4$

This type of hardness is referred to as permanent because unlike temporary hardness, it cannot be removed by simple methods like boiling.

Degree of hardness

Hardness is generally represented in terms of ppm of $CaCO_3$.

$$\textbf{Hardness of water in } \boldsymbol{ppm} = \frac{\textbf{Mass of } \mathbf{CaCO_3}}{\textbf{Mass of hard water}} \times 10^6$$

If there is no information about the given salt, then the hardness of water is calculated in terms of $CaCO_3$.

The hardness of water can also be represented in terms of other salts like $CaCl_2$, $MgCl_2$, $CaSO_4$, and more.

For the same hard water sample,

1 *g equivalent* of $CaCO_3$ ($n_f = 2$) = 1 *g equivalent* of $MgCl_2$ ($n_f = 2$) = 1 *g equivalent* of $CaCl_2$ ($n_f = 2$)

$$\text{Number of equivalents} = \frac{\text{Given mass}}{\text{Equivalent mass}}$$

Number of equivalents of all three are 1, so given mass = equivalent mass.

$$\text{Equivalent mass} = \frac{\text{Molar mass}}{\text{n-factor}}, \text{ so}$$

$$\frac{100}{2}\ g \text{ of } CaCO_3 = \frac{95}{2}\ g \text{ of } MgCl_2 = \frac{111}{2}\ g \text{ of } CaCl_2$$

100 *g* of $CaCO_3$ = 95 *g* of $MgCl_2$ = 111 *g* of $CaCl_2$

100 *ppm* $CaCO_3$ = 95 *ppm* of $MgCl_2$ = 111 *ppm* of $CaCl_2$

Based on calculating the degree of hardness in terms of $CaCO_3$

A sample of water contains 2 *mg* of $MgCl_2$ and 2 *mg* of $CaCl_2$ per litre. Calculate the degree of hardness in terms of $CaCO_3$.

Solution

100 *g* of $CaCO_3$. = 95 *g* of $MgCl_2$

100 *g* of $CaCO_3$. = 111 *g* of $CaCl_2$

$$2\ mg \text{ of } MgCl_2 = \frac{2 \times 10^{-3}}{95} \times 100\ g \text{ of } CaCO_3$$

$$2\ mg \text{ of } CaCl_2 = \frac{2 \times 10^{-3}}{111} \times 100\ g \text{ of } CaCO_3$$

$$\text{Total mass of } CaCO_3 = \left(\frac{2 \times 10^{-3}}{95} \times 100\ g\right) + \left(\frac{2 \times 10^{-3}}{111} \times 100\ g\right)$$

Total mass of $CaCO_3 = (0.0021) + (0.0018)\ g = 0.0039\ g$

$1\ L$ of solution $= 1000\ g$ (Density $= 1\ g\ L^{-1}$ for water)

Hardness of water in *ppm* $= \dfrac{\textbf{Mass of } \mathbf{CaCO_3}}{\textbf{Mass of hard water}} \times \mathbf{10^6}$

Hardness of water in *ppm* $= \dfrac{0.0039}{1000} \times 10^6 = 3.9\ ppm$

The degree of hardness in terms of $CaCO_3$ is 3.9 *ppm*

BOARDS **MAIN** **ADVANCED**

Concept of Available Chlorine

Bleaching Powder is $CaOCl_2$.

Available chlorine

The weight of available Cl_2 released from the given sample of bleaching powder on reaction with dilute acids or CO_2 is known as available chlorine.

$CaOCl_2$ is dissolved in water to form a suspension.

Bleaching powder

$$CaOCl_2(aq) + H_2SO_4(aq) \rightarrow CaSO_4(s) + Cl_2(g) + \rightarrow H_2O(l)$$

$$CaOCl_2(aq) + 2HCl(aq) \rightarrow CaCl_2(s) + Cl_2(g) + H_2O(l)$$

$$CaOCl_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + Cl_2(g)$$

Sample of bleaching powder

$$CaOCl_2(aq) + 2CH_3COOH(aq) \rightarrow Ca(CH_3COO)_2 + Cl_2(g) + H_2O(l)$$

$$Cl_2(g) + 2KI(aq) \rightarrow 2KCl(s) + I_2(aq)$$

$$I_2(aq) + 2Na_2S_2O_3(aq) \rightarrow Na_2S_4O_6(aq) + 2NaI(aq)$$

v.f. (of I_2) = 2 and v.f. (of $Na_2S_2O_3$) = 1

Where v.f. is the valency factor

The endpoint is indicated by the disappearance of blue colour.

$\dfrac{M \times V}{2}$ = Millimoles of Cl_2 produced = Millimoles of I_2 used by hypo

M = Molarity of $Na_2S_2O_3$,

V = Volume of $Na_2S_2O_3$

If, W = Amount of bleaching powder taken in gram.

Mass of Cl_2 produced $= \dfrac{M \times V \times 10^{-3}}{2} \times 71$

Mass of Cl_2 produced $= 35.5 \times M \times V \times 10^{-3}$

% of available chlorine $= \dfrac{35.5 \times M \times V \times 10^{-3}}{W} \times 100$

% of available chlorine $= \dfrac{\mathbf{3.55 \times M \times V}}{\mathbf{W}}$