NEET Class Companion Chemistry

Module 2

Contents

CHAPTER

8

Redox Reaction

Learning Objectives

During the course of this chapter, you will be able to:

- ☑ know redox reactions.
- ☑ illustrate the terms oxidation, reduction, oxidant and reductant.
- ☑ elucidate mechanism of redox reactions through electron transfer process.
- ☑ apply the concept of oxidation number for identification of oxidant and reductant in a reaction.
- ☑ categorize different types of redox reaction.
- ☑ balance the chemical equations using oxidation number method and half reaction method.
- ☑ understand the concept of redox reactions in terms of electrode processes.

INTRODUCTION

Redox reactions are those in which oxidation and reduction take place simultaneously. Oxidizing agent can gain electron whereas reducing agent can lose electron easily. The oxidation state of any element can never be in fraction. If oxidation number of any element comes out be in fraction, it is average oxidation number of that element which is present in different oxidation states.

The equivalent weight of a species if acts as oxidant or reductant should be derived by:

Eq. weight of oxidant or reductant

$$= \frac{\text{Mol. wt. of oxidant or reductant}}{\text{Number of electrons lost or gained by one molecule of oxidant or reductant}}$$

CLASSICAL IDEA OF REDOX REACTIONS – OXIDATION AND REDUCTION REACTIONS

Oxidation is the process involving increase in oxidation state of one or more element while reduction is the process involving decrease in oxidation state of one or more elements.

Those reactions which involve increase in oxidation number and decrease in oxidation number simultaneously are known as oxidation reduction or redox reaction.

The following reactions represent oxidation process according to the limited definition of oxidation.

- Addition of oxygen:
  $2Mg + O_2 \rightarrow 2MgO$
  $C + O_2 \rightarrow CO_2$
- Removal of hydrogen:
  $H_2S + Cl_2 \rightarrow 2HCl + S$
  $4HI + O_2 \rightarrow 2I_2 + 2H_2O$
- Addition of electronegative element:
  $Fe + S \rightarrow FeS$
  $SnCl_2 + Cl_2 \rightarrow SnCl_4$
- Removal of electropositive element:
  $2NaI + H_2O_2 \rightarrow 2NaOH + I_2$

The following reactions represent reduction.

- Addition of hydrogen:
  $N_2 + 3H_2 \rightarrow 2NH_3$
  $H_2 + Cl_2 \rightarrow 2HCl$
- Removal of oxygen:
  $CuO + C \rightarrow Cu + CO$
  $H_2O + C \rightarrow CO + H_2$

- Addition of electropositive element:
  $CuCl_2 + Cu \rightarrow Cu_2Cl_2$
  $HgCl_2 + Hg \rightarrow Hg_2Cl_2$
- Removal of electronegative element:
  $2FeCl_3 + H_2 \rightarrow 2FeCl_2 + 2HCl$

REDOX REACTIONS IN TERMS OF ELECTRON TRANSFER REACTIONS

De-electronation

- In oxidation process there is one or more e^-s are lost by an atom, ion or molecule.

Examples:

(a) $Zn \rightarrow Zn^{+2} + 2e^-$
$M \rightarrow M^{n+} + ne^-$

(b) $Sn^{+2} \rightarrow Sn^{+4} + (4-2)\,e^-$
$M^{+n_1} \rightarrow M^{+n_2} + (n_2-n_1)e^-$

(c) $Cl^- \rightarrow Cl + e^-$
$A^{-n} \rightarrow A + ne^-$

(d) $MnO_4^{-2} \rightarrow MnO_4^- + (2-1)e^-$
$A^{-n_1} \rightarrow A^{-n_2} + (n_1-n_2)e^-$

Electronation

In reduction process, one or more e^-s are gained by an atom, ion or molecule.

Examples:

(a) $Cu^{+2} + 2e^- \rightarrow Cu$
(b) $Fe^{+3} + (3-2)\,e^- \Rightarrow Fe^{+2}$
(c) $O + 2e^- \rightarrow O^{2-}$
(d) $[Fe(CN)_4]^{3-} + (4-3)e^- \rightarrow [Fe(CN)_4]^{-4}$

Oxidant are those substances which:

- Oxidizes others and reduces themselves.
- Accepts electron, i.e., electron acceptors
- Show decrease in oxidation State
- Acts as a lewis acid

Examples: All electronegative element like F_2, Cl_2, N_2, O and Compounds which have effective element in maximum oxidation state (E.g., $KMnO_4$ $K_2Cr_2O_7$)

Reductant are those substances which:

- Reduces others and oxidizes themselves.
- Donates electron, i.e., electron donors
- Show increase in oxidation state
- Acts as a Lewis base
- Some non-metals like, C, H, S

Examples: Some hydrides like LiH, CaH_2, $LiAlH_4$ etc., and compounds having effective element in minimum O.S. (E.g., PH_3, NH_3....)

Competitive electron transfer reaction

Case 1:

If we will place zinc strip in solution of copper nitrate we will observe that Zn being oxidized and converted into Zn^{+2} while Cu^{+2} gets reduced to convert in Cu as per the given reaction.

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

Case 2:

A strip of copper placed in silver nitrate solution will get oxidized into Cu^{+2} and will reduce silver from Ag+ to Ag.

$$Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$$

It is observed here that different metals are in competition of releasing electron. This suggests to develop a table in which metals are sorted according to their tendency to loose electrons. This table is called metal activity series.

SOLVED EXAMPLES – I

EXAMPLE 1

State which of the following reactions are neither oxidation nor reduction?

(A) $Na \rightarrow NaOH$
(B) $Cl_2 \rightarrow Cl^- + ClO_3^-$
(C) $P_2O_5 \rightarrow H_4P_2O_7$
(D) $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$

SOLUTION: (C)

In the reaction $P_2O_5 \rightarrow H_4P_2O_7$
The O.S. of P in P_2O_5 is
$2x + 5(-2) = 0$ or $x = +5$
The O.S. of P in $H_4P_2O_7$ is
$4(+1) + 2(x) + 7(-2) = 0$
$2x = 10$ or $x = +5$
Since there is no change in O.S. of P, hence, the above reaction is neither oxidation nor reduction.

EXAMPLE 2

Which of the following is not a redox reaction?

(A) $\frac{1}{2}H_2 + \frac{1}{2}I_2 \rightarrow HI$
(B) $PCl_5 \rightarrow PCl_3 + Cl_2$
(C) $2CuSO_4 + 4KI \rightarrow Cu_2I_2 + 2K_2SO_4 + I_2$
(D) $CaOCl_2 \rightarrow Ca^{+2} + OCl^- + Cl^-$

SOLUTION: (D)

In all the above reaction, except (D) there is change in oxidation states of reactant and product atoms, hence, they are all redox reactions. In reaction (D), the oxidation states of the atoms of the reactants and products remain unchanged hence, it is not a redox reaction.

EXAMPLE 3

Identify the substance acting as oxidant or reductant if any in the following:

(A) $AlCl_3 + 3K \longrightarrow Al + 3KCl$

(B) $SO_2 + 2H_2S \longrightarrow 3S + H_2O$

(C) $BaCl_2 + Na_2SO_4 \longrightarrow BaSO_4 + 2NaCl$

(D) $3I_2 + 6NaOH \longrightarrow NaIO_3 + 5NaI + 3H_2O$

SOLUTION:

In a conjugate pair, oxidant has higher Oxidation number.

(A) **For $AlCl_3$:** $Al^{3}+ + 3e^- \longrightarrow Al^0$; oxidation $AlCl_3$

For K: $K^0 \longrightarrow K^1 + + e$ and reductant K.

(B) **For SO_2:** $S^{4+} + 4e^- \longrightarrow S^0$;

For H_2S: $S^{2-} \longrightarrow S^0 + 2e^-$

(C) No change in oxidation number of either of the conjugate pair.

∴ None is oxidant or reductant.

(D) **For I_2:** $I_2^0 \longrightarrow 2I^{5+} + 10e^-$ and $I_2^0 + 2e \longrightarrow 2I^-$

∴ I_2 acts as oxidant and reductant both.

EXAMPLE 4

Evaluate equivalent weight of reductant or oxidant given on left-hand side of each reaction:

(A) $As_2O_3 + 5H_2O \longrightarrow 2AsO_4^{3-} + 10H^+ + 4e^-$

(B) $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

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

(D) $C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$

(E) $FeC_2O_4 \longrightarrow Fe^{3+} + 2CO_2 + 3e^-$

(F) $2CuSO_4 + 2e^- \longrightarrow Cu_2^+ + SO_4^{2-}$

SOLUTION:

$E_{red./oxi.}$ = one molecular of reductant or oxidant or value factor.

$$\frac{\text{Mol. weight of reductant or oxidant}}{\text{Number of element sgained or lost}}$$

(A) $E_{As_2O_3} = \frac{M_{As_2O_3}}{4} (As_2^{3+} \longrightarrow 2As^{5+} + 4e^-)$

(B) $E_{MnO_4^-} = \frac{M_{MnO_4^-}}{5} (Mn^{7+} + 5e^- \longrightarrow Mn^{2+})$

(C) $E_{Cr_2O_7^{2-}} = \frac{M_{Cr_2O_7^{2-}}}{6} (Cr_2^{6+} \longrightarrow 2Cr^{3+} + 6e^-)$

(D) $E_{C_2O_4^{2-}} = \frac{M_{CrO_4^{2-}}}{2} (C_2^{3+} \longrightarrow 2C^{4+} + 2e^-)$

(E) $E_{FeC_2O_4} = \frac{M_{FeC_2O_4}}{3}$

$(Fe^{2+} + C_2^{3+} \longrightarrow Fe^{3+} + 2C^{4+} + 3e^-)$

(F) $E_{CuSO_4} = \frac{M_{CuSO_4}}{1} \quad (2Cu^{2+} + 2e^- \longrightarrow Cu_2^+)$

EXAMPLE 5

Equivalent weight of FeC_2O_4 during its reaction with $KMnO_4$ is:

(A) M/3 (B) M/1
(C) M/2 (D) M/4

SOLUTION: (A)

Reaction of FeC_2O_4 with $KMnO_4$ is,

$5FeC_2O_4 + 6KMnO_4 + 24H_2SO_4 \longrightarrow 3K_2SO_4 + 6KMnSO_4 + 5Fe(SO_4)_3 + 24H_2O + 10CO_2$

So, Fe is oxidized from +2 to +3

C is oxidized from +3 to +4

So, n-factor $= 1 + 2 \times 1 = 3$

$$\text{Equivalent weight} = \frac{\text{Molecular weight}}{n\text{-factor}}$$

$$= \frac{M}{3}$$

EXAMPLE 6

Which of the following ion is spectator ion in the reaction given below?

$Zn + 2H^+ + 2Cl^- \longrightarrow Zn^{2+} + 2Cl^- + H_2$

(A) Zn^{2+} (B) H^+
(C) Cl^- (D) None of these

SOLUTION: (C)

The species present in solution but does not take part in the reaction is called spectator ion. It may be omitted while writing the net ionic reaction.

$Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$

EXAMPLE 7

Which reaction does not represent auto redox or disproportionation?

(A) $Cl_2 + OH^- \longrightarrow Cl^- + ClO_3^- + H_2O$

(B) $2H_2O_2 \longrightarrow H_2O + O_2$

(C) $2Cu^+ \longrightarrow Cu^{2+} + Cu$

(D) $(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$

SOLUTION: (D)

In auto redox or disproportionation, same element is oxidized as well as reduced. In (A) Cl_2 (B) H_2O_2 and (C) Cu^+ is oxidized as well as reduced. In (D) N is oxidized and Cr is reduced in one molecule of $(NH_4)_2Cr_2O_7$ and thus, it is intramolecular redox.

EXAMPLE 8

In which triplet each species can act as oxidant and reductant?

(A) H_2O_2, HNO_2, $HClO_4$ (B) HNO_2, SO_2, H_2O_2

(C) HNO_3, SO_2, H_2SO_4 (D) $KMnO_4$, SO_3, O_3

SOLUTION: (B)

The species in which an element has oxidation number lying in between its minimum and maximum values can acts as oxidant and reductant both.

	Minimum O.S.	Maximum O.S.
N^{3+} in HNO_2	–3	+5
S^{4+} in SO_2	–2	+6
O^{1-} in H_2O_2	–2	0

EXAMPLE 9

State the equivalent mass of each reactant and product in following half-reactions:

(A) $2CuI_2 \longrightarrow Cu_2I_2$ (B) $As_2O_3 \longrightarrow H_3AsO_4$

(C) $HNO_3 \longrightarrow NO$ (D) $KMnO_4 \longrightarrow K_2MnO_4$

(E) $PH_3 \longrightarrow H_3PO_3$

SOLUTION:

(A) $E_{CuI_2} = \frac{M}{1}$; $E_{Cu_2I_2} = \frac{M}{2}$

(B) $E_{As_2O_3} = \frac{M}{4}$; $E_{H_3As_2O_3} = \frac{M}{2}$

(C) $E_{HNO_3} = \frac{M}{3}$; $E_{NO} = \frac{M}{3}$

(D) $E_{KMnO_4} = \frac{M}{1}$; $E_{K_2MnO_4} = \frac{M}{1}$

(E) $E_{PH_3} = \frac{M}{6}$; $E_{H_3PO_3} = \frac{M}{6}$

EXAMPLE 10

Calculate the equivalent mass of each oxidant and reductant in:

(A) $KI + K_2Cr_2O_7 \longrightarrow Cr^{3+} + 3I_2$

(B) $Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$

(C) $NO_3^- \longrightarrow N_2$

(D) $FeSO_4 + KClO_3 \longrightarrow KCl + Fe_2(SO_4)_3$

(E) $Fe_3O_4 + KMnO_4 \longrightarrow Fe_2O_3 + MnO_2$

(F) $FeC_2O_4 \longrightarrow Fe^{3+} + CO_2$

(G) $Na_2SO_3 + Na_2CrO_4 \longrightarrow Na_2SO_4 + Cr(OH)_3$

SOLUTION:

$$E_{oxidant/reductant} = \frac{\text{M. mass of oxidant or reductant}}{\text{No. of 'e' lost or gained by one molecule of oxidant or reductant}}$$

(A) $2I^- \longrightarrow I_2^0 + 2e$; $E_{KI} = \frac{M}{1} = \frac{166}{1} = 166$

$6e^- + Cr_2^{6+} \longrightarrow 2Cr^{3+}$; $E_{K_2Cr_2O_7} = \frac{M}{6} = \frac{294}{6} = 49$

(B) $2S_2^{2+} \longrightarrow S_4^{(5/2)+} + 2e$; $E_{Na_2S_2O_3} = \frac{M}{1} = \frac{158}{1} = 158$

$2e^- + I_2^0 \longrightarrow 2I^{1-}$; $E_{I_2} = \frac{M}{2} = \frac{254}{2} = 127$

(C) $10e^- + 2N^5 + \longrightarrow N_2^0; E_{NO_3^-} = \frac{\text{Ionic M. mass}}{5}$

$= \frac{62}{5} = 12.4$

(D) $2Fe^2 + \longrightarrow Fe_2^{3+} + 2e; E_{FeSO_4} = \frac{M}{1} = \frac{152}{1} = 152$

$6e + Cl^{5+} \longrightarrow Cl^-; E_{KClO_3} = \frac{M}{6} = \frac{122.5}{6} = 20.42$

(E) $2Fe_3^{(8/3)+} \longrightarrow 3Fe_2^{3+} + 2e; E_{Fe_3O_4} = \frac{M}{1} = \frac{232}{1} = 232$

$3e + Mn^{7+} \longrightarrow Mn^{4+}; E_{KMnO_4} = \frac{M}{3} = \frac{158}{3} = 52.67$

(F) $FeC_2O_4 \longrightarrow Fe^{3+} + CO_2$

$Fe^{2+} \longrightarrow Fe^{3+} + e$

$C_2^{3+} \longrightarrow 2C^{4+} + 2e$

$FeC_2O_4 \longrightarrow Fe^{3+} + 2C^{4+} + 3e^-$

$E_{FeC_2O_4} = \frac{M}{3} = \frac{144}{3} = 48$

(G) $S^{4+} \longrightarrow S^{6+} + 2e$

$E_{Na_2SO_3} = \frac{M}{2} = \frac{126}{2} = 63$

$3e + Cr^{6+} \longrightarrow Cr^{3+}$

$E_{Na_2CrO_4} = \frac{M}{3} = \frac{162}{3} = 54$

CHECK YOUR UNDERSTANDING - I

1. Which of the following acts as both oxidant and reductant?
   (A) HNO_3
   (B) HNO_2
   (C) Both HNO_3 and HNO_2
   (D) Neither HNO_3 nor HNO_2

2. In the reaction $C_2O_4^{-2} + MnO^-_4 + H^+ \rightarrow Mn^{+2} + CO_2$ the reductants is:
   (A) $C_2O_4^{-2}$ (B) H^+
   (C) MnO^-_4 (D) None of these

3. In the reaction Al + $Fe_3O_4 \rightarrow Al_2O_3$ + Fe, what is the total number of electrons transferred during the change?
   (A) 16 (B) 24 (C) 8 (D) 12

4. Select the nature or type of redox change in the following reactions:
   (A) $2Cu^+ \longrightarrow Cu^{2+} + Cu^0$
   (B) $Cl_2 \longrightarrow ClO^- + Cl^-$
   (C) $2KClO_3 \longrightarrow 2KCl + 3O_2$
   (D) $(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$
   (E) $10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \longrightarrow 2MnSO_4 + 5Fe_2(SO_4)_3 + K_2SO_4 + 8H_2O$
   (F) $5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$

5. Which of the following can be both oxidizing as well as reducing agent?
   (A) H_2 (B) I_2
   (C) H_2O_2 (D) All of these

6. The number of electrons lost or gained during the change,

   $Fe + H_2O \longrightarrow Fe_3O_4 + H_2$

   (A) 2 (B) 4 (C) 6 (D) 8

7. The equivalent weight of the salt $KHC_2O_4 \cdot H_2C_2O_4 \cdot 4H_2O$ used as reducing agent is:
   (A) Mol. wt./1 (B) Mol. wt./2
   (C) Mol. wt./3 (D) Mol. wt./4

8. In a reaction, 4 mole of electrons are transferred to 1 mole of HNO_3, the possible product obtained due to reduction is:
   (A) 0.5 mol of N_2 (B) 0.5 mol of N_2O
   (C) 1 mol of NO_2 (D) 1 mol of NH_3

9. Which species are oxidized and reduced in the following reaction?
$FeC_2O_4 + KMnO_4 \longrightarrow Fe^{2+} + CO_2 + Mn^{2+}$
(A) Oxidized: Fe, C Reduced: Mn
(B) Oxidized: Fe Reduced: Mn
(C) Reduced: Fe, Mn Oxidized: C
(D) Reduced: C Oxidized: Mn, Fe

10. Which of the following is not intramolecular redox reaction?
(A) $(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$
(B) $2KClO_3 \longrightarrow 2KCl + 3O_2$
(C) $2Mn_2O_7 \longrightarrow 4MnO_2 + 3O_2$
(D) $2ClO_2 + 5H_2O_2 \xrightarrow{2OH^-} 2Cl^- + 5O_2 + 6H_2O$

11. Equivalent weight of Fe_2O_3 in terms of its mol. weight in the change $Fe_3O_4 \longrightarrow Fe_2O_3$ is:
(A) M (B) M/2 (C) M/3 (D) 3M/2

12. Equivalent weight of N_2 and NH_3 in the change $N_2 \longrightarrow NH_3$ respectively is:
(A) 4.67, 12.4 (B) 9.3, 12.4
(C) 4.67, 5.34 (D) 5.34, 4.67

13. Select the type of redox reaction from the following on the basis of type of redox changes (a) intermolecular redox; (b) intramolecular redox; (c) auto-redox. If none, write none.
(A) $C_6H_5CHO \xrightarrow{NaOH} C_6H_5CH_2OH + C_6H_5COONa$
(B) $Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$
(C) $2Mn_2O_7 \longrightarrow 4MnO_2 + 3O_2$
(D) $NO_3^- + H_2S + H_2O + H+ \longrightarrow NH_4^+ + HSO_4$
(E) $Fe + N_2H_4 \longrightarrow NH_3 + Fe(OH)_2$
(F) $2KOH + Br_2 \longrightarrow KBr + KBrO$
(G) $2Cu^+ \longrightarrow Cu + Cu^{2+}$
(H) $Ag(NH_3)_2^+ \xrightarrow{2H^+} Ag^+ + 2NH_4^+$
(I) $5KI + KIO_3 + 6HCl \longrightarrow 3I_2 + 6KCl + 3H_2O$

14. Identify the oxidized and reduced species in the following reactions:
(A) $CH_4(g) + 4Cl_2(g) \longrightarrow CCl_4(g) + 4HCl(g)$
(B) $MnO_2(s) + C_2H_2O_4(aq) \xrightarrow{2H^+} Mn^{2+}(aq) + 2CO_2(g) + 2H_2O(l)$
(C) $I_2(aq) + 2S_2O_3^{2-}(aq) + S_4O_6^{2-} \longrightarrow Cl_2(g) + 2Br^-(aq)$
(D) $2Cl^-(aq) + Br_2(aq) \longrightarrow Cl_2(aq) + 2Br^-(aq)$

OXIDATION NUMBER

Oxidation state of an atom is the charge present on an atom when it is in combined state.

or

Oxidation state of any atom in any molecule or ion may be defined as arbitrary charge assigned to that atom according to some well-defined rules.

Some important points concerning oxidation number:

- No two elements have same electronegativity values.
  S > C   C > H
  P > H   Cl > N
- Element can have positive or negative oxidation number.
- Oxidation number can be whole number, zero, or a fractional value.

E.g.,

$Ni(CO)_4 \Rightarrow$ O.S of Ni = 0
$N_3H \Rightarrow$ O.S of N = −1/3
$HCl \Rightarrow$ O.S of Cl = −1

- Oxidation state of same element can be different in different or same compounds.

E.g.,

$H_2S \Rightarrow$ O.S of S = −2
$H_2SO_3 \Rightarrow$ O.S of S = +4
$H_2SO_4 \Rightarrow$ O.S of S = +6

Some helping rules for calculating oxidation number:

- In case of a covalent bond:
  (a) For a homoatomic molecule,

$$\underset{0\ \ 0}{A - A} \quad \underset{0\ \ 0}{A = A} \quad \underset{0\ \ 0}{A \equiv A}$$

(b) For heteroatomic molecule (EN of B > A)

A – B	A = B	A ≡ B
↓ ↓	↓ ↓	↓ ↓
+1 –1	+2 –2	+3 –3

- In case of coordinate bond (EN of B > A):

A → A	B → B	A → B
↓ ↓	↓ ↓	↓ ↓
+2 –2	+2 –2	+2 –2

- In case of ionic bond:

  Charge on cation = O.S of cation

  Charge on anion = O.S of anion

E.g., NaCl → Na^+ + Cl^-
↓ ↓
+1 –1

$MgCl_2$ → Mg^{+2} + 2Cl–
↓ ↓
+2 –1

- Oxidation number is zero in following cases:
  (a) The element in its free state has zero oxidation number. For example, oxidation number of Na,Cl, Cu, I, O, etc., is zero.
  (b) In homoatomic molecules, oxidation number of atoms present is zero.

E.g., H_2, O_2, N_2, P_4, S_8 = zero

  (c) Element in any of its allotropic form has oxidation number zero.

E.g., $C_{Diamond}$, $C_{Graphite}$, $S_{Monoclinic}$, $S_{Rhombic}$ = 0

  (d) Oxidation number of all the components of an alloy are zero.

- Fluorine in all its compounds has oxidation number of –1.
- I A and II A group elements are +1 and +2 oxidation number.
- Hydrogen in most of its compounds has +1 oxidation number except in metal hydrides (–1).

E.g,

NaH	LiH	CaH_2	MgH_2
↓ ↓	↓ ↓	↓ ↓	↓ ↓
+1 –1	+1 –1	+2 –1	+2 –1

- Oxygen in most of its compounds has –2 oxidation number except in:
  (a) Peroxides (O_2^{-2}) → Oxidation number (O) = –1

E.g., H_2O_2, BaO_2

  (b) Superoxides (O_2^{-1}) → Oxidation number (O) = –1/2

E.g., KO_2
↓
–1/2

  (c) Ozonide (O_3^{-1}) → Oxidation number (O) = –1/3

E.g., KO_3
↓
–1/3

  (d) OF_2 (Oxygen difluoride)

F – O – F
↓
+2

  (e) O_2F_2 (dioxygen difluoride)
↓
+1

- Monoatomic ions have oxidation number equal to the charge present on the ion.

  E.g., Mg^{2+} → Oxidation number = +2

- The algebric sum of oxidation number of all the atoms present in a polyatomic neutral molecule is 0.

  E.g., H_2SO_4

  If O.S of S is x then
  $2(+1) + x + 4(-2) = 0$
  $x - 6 = 0$
  $x = +6$

  E.g., H_2SO_3

  If O.S of S is x then
  $2(+1) + x + 3(-2) = 0$
  $x - 4 = 0$
  $x = +4$

- All the atoms in a polyatomic complex ion has the oxidation number equal to the algebric sum of the charge present on the ion.

  E.g., SO_4^{-2}

  If O.S of S is x then
  $x + 4(-2) = -2$
  $x - 6 = 0$
  $x = +6$

  E.g., HCO_3^-

  If O.S of C is x then
  $+1 + x + 3(-2) = -1$
  $x - 4 = 0$
  $x = +4$

- In complex compounds, oxidation number of some neutral molecules (ligands) is zero. Example: CO, NO, NH_3, H_2O.

Applications of Oxidation Number

- **To compare the strength of acid and base:**

$$\text{Strength of base} \propto \frac{1}{\text{Oxidation Number}}$$

$$\text{Strength of acid} \propto \text{Oxidation Number}$$

- **To determine the reducing and oxidizing nature of the substances:**

  (a) The compound acts as an oxidizing agent, if effective element in a compound is present in maximum an oxidation state.

E.g., $KMnO_4 \downarrow +7$, $K_2Cr_2O_7 \downarrow +6$, $H_2SO_4 \downarrow +6$

$SO_3 \downarrow +6$, $H_3PO_4 \downarrow +5$, $HNO_3 \downarrow +5$, $HClO_4 \downarrow +7$

(b) The compound acts as a reducing agent, if the effective element in a compound is present in minimum oxidation state.

$PH_3 \downarrow -3$, $NH_3 \downarrow -3$, $CH_4 \downarrow -4$

(c) The compound can act as an oxidizing agent as well as a reducing agent, If effective element in a compound is present in intermediate oxidation state.

$HNO_2 \downarrow +3$, $H_3PO_3 \downarrow +3$, $SO_2 \downarrow +4$, $H_2O_2 \downarrow -1$

- **Equivalent weight of compounds:** The equivalent weight of an oxidizing agent is that weight of an element which accepts one mole of electrons in a chemical reaction.

  (a) Equivalent wt. of an oxidant (get reduced)

$$= \frac{\text{Molecular weight}}{\text{No. of electrons gained by one mole}}$$

In acidic medium,

$$6e^- + Cr_2O_7^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O$$

In this reaction, atom undergoing reduction is Cr. Its oxidation state is decreasing from +6 to +3.

Eq. wt. of $K_2Cr_2O_7$

$$= \frac{\text{Mol. wt. of } K_2Cr_2O_7}{3 \times 2} = \frac{\text{Mol. wt.}}{6}$$

NOTES

6 electrons were gained by Cr_2O_72- as indicated by 6 in the denominator that as it can be seen from the given balanced equation

(b) Similarly equivalent wt. of a reducant:

$$= \frac{\text{Mol. wt.}}{\text{No.of electrons lost by one mole}}$$

In acidic medium, $C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$

Total electrons lost = 2

So, eq. wt. = $\frac{\text{Mol. wt.}}{2}$

(c) A compound may have different equivalent weights different conditions. Since, it depends upon the number of electrons lost or gained by that compound that reaction.

(i) $MnO_4^- \longrightarrow Mn^{+2}$ (acidic medium)
(+7) (+2)

Here, 5 electrons are taken.

So, Eq., wt. = $\frac{\text{Mol. wt. of } KMnO_4}{5} = \frac{158}{5} = 31$

(ii) $MnO_4^- \longrightarrow MnO_2$ (neutral medium) or (weakly alkaline medium)
(+7) (+4)

Here, only 3 electrons are gained.

So eq., wt.

$$= \frac{\text{Mol. wt. of } KMnO_4}{3} = \frac{158}{3} = 52.7$$

NOTES

When alkaline medium is given in the question consider it as weakly alkaline medium.

(iii) $MnO_4^- \longrightarrow MnO_4^{-2}$ (strong alkaline medium)
(+7) (+6)

Here, only one electron is gained.

So, eq. wt. = $\frac{\text{Mol. wt. of } KMnO_4}{1} = 158$

NOTES

$KMnO_4$ acts as an oxidant in every medium but with different strengths which follows the following order acidic medium > neutral medium > alkaline medium

While, potassium dichromate acts as an oxidant only in acidic medium as follows:

$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$
$(2 \times 6) \longrightarrow (2 \times 3)$

Here, 6 electrons are gained.

So, eq., wt.= $\frac{\text{Mol. wt. of } K_2Cr_2O_7}{6} = \frac{294.21}{6} = 49.$

- **To find the possible molecular formula of compound:** The sum of oxidation number of all the atoms present in a compound is zero hence, the validity of formula can be confirmed.

ock Notation

ne oxidation number state of a metal in a compound is ometimes expressed by putting a roman numeral repre- enting the oxidation number in parenthesis after the sym- ol of metal in molecular formula. Thus aurous chloride nd auric chloride are written as Au(I)Cl and Au(III)Cl_3 espectively. It is popularly known as **Stock Notation.**

ypes of Redox Reactions

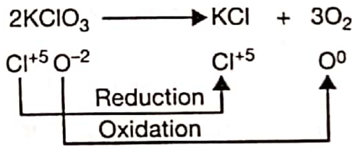
- **Intermolecular redox reaction:** It is when both the oxidation and reduction takes place separately in different compounds, then the reaction.

  $SnCl_2 + 2FeCl_3 \longrightarrow SnCl_4 + 2FeCl_2$

  $Sn^{+2} \longrightarrow Sn^{+4}$ (Oxidation)

  $Fe^{+3} \longrightarrow Fe^{+2}$ (Reduction)

- **Intramolecular redox reaction or decomposition reaction:** It is when during a chemical reaction, oxidation and reduction takes place in a single compound, then the reaction is called intramolecular redox reaction.



- **Displacement Reaction:** An atom or ion gets replaced by another atom or ion.

  X+YZ → XZ+Y

  It is further classified as metal displacement and non-metal displacement reaction.

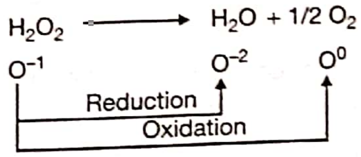
  e. g. Metal Displacement

  $$\overset{+2\ +6\ -2}{CuSO_4}(aq) + \overset{0}{Zn}(s) \longrightarrow \overset{0}{Cu}(s) + \overset{+2\ +6\ -2}{ZnSO_4}(aq)$$

  e.g. Non-Metal Displacement

  $$2\overset{0}{Na}(s) + 2\overset{+1\ -2}{H_2O}(l) \longrightarrow 2\overset{+1\ -2\ +1}{NaOH}(aq) + \overset{0}{H_2}(g)$$

- **Disproportionation reaction:** It is when both the reduction and oxidation takes place in the same element of the same compound, during the chemical reaction.

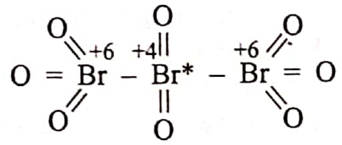


The Paradox of Fractional Oxidation Number

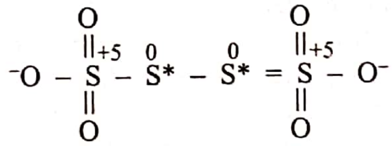
Sometimes, the oxidation number of a particular element in the compound is in fraction. Actually this fractional oxidation state is the average oxidation state of element under examination. This can be understood with structural parameters which reveal that element is present in different oxidation states.

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

Structure of C_3O_2 (carbon suboxide)



Structure of Br_3O_8 (tribromooctaoxide)



Structure of $S_4O_6^{2-}$ (tetrathionate ion)

Balancing of Redox Reaction

Oxidation Number Change Method

In a balanced redox reaction, total increase in oxidation number should be equal to the total decrease in the oxidation number. This equivalence has provided the basis for balancing redox reactions.

This procedure involves the following steps:

- Atom in oxidizing agent has been selected, whose oxidation number decreases and indicates the electron gain.
- Atom in reducing agent has been selected whose oxidation number increases and indicates the electrons loss.
- Now, these two are cross multiplied, i.e., multiply oxidizing agent by the number of loss of electrons and reducing agent by number of gain of electrons.
- Number of atoms on both sides are balanced, whose oxidation numbers change in the reaction.
- In order to balance oxygen atoms, H_2O molecules are added on the side deficient in oxygen.
- Then number of H atoms are balanced by adding H^+ ions to the side deficient in hydrogen.

Ion-electron Method or Half Reaction Method

The following steps are followed while balancing redox reaction (equations) using this method.

- Equation is written in the ionic form.
- Redox equation is to split into two half reactions one representing oxidation and the other representing reduction.
- These half-reactions are then balanced separately and then added by multiplying with suitable coefficients so that the electrons are cancelled. Balancing is done with the help of following sub-steps:

(a) All other atoms are balanced except H and O.

(b) Then balance oxygen atoms by adding H_2O(water) molecules to the side deficient in oxygen. The number of H_2O molecules added are equal to the deficiency of oxygen atoms.

(c) Hydrogen atoms are balanced by adding H^+ ions equal to the deficiency in the side which is deficient in hydrogen atoms.

(d) Charge is balanced by adding electrons to the side which is rich in +ve charge, i.e., deficient in electrons. Number of electrons added are equal to the deficiency.

(e) Number of electrons are equalized by multiplying the half-equations with suitable coefficients.

- These half-equations are then added to get an equation which is balanced with respect to charge and atoms.
- If the reaction medium is basic, OH^- ions are added to both the sides of balanced equation, which is equal to number of H^+ ions in balanced equation.

Acidic Medium:

- $Cr_2O_7^{2-} + C_2O_4^{2-} \longrightarrow Cr^{3+} + CO_2$
- Write both the half-reaction.

$Cr_2O_7^{2-} \longrightarrow Cr^{3+}$ (Reduction half-reaction)

$C_2O_4^{2-} \longrightarrow CO_2$ (Oxidation half-reaction)

- Atoms other than H and O are balanced.

$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$

$C_2O_4^{2-} \longrightarrow 2CO_2$

- Balance O-atoms by the addition of H_2O to another side.

$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$

$C_2O_4^{2-} \longrightarrow 2CO_2$

- Balance H-atoms by the addition of H^+ to another side

$Cr_2O_7^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O$

$C_2O_4^{2-} \longrightarrow 2CO_2$

- Now, balance the charge by the addition of electron (e^-).

$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$ (1)

$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$ (2)

- Multiply equations by a constant to get the same number of electrons on both side. In the above case, second equation is multiplied by 3 and then added to first equation.

$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$

$3C_2O_4^{2-} \longrightarrow 6CO_2 + 6e^-$

$Cr_2O_7^{2-} + 3C_2O_4^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 6CO_2 + 7H_2O$

Alkaline Medium:

- Consider the reaction.

$Cr(OH)_3 + IO_3^- \xrightarrow{OH^-} I^- + CrO_4^{2-}$

- Separate the two-half reactions.

$Cr(OH)_3 \longrightarrow CrO_4^{2-}$ (Oxidation half reaction)

$IO_3^- \longrightarrow I^-$ (Reduction half reaction)

- O-atoms are balanced by adding H_2O molecules

$H_2O + Cr(OH)_3 \longrightarrow CrO_4^{2-}$

$IO_3^- \longrightarrow I^- + 3H_2O$

- H-atoms are balanced by adding H^+ to the side having deficiency and add equal number of OH^- ions to other side (∴ medium is known)

$H_2O + Cr(OH)_3 \longrightarrow CrO_4^{2-} + 5H^+$

$5OH^- + H_2O + Cr(OH)_3 \longrightarrow CrO_4^{2-} + 5H^+ + 5OH^-$

or $5OH^- + Cr(OH)_3 \longrightarrow CrO_4^{2-} + 4H_2O$

$IO_3^- + 6H^+ \longrightarrow I^- + 3H_2O$

$IO_3^- + 6H^+ + 6OH^- \longrightarrow I^- + 3H_2O + 6OH^-$

or $IO_3^- + 3H_2O \longrightarrow I^- + 6OH^-$

- Charge is balanced by adding electrons

$5OH^- + Cr(OH)_3 \longrightarrow CrO_4^{2-} + 4H_2O + 3e^-$

$IO_3^- + 6H_2O + 6e^- \longrightarrow I^- + 3H_2O + 6OH^-$

- First equation is multiplied by 2 and then add to second to give

$10OH^- + 2Cr(OH)_3 \longrightarrow 2CrO_4^{2-} + 8H_2O + 6e^-$

$IO_3^- + 6H_2O + 6e^- \longrightarrow I^- + 3H_2O + 6OH^-$

Balanced half-reactions are added to give the complete balanced reaction.

$4OH^- + 2Cr(OH)_3 + IO_3^- \longrightarrow 5H_2O + 2CrO_4^{2-} + I^-$

Redox Reaction as basis of Titrations:

The titration methods are adopted for determination of strength of reductant or oxidant by indicator which is sensitive to redox reaction.

If indicator is used in $KMnO_4$ titirations, it itself acts as indicator. After the oxidation of last reductant the visible end point is achieved.

If $K_2Cr_2O_7$ is used, it oxidizes the indicator substance just after the equivalence point producing colour, hence can not be used as self indicator.

In iodometric and iodimetric titrations, starch (which produces blue colour) is used as indicator to detect whether I_2 reduces to I^- or I^- gets oxidized to I_2.

REDOX REACTIONS AND ELECTRODE PROCESSES

When the oxidized and reduced forms of a substance taking part in an oxidation or reduction half reaction, it is known as a redox couple. It is represented by separating the oxidized form from the reduced form by a vertical line or slash which represents an interface.

Electrode potential is the potential associated with each electrode. If the concentration of each species taking part in the electrode reaction is unity and the reaction is carried out at 298 K, then the potential of each electrode is called Standard Electrode Potential. The electrode potential of each electrode process measures the relative tendency of the active species to remain in the oxidized or reduced form

Table 8.1 The Standard Electrode Potentials at 298 K. Ions are present as aqueous species and H_2O as liquid; gases and solids are shown by g and s respectively.

Increasing strength of oxidising agent ↑

Reaction (Oxidised form + ne^-	→ Reduced form)	E^0/V
$F_2(g) + 2e^-$	$\rightarrow 2F^-$	2.87
$Co^{3+} + e^-$	$\rightarrow Co^{2-}$	1.81
$H_2O_2 + 2H^+ + 2e^-$	$\rightarrow 2H_2O$	1.78
$MnO_4^- + 8H^+ + 5e^-$	$\rightarrow Mn^{2+} + 4h_2O$	1.51
Au^{3+}	$\rightarrow Au(s)$	1.40
$C1_2(g) + 2e^-$	$\rightarrow 2Cl^-$	1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^-$	$\rightarrow 2Cr^{3+} + 7H_2O$	1.33
$O2(g) + 4H^+ + 4e^-$	$\rightarrow 2H_2O$	1.23
$MnO_2(s) + 4H^+ + 2e^-$	$\rightarrow Mn^{2+} + 2H_2O$	1.23
$Br_2 + 2e^-$	$\rightarrow 2Br$	1.09
$NO_3^- + 4H^+ + 3e^-$	$\rightarrow NO(g) + 2H_2O$	0.97
$2Hg^{2+} + 2e^-$	$\rightarrow Hg_1^{2+}$	0.92
$Ag^+ + e^-$	$\rightarrow Ag(s)$	0.80
$Fe^{3+} + e^-$	$\rightarrow Fe^{2+}$	0.77
$O_2(g) + 2H^+ + 2e^-$	$\rightarrow H_2O_2$	0.68
$I_2(s) + 2e^-$	$\rightarrow 2I^-$	0.54
$Cu^+ + e^-$	$\rightarrow Cu(s)$	0.52
$Cu^{2-} + 2e^-$	$\rightarrow Cu(s)$	0.34
$AgCl(s) + e^-$	$\rightarrow Ag(s) + Cl^-$	0.22
$AgBr(s) + e^-$	$\rightarrow Ag(s) + Br^-$	0.10
$2H^+ + 2e^-$	**$\rightarrow H_2(g)$**	0.00
$Ph^{2+} + 2e^-$	$\rightarrow Pb(s)$	-0.13
$Sn^{2-} + 2e^-$	$\rightarrow Sn(s)$	-0.14
$Ni^{2+} + 2e^-$	$\rightarrow Ni(s)$	-0.25
$Fe^{3+} + 2e^-$	$\rightarrow Fe(s)$	-0.44
$Cr^{3+} + 3e^-$	$\rightarrow Cr(s)$	-0.74
$Zn^{2+} + 2e^-$	$\rightarrow Zn(s)$	-0.76
$2H_2O + 2e^-$	$\rightarrow H^2(g) + 2OH^-$	-0.83
$AF^+ + 3e^-$	$\rightarrow Al(s)$	-1.66
$Mg^{2+} + 2e^-$	$\rightarrow Mg(s)$	-2.36
$Na^+ + e^-$	$\rightarrow Na(s)$	-2.71
$Ca^{2+} + 2e^-$	$\rightarrow Ca(s)$	-2.87
$K^+ + e^-$	$\rightarrow K(s)$	-2.93
$Li^+ + e^-$	$\rightarrow Li(s)$	-3.05

Increasing strength of oxidising agent ↓

1. A negative E^θ means that the redox couple is a stronger reducing agent than the H^+/H_2 couple.
2. A positive E^θ means that the redox couple is a weaker reducing agnent than the H^+/H_2 couple.