Redox Reactions

- “Oxidation” is defined as the addition of oxygen/electronegative element to a substance or removal of hydrogen/electropositive element from a substance.
- Removal of oxygen/electronegative element from a substance or addition of hydrogen/ electropositive element to a substance is reduction.
- Half reactions that involve loss of electrons are called oxidation reactions. Similarly, the half reactions that involve gain of electrons are called reduction reactions.
- Oxidation: Loss of electron(s) by any species.
- Reduction: Gain of electron(s) by any species.
- Oxidising agent : Acceptor of electron(s).
- Reducing agent : Donor of electron(s).
- Oxidation number denotes the oxidation state of an element in a compound ascertained according to a set of rules formulated on the basis that electron in a covalent bond belongs entirely to more electronegative element.

- **Rules for Calculation of Oxidation number**
  - In elements, in the free or the uncombined state, each atom bears an oxidation number of zero. Evidently each atom in H_2, O_2, Cl_2, O_3, P4, S_8, Na, Mg, Al has the oxidation number zero.
  - The oxidation number of oxygen in most compounds is –2. However, we come across two kinds of exceptions here. One arises in the case of peroxides and superoxides. While in peroxides each oxygen atom is assigned an oxidation number of –1, in superoxides each oxygen atom is assigned an oxidation number of –(½).
  - For ions composed of only one atom, the oxidation number is equal to the charge on the ion. Thus Na+ ion has an oxidation number of +1.
  - The oxidation number of hydrogen is +1, except when it is bonded to metals in binary compounds (that is compounds containing two elements). For example, in LiH, NaH its oxidation number is –1.
  - In all its compounds, fluorine has an oxidation number of –1. Other halogens (Cl, Br, and I) also have an oxidation number of –1, when they occur as halide ions in their compounds. Chlorine, bromine and iodine when combined with oxygen, for example in oxoacids and oxoanions, have positive oxidation numbers.
  - The algebraic sum of the oxidation number of all the atoms in a compound must be zero. In polyatomic ion, the algebraic sum of all the oxidation numbers of atoms of the ion must equal the charge on the ion.

- **Types of Redox Reactions**

  - Combination Reaction
    A combination reaction may be denoted in the manner:
    $A + B \rightarrow C$
    Either A and B or both A and B must be in the elemental form for such a reaction to be a redox reaction.

  - Decomposition reactions
    Decomposition reactions are the opposite of combination reactions. Precisely, a decomposition reaction leads to the breakdown of a compound into two or more components at least one of which must be in the elemental state.

  - Displacement reactions
    In a displacement reaction, an ion (or an atom) in a compound is replaced by an ion (or an atom) of another element. It may be denoted as:
    $X + YZ \rightarrow XZ + Y$
    Displacement reactions fit into two categories: metal displacement and non-metal displacement.

  - Disproportionation reactions
    Disproportionation reactions are a special typeof redox reactions. In a disproportionationreaction an element in one oxidation state issimultaneously oxidised and reduced. One ofthe reacting substances in adisproportionation reaction always containsan element that can exist in at least threeoxidation states. The element in the form ofreacting substance is in the intermediateoxidation state; and both higher and loweroxidation states of that element are formed inthe reaction.

- **Balancing of Redox Reactions by Oxidation Number Method.**

    - Write the correct formula for each reactant and product.
    - Identify atoms which undergo change in oxidation number in the reaction by assigning the oxidation number to all elements in the reaction.
    - Calculate the increase or decrease in the oxidation number per atom and for the entire molecule/ion in which it occurs. If these are not equal then multiply by suitable coefficients so that these become equal.
    - Ascertain the involvement of ions if the reaction is taking place in water, add H^+ or OH^- ions to the expression on the appropriate side so that the total ionic charges of reactants and products are equal. If the reaction is carried out in acidic solution, use H^+ ions in the equation; if in basic solution, use OH^- ions.
    - Make the numbers of hydrogen atoms in the expression on the two sides equal by adding water (H2O) molecules to the reactants or products.

- **Balancing of Redox Reactions by Half Reaction Method**

    - Produce unbalanced equation for the reaction in ionic form.
    - Separate the equation into half-reactions.
    - Balance the atoms other than O and H in each half reaction individually.
    - For reactions occurring in acidic medium, add H_2O to balance O atoms and H^+ to balance H atoms.
    - Add electrons to one side of the half reaction to balance the charges. If need be, make the number of electrons equal in the two half reactions by multiplying one or both half reactions by appropriate coefficients.
    - We add the two half reactions to achieve the overall reaction and cancel the electrons on each side. This gives the net ionic equation.
    - Verify that the equation contains the same type and number of atoms and the same charges on both sides of the equation. This last check reveals that the equation is fully balanced with respect to number of atoms and the charges.

- A redox couple is defined as having together the oxidised and reduced forms of a substance taking part in an oxidation or reduction half reaction.

Sample Examples

- Permanganate ion reacts with bromide ionin basic medium to give manganese dioxide and bromate ion. Write the balanced ionic equation for the reaction.

  Solution

  Step 1 : The skeletal ionic equation is :

  $MnO_4^-(aq) + Br^-(aq) \rightarrow MnO_2(s) + BrO_3^-(aq)$

  Step 2 : Assign oxidation numbers for Mn and Br

  +7 -1 +4 +5

  $MnO_4^-(aq) + Br^-(aq) \rightarrow MnO_2(s) + BrO_3^-(aq)$

  Step 3 : Calculate the increase and decrease of oxidation number, and make the increase equal to the decrease.

  $2MnO_4^-(aq) + Br^-(aq) \rightarrow 2MnO_2(s) + BrO_3^-(aq)$

Step 4 : As the reaction occurs in the basic medium, and the ionic charges are not equal on both sides, add 2 OH^- ions on the right to make ionic charges equal.

$2MnO_4^-(aq) + Br^-(aq) \rightarrow 2MnO_2(s) + BrO_3^-(aq) + 2OH^-$

Step 5 : Finally, count the hydrogen atoms and add appropriate number of water molecules (i.e. one H2O molecule) on the left side to achieve balanced redox change.

$2MnO_4^-(aq) + Br^-(aq) + H_2O \rightarrow 2MnO_2(s) + BrO_3^-(aq) + 2OH^-$

- Justify that the reaction : 2 Na(s) + H_2(g) → 2 NaH (s) is a redox change.

  Solution

  Since in the above reaction the compound formed is an ionic compound, which may also be represented as Na^+H^- (s), this suggests that one half reaction in this process is :

  2 Na (s) → 2 Na^+(g) + 2e^-

  and the other half reaction is:

  H^2 (g) + 2e^- → 2 H^-(g)

  This splitting of the reaction under examination into two half reactions automatically reveals that here sodium is oxidised and hydrogen is reduced, therefore, the complete reaction is a redox change.