>>Nothing is Is~~m~~possible.!

REDOX

REDOX Rx^N

Oxidation :-

↳ De-electronation.

↳ The process in which one or more e^- are lost by an atom, ion or molecule.

↳ e.g., $Zn^{\cancel{2+}} \rightarrow Zn^{2+} + 2e^-$

$Na \rightarrow Na^+ + e^-$

$X \rightarrow X^{n+} + ne^-$

Reduction :-

↳ Electronation.

↳ The process in which one or more e^- are gained by an atom, ion or molecule.

↳ e.g., $O^{2-} + 2e^- \rightarrow O$

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

$X^{n+} + ne^- \rightarrow X$

Redox Reaction (Oxidation - Reduction Rx^n) :-

↳ Rx^n involving transfer of e^- from one chemical substance to another.

↳ Rx^n involving oxidation and reduction both simunteneously.

↳ Rx^n in which increase as well as decrease in oxidation number of same or different atoms occurs.

Oxidation state :- of an atom

- O.S. in a molecule or ion is the hypothetical or real charge present on an atom due to electronegativity change

- O.S. of an element in a compound represents the number of electron are lost or gained during its change from free elemental state into that compound.

- can be +ve or -ve.

- can be zero, fractional value or whole number.

- can be different in same or different compound.

- Some helping Rules for calculating oxidation number :-

1) The O.S. of an element in its free (elemental) state is zero. (e.g., Na, Zn, O_2 etc. are 0).
2) The O.S. of an element in its allotropic form (e.g., $C_{diamond}$, $C_{graphite}$, $S_{monoclinic}$, $S_{Rhombic}$) is 0.
3) The O.S. of all the components of an alloy are zero.

Oxidising Agent or Oxidant :

↳ compounds which can oxidises others and reduce itself in a chemical rx^n.

↳ reagent in which for an element, oxidation number decreases or which undergoes gain of e^- in a redox rx^n.

↳ e.g., $KMnO_4$, HNO_3, $K_2Cr_2O_7$, conc. H_2SO_4.

Reducing Agent or Reductant :-

↳ compound which can reduce other and oxidises itself during the chemical rx^n.

↳ reagent in which for an element, oxidation number increases or which undergoes loss of e^- in a redox rx^n.

↳ e.g., KI, $Na_2S_2O_3$, etc.

TYPES OF REDOX RX^n :

1) Intermolecular Redox Rx^n :-

↳ A redox rx^n in which the oxidising agent and reducing agent are two different compound.

↳ e.g.,

$$\underline{10}\ \overset{2+}{Fe}SO_4 + 2K\overset{7+}{Mn}O_4 + \underline{8}\ H_2SO_4 \longrightarrow \underline{5}\ \overset{3+}{Fe_2}(SO_4)_3 + \overset{2+}{Mn}SO_4 + K_2SO_4 + \underline{8}H_2O$$

2) Disproportion Redox Rx^n :-

↳ ~~a~~ redox rx^n in which ~~redox~~ same element in a particular compound in a definite oxidation state is oxidized as well as reduced simutenously.

↳ e.g., $2H_2\overset{(-1)}{O_2}(aq) \longrightarrow 2H_2\overset{(-2)}{O}(l) + \overset{(0)}{O_2}(g)$

↳↳ Oxygen is the common element in the above rxn,

3) Intra molecular Redox Rx^n :-

↳ Both elements undergoing oxidation & reduction belongs to the same compound

↳ e.g., $2KClO_3 \longrightarrow 2KCl + 3O_2$

↳↳ $KClO_3$ plays the roles of both oxidant & reductant.

4) comproportion Redox Rx^n :-

↳ $NH_4NO_2 \longrightarrow N_2 + 2H_2O$

↳↳ Here, nitrogen in this compound has +3 and -3 oxidation number, which is not a definite value.

↳ A redox rx^n in which an element from two different oxidation state converted into a single oxidation state.

Balancing a Redox Rx^n :-

1) Ion - Electron Method :-

① Assign the oxidation number to each element present in the rx^n.

$$\overset{2+}{Fe}\overset{6+}{S}\overset{2-}{O_4} + \overset{1+}{K}\overset{7+}{Mn}\overset{2-}{O_4} + \overset{1+}{H_2}\overset{6+}{S}\overset{2-}{O_4} \rightarrow \overset{3+}{Fe_2}(\overset{6+}{S}\overset{2-}{O_4})_3 + \overset{2+}{Mn}\overset{6+}{S}\overset{2-}{O_4} + \overset{1+}{H_2}\overset{2-}{O} + \overset{2+}{K_2}S\overset{2-}{O_4}$$

② Convert the eq^n in ionic form, by eliminating the species, which are not undergoing either oxidation and reduction.

undergoes reduction

$$Fe^{2+} + MnO_4^{\cancel{2}-} \rightarrow Fe^{3+} + Mn^{2+}$$

undergoes oxidation

③ Split the Ionic Rx^n in two half rx^n, (one for oxidation and other for reduction)

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

$$MnO_4^{\cancel{2}-} \longrightarrow Mn^{2+}$$

④ Balance the atom other than O_2 & H_2 atom in both half rx^ns.

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

$$MnO_4^{-} \longrightarrow Mn^{2+}$$

(Both are balanced on both side).

⑤ Balance O and H atom by H_2O & H^+ respectively by the following way :- For one excess oxygen atom, add one H_2O on the other side and two H^+ on the same side.

$$Fe^{2+} \rightarrow Fe^{3+}$$ (no Oxygen atom)

$$8H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4H_2O$$

⑥ Balance the eq^ns chargewises by adding e^- to the electrically positive side.

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

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

⑦ The no. of e^- gained & lost in each half-rxn are equalised by multiplying both the half rxn with a suitable factor & finally the half rxn are added to give the overrall balanced rxn.

$$(Fe^{2+} \rightarrow Fe^{3+} + e^-) \times 5$$
$$(5e^- + 8H^+ + MnO_4^- \rightarrow Mn^{2+} + 4H_2O) \times 1$$

$$5Fe^{2+} + 8H^+ + MnO_4^- \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

⑧ Convert the Ionic Rxn into molecular form by adding the elements or species, which are removed in step (2).

$$10\,Fe(SO_4) + 2KMnO_4 + 8H_2SO_4 \rightarrow 5\,Fe_2(SO_4)_3 + 2MnO_4 + 8H_2O + K_2SO_4$$

~~# Applications of Oxidation Number :-~~

~~ⓐ~~

2) Oxidation Number Method :-

ⓐ Write the oxidation number of all the atoms.

$$Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO_2 + H_2O$$

$$\overset{(0)}{Cu} + \overset{(1+)}{H}\overset{(5+)}{N}\overset{(2-)}{O_3} \rightarrow \overset{(2+)}{Cu}(\overset{(5+)}{N}\overset{(2-)}{O})_3 + \overset{(4+)}{N}\overset{(2-)}{O_2} + \overset{(1+)}{H_2}\overset{(2-)}{O}$$

ⓑ Select the atom in oxidant/reductant whose O.N. decrease/increases and indicate the number of gain of e^- / loss of e^- per molecules.

$$\overset{(0)}{Cu} \rightarrow \overset{2+}{Cu}(\overset{5+}{N}\overset{2-}{O_3})_2$$ ---- (i) (O.N. of Cu is increased by 2)

$$H\overset{(5+)}{N}O_3 \rightarrow \overset{(4+)}{N}O_2$$ -- (ii) (O.N. of N is decreased by 1)

ⓒ Cross multiply, i.e., multiplying oxidant by no. of lossed e^- & reductant by no. of gained e^-.

$$Cu + 2HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + H_2O$$

(d) Balance the no. of atom on both sides whose O.N. change in the rx^{n}.

$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

(c) Balance O_2 atoms by adding required no. of H_2O molecules to the side of deficient of oxygen. Balance the required no. of H atoms by adding H^+ ions to the side deficient of Hydrogen.

Application of Oxidation Number :-

1) To compare the strength of oxyacid.
2) To determine the oxidising and reducing nature of the substances.

↳ If effective element in a compound is present in maximum O.S. then the compound acts as Oxidant.

Effective Element → maximum O.S. pressence → Oxidant.

↳ If effective element in a compound is present in minimum O.S. then the compound acts as Reductant.

Effective Element → minimum O.S. pressence → Reductant.

↳ If Effective element in a compound is present in intermediate O.S. then the compound can act as Oxidant as well as Reductant.

Effective Element → intermediate O.S. pressence → Both Oxidant & Reductant.

*** **EQUIVALENT WEIGHT** :- of an oxidising agent or reducing agent is that weight which accept 1 mole electrons in a chemical rxn or loses 1 mole electrons in a chemical rxn.

3) To calculate the equivalent weight of ~~the~~ compounds.

↳ E.W. of oxidant $= \dfrac{\text{Molecular Weight}}{\text{No. of } e^- \text{ gained by 1 molecule}}$

$= M \,/\, \text{Net change in O.N. per molecule}$

↳ E.W. of Reductant $= \dfrac{\text{Molecular Weight}}{\text{No. of } e^- \text{ losed by 1 molecule}}$

$= \dfrac{M}{\text{Net change in O.N. per Molecule}}$

↳ ~~So~~ ~~Different~~ equivalent wt. of a compound is different in different condition.

4) To determine the possible molecular formula of compound.

Key Note

* Max. O.S. = No. of valence e^-
* Min. O.S. = 8 − (max. O.S.)
} (for an element)

Concept of n-factor / Valency Factor

1. n_f = No. of e^- exchanged per molecule
 = Net change in O.N. per molecule.

2. $E = \dfrac{M}{n_f}$ (E = eq. wt., M = molecular wt.)

3. Number of eqv. = No. of moles × n_f.

e.g., Suppose there are 3 atoms A, B and C and their ~~eq~~ oxidation number are 12, -2 and -4 respectively. Then the molecular formula will be -

Ans : Net charge on a free compound is zero.

$\therefore +12 = (-2)(x) + (-4)(y)$

$\Rightarrow +12 = (-2)(2) + (-4)(2)$

$\Rightarrow +12 = -4 \cancel{+} -8 = -12$

or, $+12 = (-2)(4) + (-4)(1)$

$\Rightarrow +12 = -8 - 4 = -12$.

So, the molecular formula is AB_2C_2 or AB_4C.

Law of Equivalence :-

↳ one equivalent of an element combine with one equivalent of the other, and in a chemical rxn same no. of equivalent (or mill equivalent) of reactants reacts to give mill equivalent of products seperately.

↳ $aA + bB \longrightarrow cC + dD$

m.eq A = meq. B = m.eq C = m.eq D [In General Rxn]

↳ In a compound M_xN_y

m.eq. of M_xN_y = m.eq M = m.eq. of N.

Key Note :-

$N_1V_1 = N_2V_2$ (always true)

$M_1V_1 = M_2V_2$ (may or may not be true).

$\rightarrow M_1 \times n_1 \times V_1 = M_2 \times n_2 \times V_2$ (always true)

— where 'n' terms represents 'n' factor.

Redox Titration :-

↳ Titrations based on Redox Processes.

↳ Titrate / Titrants are oxidising / reducing agents.

↳ Titrate + Titrants → Products.

M. eq. of Titrate = M. eq. of Titrants (at equivalent point)

→ Titration using Acidified $KMnO_4$:-

↳ In Redox Rx^n, use of $KMnO_4$ as oxidising agent was 1st made for Fe^{2+} ions.

Imp. titrations using $KMnO_4$:-

1) $KMnO_4$ v/s Oxalic Acid :-

↳ $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + \overset{10CO_2}{\cancel{5O_2}} + 8H_2O$

end point :- Light Pink color of MnO_4^- soln, $KMnO_4$ acts as self indicator.

↳ Mill equivalent of $KMnO_4$ = Mill equivalent of Oxalic Acid

$\Rightarrow N_{KMnO_4} \times V_{KMnO_4} = N_{oxalic\ acid} \times V_{oxalic\ acid}$

2) $KMnO_4$ v/s Fe^{2+} ions :-

↳ Fe^{2+} gets readily oxidised by MnO_4^- to Fe^{3+}.

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

End Point :- MnO_4^- acts as self indicator and light pink color of soln indicates end point.

↳ At equivalent point :-

1 mol MnO_4^- reacts with 5mol Fe^{2+}

$\Rightarrow$ M.eq. of MnO_4^- = M.eq. of Fe^{2+}

$\Rightarrow N_{KMnO_4} \times V_{KMnO_4} = N_{Fe^{2+}} \times V_{Fe^{2+}}$

$\Rightarrow 5 \times M_{KMnO_4} \times V_{KMnO_4} = 1 \times M_{KMnO_4} \times V_{KMnO_4}$

3) Estimation of Fe^{2+} and Fe^{3+} ions in a solution :-

↳ In this estimation, the solution is titrated twice. first without reduction ~~with~~

in which only Fe^{2+} reacts and Fe^{3+} ~~ion~~ remains unreacted. In 2nd step same volume of solution is taken, Fe^{3+} ions are reduced to Fe^{2+} and then titrated.

Here :-

i) In step I :- M.eq. of $KMnO_4$ (let x) = M.eq. of Fe^{2+}

ii) In step-II :- M.eq. of $KMnO_4$ (y) = M.eq. of Fe^{2+} + M.eq. of Fe^{3+}

4) Analysis of sample containing oxalic acid and sodium oxalate :-

Same volume of solution are titrated seperately with NaOH and $KMnO_4$ sol^n.

M.eq. of NaOH = M.eq. of ~~[illegible]~~ Oxalic Acid

and M.eq. of $KMnO_4$ = M.eq. of oxalic acid + M.eq of Sodium oxalate.

→ Titration Using Acidified $K_2Cr_2O_7$:-

In volumetric analysis,

$Cr_2O_7^{2-}$ is also used as oxidant. (weaker than MnO_4^-)

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

$$E_{Cr_2O_7^{2-}} = \frac{M_{Cr_2O_7^{2-}}}{6} = \frac{296}{6} = 49.$$

These titrations are made in 1-2 N acid sol^n. In neutral or alkaline medium, it is not used. In alkaline medium orange $Cr_2O_7^{2-}$ changes to yellow CrO_4^{2-}

Iodometric and Iodimetric Titration :-

↳ Iodine acts as mild oxidising agent.

↳ These titrations fall into 2 categories :-

ⓐ Iodimetry :- standard I_2 solⁿ is used to titrate easily oxidisable substances.

ⓑ Iodometry :- In iodiometric titrations, an oxidant is allowed to react with excess KI (or I^-) solⁿ. The I_2 liberated is titrated with hypo solⁿ.

I_2 (insoluble in water) remains in the solⁿ containing KI as KI_3.

miscellaneous :-

1. n_f for species undergoes disproportion

$$= \frac{n_R \times n_O}{n_R \times n_O}$$ (where n_R and n_O are n_f for Reduction & Oxidation Process)

2. Oxidation species :-

$\left.\begin{matrix} H_2SO_5 \\ H_2S_2O_8 \end{matrix}\right\} S(+6)$

$CrO_5 \} Cr(+6)$

$K_3CrO_8 \} Cr(+5)$

$CaTiO_4 \} Ti(+4)$