Redox Reactions

1) Oxidation number is the charge which an atom appears to acquire in a molecule, when all the bonding electrons are counted to more electro negative element. It may be positive, negative, zero or fractional.

2) The rules useful for the oxidation number are

i. In elementary state oxidation number of an element is zero.

E.g.: Oxidation number of H in hydrogen (H_2) is zero, Au in gold is zero and S in -sulphur (S_8) is zero

ii. Oxidation number of an atom in its charged monoatomic ion is equal to the charge on the ion.

E.g.: Oxidation state of P in phosphide is –3; Fe in ferrous ion is +2.

iii. Oxidation state of a metal in an alloy and in metal carbonyl is zero.

E.g.: Oxidation state of Sodium in sodium amalgam is zero.

Oxidation state of Fe in Iron pentacarbonyl i.e. $Fe(CO)_5$ is zero.

iv. The oxidation number of fluorine is always –1in all of its compounds.

Fluorine does not exhibit positive oxidation states. This is due to its highest electro negativity.

a) Oxidation number of F in hydrogen fluoride is –1

b) Oxidation number of F in sulphur hexafluoride is –1

v) Oxidation number of alkali metal in all its compounds is +1 and of an alkaline earth metal in all its compounds is +2.

vi. Oxidation state of hydrogen in covalent or molecular hydrides is +1. It is –1 in ionic or saline hydrides.

vii. Oxidation number of oxygen in its compounds is usually –2.

E.g. Oxidation number of O in alumina is –2

However, oxidation state of oxygen in peroxides like H_2O_2, Na_2O_2, BaO_2, etc., is –1 and in super oxides like KO_2, RbO_2, CsO_2, etc., is – 1/2. Oxygen exhibits +1 and +2 in O_2F_2 and OF_2 respectively because fluorine is more electronegative than oxygen.

viii. Oxidation number of sulphur in $H_2S_2O_8$, $K_2S_2O_8$, $S_2O_8^{2-}$ and H_2SO_5 is + 6 [These contain one peroxy linkage].

ix. In some compounds all the atoms of the same element may not have the same oxidation number. When we calculate the oxidation number we get the average value.

For example, in $Na_2\ S_2\ O_3$ the oxidation number of one sulphur atom is +6 and that of the other Sulphur atom is _2. So the average oxidation number of sulphur in $Na_2S_2O_3$ is +2.

x. In NCl_3 the oxidation number of Nitrogen is _3. In HN_3 [Hydrazoic acid] the oxidation number of Nitrogen is –1/3.

xi. The maximum oxidation number exhibited is equal to its group (Roman) number in the long form of the periodic table.

xii. The algebraic sum of oxidation numbers of all the atoms in a neutral molecule is zero. If the species is an ion, the algebraic sum of oxidation numbers of all atoms in the ion is equal to the charge of the ion.

xiii. The highest oxidation state possible for elements in periodic table is +8.it is shown by osmium (in OsO_4), Ruthenium (in RuO_4) and Xenon in XeO_4 . The lowest oxidation state possible for elements in periodic table is -4.it is shown by Carbon.

Oxidation, Reduction,

3. According to modern electronic concept,

   i) Oxidation is a process in which electrons are removed from an atom or ion. i.e de-electro nation is oxidation.

   ii) Reduction involves addition of electrons to an atom or ion i.e. electro nation.

4. Terms used in oxidation and reduction.

Term	Oxidation Number	In terms of electrons
Oxidation	Increases	Loss of electrons
Reduction	Decreases	Gain of electrons
Oxidising agent	Decreases	Accepts electrons
Reducing agent	Increases	Loses electrons
Substance oxidised	Increases	Loses electrons
Substance reduced	Decreases	Gains electrons

5. In a redox reaction, electrons are transferred from the reducing agent [reductant] to the oxidising agent [oxidant]. In a redox reaction the oxidant gets reduced and the reductant gets oxidised. The oxidation number of the reductant increases and that of the oxidant decreases.

6. Metals are reducing agents. Alkali metals are powerful reducing agents.

   Caesium is the most powerful reducing agent. In aqueous medium, Lithium is the most powerful reducing agent.

   Non-metals are oxidising agents. Fluorine is the most powerful oxidising agent. Next to Fluorine, Ozone is the most powerful oxidising agent.

7. An element present in its lowest oxidation state in a compound can act as a reducing agent.

E.g.: H_2S, $Na_2S_2O_3$, $FeSO_4$, $SnCl_2$ etc

8. An element present in its highest oxidation state in a compound can generally act as an oxidising agent.

   E.g.: $KMnO_4$, $K_2Cr_2O_7$, HNO_3, Conc. H_2SO_4, $HOCl$ etc

9. An element present in its intermediate oxidation state in a compound can act as a reducing as well as oxidising agent.

   E.g.: $NaNO_2$, SO_2

10. During redox reactions

    i. Halogens are reduced to halide ions $[X^-]$

    ii Potassium permanganate is reduced to Mn^{2+} in acid medium. In dilute alkaline medium or neutral medium MnO_4^- is reduced MnO_2. In strong alkaline medium MnO_4^- is reduced to MnO_4^{2-}

    iii. $K_2Cr_2O_7$ and K_2CrO_4 are reduced to Cr^{3+} in acid medium

11. All combustion reactions which make use of elemental dioxygen as well as other reactions involving elements other than dioxygen, are redox reactions. In combustion reactions, oxygen undergoes reduction (oxi.state decrease from 0 to –2)

    Eg: $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$

12. Decomposition reactions are the opposite of combination reactions.

    Eg: 1) $2HgO \rightarrow 2Hg + O_2$

    2) $2H_2O_{(g)} \rightarrow 2H_{2(g)} + O_{2(g)}$

    3) $2KClO_3 \rightarrow 2KCl_{(s)} + 3O_{2\,(g)}$

13. All decomposition reactions are not redox reactions.

E.g.: $MgCO_{3(s)} \rightarrow MgO_{(s)} + CO_{2(g)}$

14. All displacement reactions are red-ox reactions.

$A + BC \rightarrow AC + B$

i. Metal displacement

E.g.: $Zn_{(s)} + CuSO_{4\,(aq)}\ ZnSO_4 + Cu$

$TiCl_{4\,(1)} + 2\,Mg_{(s)}\ Ti_{(s)} + 2MgCl_{2(s)}$

ii. Non-metal displacement

E.g.: $2KCl_{(aq)} + F_2 \rightarrow 2KF_{(aq)} + Cl_2$.

iii. Metal-non metal displacement

E.g.: $2HCl_{(aq)} + Zn \rightarrow ZnCl_2 + H_{2\,(g)}$

15. Disproportionate reactions involve the same element in the given form to undergo both oxidation and reduction simultaneously. To show disproportination an element should has at least three different oxidation states.

E.g. $P_4 + 3NaOH + 3H_2O \rightarrow 2NaH_2PO_2 + PH_3$, in this the oxidation state of P in P_4 is zero and it changes to +1 in NaH_2PO_2 and -3 in PH_3

16. The inverse of disproportionation is comproportionation. In comproportionation reactions, two species with the same element in two different oxidation states form a single product in which the element is in an intermediate oxidation state.

E.g.: $2H_2S + SO_2 \rightarrow 2H_2O + 3S$

-2 +4 0

17. In titrimetric analysis the substance of known concentration is called the titrant and the substance being titrated is called the titrand.

18. The process of adding the standard solution until the reaction is just complete is called titration.

19. The point at which the titrand just completely reacts is called the equivalence point or the theoretical point or stoichiometric end point.

20. In the redox reactions the completion of the titration is detected by a suitable methods

    i) Observing a physical change

    ii) By using a reagent known as indicator

21. A compound added to reacting solutions that undergo an abrupt change in a physical property usually colour is called indicator.

22. Oxidation - reduction titrations based on oxidation - reduction reactions are called redox titrations.

23. If a zinc rod is kept in copper sulphate solution the redox reaction takes place and heat is also evolved.

$$Zn_{(s)} + Cu^{2+}_{(aq)} \quad Zn^{2+}_{(aq)} + Cu_{(s)}$$

24. The species participating in oxidation and reduction half reactions is called redox couple.

25. Redox couple are separated by a vertical line or a slash that represent an interface with $Zn_{(s)} / Zn^{2+}_{(aq)}$

26. The two redox couples are represented by Zn^{2+} / Zn and Cu^{2+} / Cu.

27. Salt bridge is a U tube containing an inert electrolyte solution like KC*l* or KNO_3, or NH_4NO_3 made in the form of semisolid in agar-agar used to connect the two half cells of a Galvanic cell. It provides an electric contact between the two solutions.

28. When the concentration of the electrolyte is 1.0 M and temperature 298 K, the potential obtained for the electrode is called standard electrode potential. Standard electrode potential for hydrogen electrode is zero.

29. When the elements arranged in the ascending or descending order of their reduction potential values. This series is called electro chemical series or activity series.

30. If the standard reduction potential is negative then it is a stronger reducing agent than H^+ / H_2 couple.

31. A metal with negative SRP value can displaces hydrogen from dilute acids. Positive SRP metal cannot displace.

E.g.: Zn (E^0 = -0.76V) displaces Hydrogen from dilute HC*l* while Cu (E^0 = + 0.34V) cannot.

Balancing redox reaction by oxidation number method

For balancing a redox reaction by oxidation number method, follow the order of steps as listed below

i) Find the oxidation numbers of the elements whose oxidation state is being changed.

ii) Balance the number of atoms in both side of the equation of the element whose oxidation number is being changed.

iii) Now, find the increase and decrease in oxidation no.

iv) To equalize the change in oxidation states, multiply the species whose oxidation state is being changed, by a suitable integer.

v) If the coefficient developed are not correct, then change them by inspection (such coefficient changes is required when an element from a compound goes in 2 different compounds, one with the same oxidation state & the other with changed oxidation state).

vi) Count the charges on both sides of the equation and balance the charges in the equation by adding requisite in acidic medium or OH^- in basic medium to the required side.

vii) Balance the hydrogen and oxygen by adding the appropriate number of H_2O molecules on the required side.

E.g.: In the equation: + I^- + H^+ $\rightarrow Cr^{3+}$ $+I_2$, the stoichiometric coefficient of, I^-, H^+ are respectively

(A) 1, 6, 14 (B) 1, 2, 14 (C) 2, 1, 14 (D) 1, 6, 12

Solution: (A)

i) Find the oxidation states of atoms undergoing redox change

$$\overset{+6\times2}{Cr_2}O_7^{2-} + I^- \longrightarrow Cr^{3+} + \overset{0}{I_2}$$

ii) Balance the number of atoms undergoing redox change.

$$\overset{(+6)x2}{Cr_2}O_7^{2-} + \overset{2x(-1)}{2I^-} \longrightarrow \overset{(+3)x2}{2Cr^{3+}} + \overset{Ox2}{I_2}$$

iii) Find the change in oxidation states and balance the change in oxidation states by multiplying the species with a suitable integer.

$$\overset{+12}{Cr_2}O_7^{2-} + \overset{-2}{2I^-} \longrightarrow \overset{+6}{2Cr^{3+}} + \overset{0}{I_2}$$

Change in ox. State = 6

As the decrease in oxidation state of chromium is 6 and increase in oxidation state of iodine is 2, so, we will have to multiply I^-/I_2 by 3 to equalize the changes in oxidation states.

Cr_2 + $6I^-$ $2Cr^{3+}$ + $3I_2$

iv) Find the total charges on both the sides and also find the difference of charges.

Charge on LHS = –2 + 6 × (-1) = –8

Charge on RHS = 2 × (+3) = +6.

Difference in charge = +6 – (–8) = 14

v) Now, as the reaction is taking place in acidic medium, we will have to add the H^+ ions, to the side falling short in positive charges, so we will add $14H^+$ on LHS to equalize the charges on both sides.

$Cr_2 + 6I^- + 14H^+ \quad 2Cr^{3+} + 3I_2$

vi) To equalize the H and O atoms, add $7H_2O$ on RHS

$Cr_2O_7^{2-} + 6I^- + 14H^+ \quad 2Cr^{3+} + 3I_2 + 7H_2O$

Balancing redox reaction by ion-electron method

This method of balancing redox reaction involves following steps.

1. Separate the reactants and products into half-reactions involving the elements that change its oxidation number. Write the skeleton equations for each half-reaction.
2. Balance each half-reaction separately involving given steps.

   i) First balance the atoms of the element undergoing oxidation or reduction.

   ii) Then balance atoms of the elements other than hydrogen and oxygen.

   iii) For balancing oxygen atoms in acidic or neutral medium, add suitable number of H_2O molecules to the side deficient in O, while in alkaline medium, add equal number of H_2O molecules as the excess of O on the side having excess of O atoms and add double the number of OH^- ions on the opposite side of the equation.

   iv) In order to balance the hydrogen atom in acidic or neutral medium, add required number of H^+ to the side deficient in H, while in alkaline medium, add equal number of OH^- ions as the excess number of atom on the side having excess H and add equal number of H_2O molecule on the opposite side of the equation
3. Multiply each half-reaction by suitable integer to make the number of electrons lost and gained same and add both the half-equations to get a completely balanced reaction.

E.g. In the equation: $H_2C_2O_4 + KMnO_4 \rightarrow CO_2 + K_2O + MnO + H_2O$, the Stoichiometric coefficients of CO_2, K_2O, MnO are respectively.

(1) 10, 1, 1 (2) 10, 2, 2 (3) 4, 1, 7 (4) 10, 1, 2

Solution: (4)

Step 1: Select the oxidant, reductant atoms and write their half reactions, one representing oxidation and other reduction.

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

$5e + Mn^{+7} \rightarrow Mn^{+2}$

Step 2: Balance the no. of electrons.

$5C_2^{+3}$' $\rightarrow 10C^{+4} + 10e$

10e + 2Mn7→ 2Mn2+

And add the two equations

$5C_2^{+3}$+ 2Mn7+ → 10C4+ + 2Mn2+

Step 3: Write complete molecule of the reductant and oxidant from which respective redox atoms were obtained.

$5H_2C_2O_4 + 2KMnO_4 \rightarrow 10CO_2 + 2MnO$

Step 4: Balance other atoms if any (Except H and O).

In above example K is unbalanced, therefore,

$5H_2C_2O_4 + 2KMnO_4 \rightarrow 10CO_2 + 2MnO + K_2O$ (Mentioned as product)

Step 5: Balance O atom using H_2O on desired side.

$5H_2C_2O_4 + 2KMnO_4 \rightarrow 10CO_2 + 2MnO + K_2O + 5H_2O$