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Oxidation Number

"The real or hypothetical charge present on one atom of an element in a molecule is called oxidation number of respective element in respective molecule."

OR

"The charge left on one atom of an element when all the atoms or groups attached to this atom are separated as ions is called oxidation number of respective element in respective molecule."

The oxidation number may be real or hypothetical and is decided by following rules-

(1) In uncombined state, oxidation number of all the elements is zero. For example, oxidation number of Na, K, Mg, Al, O_2, N_2, P_4, S_8 etc. is zero.

(2) In combined state, oxidation number of alkalis metals (Li, Na, K etc.) is always +1, alkaline earth metals (Be, Mg, Ca etc.) is always +2 and that of Al is always +3.

(3) In combined state, oxidation number of hydrogen is usually +1 but in metal hydrides (such as LiH, NaH, CaH_2 etc.) it is -1.

(4) In combined state, oxidation number of fluorine is always -1 but that of other halogens (Cl, Br, I) is usually -1. When these halogens are attached with more electronegative atoms such as F, O and N then their oxidation number is some positive number. For example, in Cl_2O the oxidation number of chlorine is +1.

(5) In combined state, oxidation number of oxygen is usually -2 but in metal peroxide (Na_2O_2, BaO_2 etc.) it is -1, in metal superoxide (KO_2, SrO_2 etc.) it is -1/2 and in F_2O it is +2.

(6) The sum of the oxidation number of all the atoms of a molecule is zero. For example,

For $KMnO_4$ molecule-

$$\text{O. N. of K} + \text{O.N. of Mn} + 4 \times \text{O.N. of O} = 0$$

(7) The oxidation number of monoatomic ion is equal to the number of charge on the ion. For example, oxidation number of Na^+, Mg^{2+} and Al^{3+} are +1, +2 and +3 respectively. Similarly, oxidation number of Cl^-, O^{2-} and N^{3-} are -1, -2 and -3 respectively.

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(8) The sum of the oxidation number of all the atoms of a polyatomic ion is equal to the number of the charge on the respective ion. For example,

For MnO_4^- ion-

O.N. of Mn + 4 × O.N. of O = -1

Q. Find per atom oxidation number of under lined element in following species-

(1) $K\underline{Mn}O_4$ (2) $K\underline{Cl}O_3$ (3) $\underline{Cr}_2O_7^{2-}$

(4) $K_4[\underline{Fe}(CN)_6]$ (5) $[\underline{Co}(NH_3)_6]^{3+}$

Ans. Let, per atom oxidation number of under lined element is x. Then,

(1) For $K\underline{Mn}O_4$

$$(+1) + x + 4 \times (-2) = 0$$

$$\therefore \quad x = +7$$

(2) For $K\underline{Cl}O_3$

$$(+1) + x + 3 \times (-2) = 0$$

$$\therefore \quad x = +5$$

(3) For $\underline{Cr}_2O_7^{2-}$

$$2x + 7 \times (-2) = -2$$

$$\therefore \quad x = +6$$

(4) For $K_4[\underline{Fe}(CN)_6]$

$$4 \times (+1) + x + 6 \times (-1) = 0$$

$$\therefore \quad x = +2$$

(5) For $[\underline{Co}(NH_3)_6]^{3+}$

$$x + 6 \times (0) = +3$$

$$\therefore \quad x = +3$$

(2) Oxidation Number Concept of Oxidation and Reduction

(a) Oxidation

"The process in which oxidation number of an element increases is called oxidation."

For example,

$$\overset{0}{Na} \rightarrow \overset{+1}{Na^+} + e^-$$

$$\overset{0}{Zn} \rightarrow \overset{+2}{Zn^{2+}} + 2e^-$$

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$$\overset{+2}{Fe^{2+}} \rightarrow \overset{+3}{Fe^{3+}} + e^-$$

$$\overset{-1}{Cl^-} \rightarrow \overset{0}{\tfrac{1}{2} Cl_2} + e^-$$

$$\overset{0}{\tfrac{1}{2} H_2} \rightarrow \overset{+1}{H^+} + e^-$$

It is clear that, in oxidation positive charge on a species increases or negative charge on the species decreases. This increase or decrease of charge is equal to the number of electrons removed.

(b) Reduction

"The process in which oxidation number of an element decreases is called reduction."

For example,

$$\overset{0}{Cl} + e^- \rightarrow \overset{-1}{Cl^-}$$

$$\overset{0}{O} + 2e^- \rightarrow \overset{-2}{O^{2-}}$$

$$\overset{+2}{Cu^{2+}} + 2e^- \rightarrow \overset{0}{Cu}$$

$$\overset{+3}{Fe^{3+}} + e^- \rightarrow \overset{+2}{Fe^{2+}}$$

$$\overset{0}{\tfrac{1}{2} H_2} + e^- \rightarrow \overset{-1}{H^-}$$

$$\overset{0}{\tfrac{1}{2} Cl_2} + e^- \rightarrow \overset{-1}{Cl^-}$$

It is clear that, in reduction the negative charge on a species increases or positive charge on the species decreases. This increase or decrease of charge is equal to the number of electrons gained.

Oxidation-Reduction Reactions or Redox Reaction

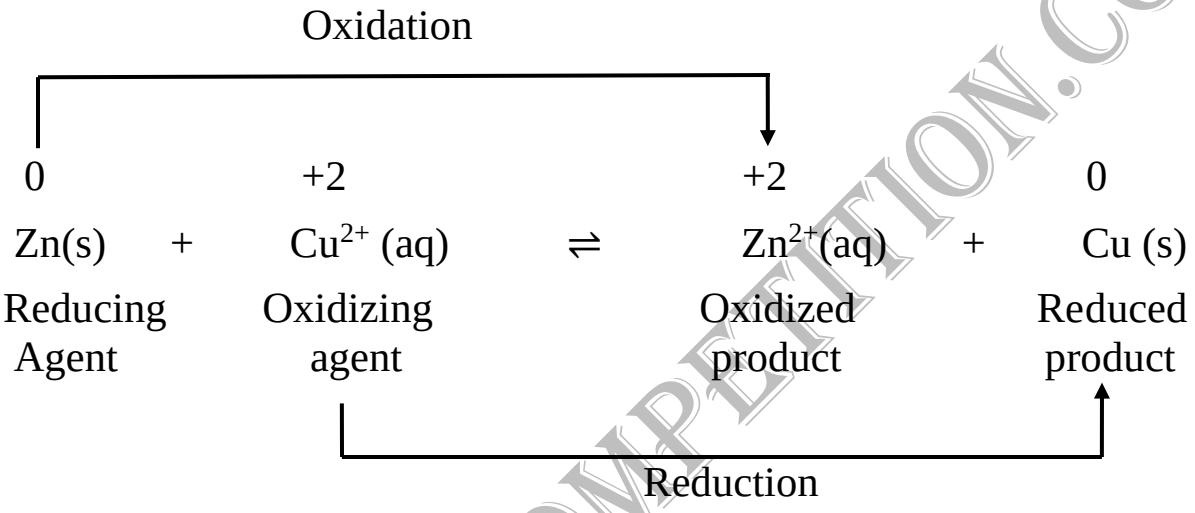
Those reactions in which both oxidation and reduction processes occur simultaneously are called oxidation-reductions reactions or redox reactions."

In oxidation number concept oxidation-reductions reactions or redox reactions have been defined in terms of change of oxidation number of different reactants. By definition,

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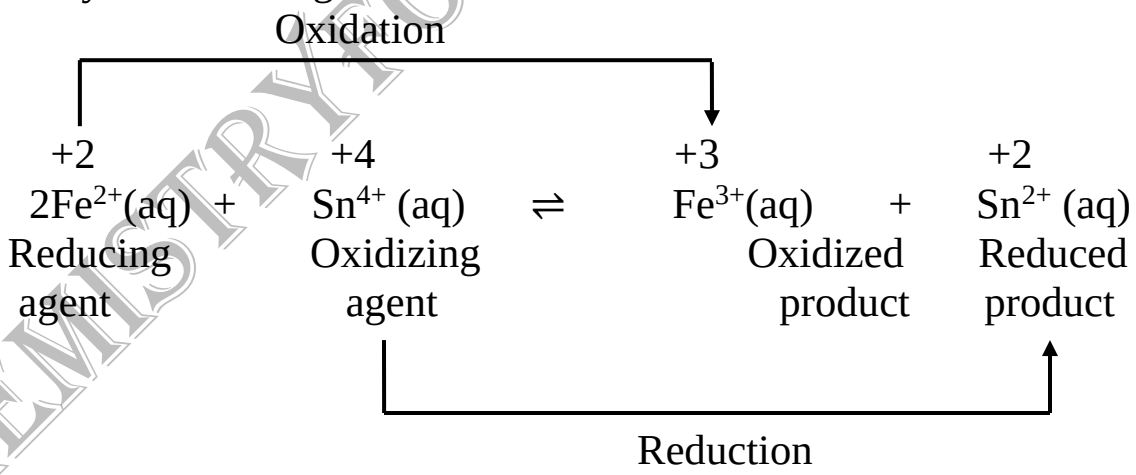
"The reactions in which oxidation number of different reactants changes are called oxidation-reductions reactions or redox reactions."

Here, the reactant whose oxidation number increases i.e. which is oxidized causes reduction of another reactant and therefore it is called reducing agent. On the other hand, the reactant whose oxidation number decreases i.e. which is reduced causes oxidation of first reactant and therefore it is called oxidizing agent. For example, in following redox reaction-



Here, oxidation number of Zn(s) increases from 0 to +2. Hence, it acts like reducing agent. On the other hand, oxidation number of Cu^{2+}(aq) decreases from +2 to 0. Hence, it acts like oxidizing agent.

Similarly, in following redox reaction-



Here, oxidation number of Fe $^{2+}$(aq) increases from +2 to +3. Hence, it acts like reducing agent. On the other hand, oxidation number of Sn^{4+} (aq) decreases from +4 to +2. Hence, it acts like oxidizing agent.

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Balancing of Redox Reactions

Following are the important criterias of a balanced redox reactions-

(1) Atoms of all the elements should be balanced on either sides of the equation.

(2)The number of electrons removed by reducing agent should be equal to the number of electrons gained by oxidizing agent.

(3)The increase of the oxidation number of reducing agent should be equal to the decrease of the oxidation number of oxidizing agent.

(4) Charge should be balanced on either sides of the equation.

Following are two important methods of balancing a redox reaction-

(1) Partial equation method or ion-electron method

(2) Oxidation number change method

(1) Partial Equation Method
or
Ion – Electron Method

The important steps involved in this method are as under-

(1) First per atom oxidation number of different elements are represented in imbalanced equation (skeletal equation). Here, it becomes clear that which element is acting like oxidizing agent and which one like reducing agent.

(2) Now, the given redox reaction is splitted into two partial equations i.e. oxidation and reduction half reactions.

(3) Now atoms other than oxygen and hydrogen are balanced in both the partial equations by multiplying different species by appropriate numbers.

(4) Now, oxygen is balanced by adding sufficient number of H_2O molecules to the side deficient in oxygen.

(5) Now, hydrogen is balanced. Here, if the reaction is occurring in acidic medium then suitable number of H^+ ions are added to the side deficient in hydrogen. But, if the reaction is occurring in basic medium then for balancing hydrogen, suitable number of H_2O molecules are added to the side deficient in hydrogen and same number of OH^- ions are added in opposite side.

(6) In this step charge is balanced in partial equations by adding appropriate number of electrons. In oxidation half reaction it is added in product side while in reduction half reactions it is added in reactant side.

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(7) Now, number of electrons removed in oxidation is balanced by number of electrons gained in reduction by multiplying partial equations by some suitable numbers (usually cross multiplication is carried out).
(8) Finally, both the partial equations are added to get balanced redox reaction.

Q. Balance following redox reaction using partial equation method-

$Fe^{2+}(aq) + Cr_2O_7^{2-}(aq)\ H^+(aq) \rightleftharpoons Fe^{3+}(aq) + Cr^{3+}(aq) + H_2O(l)$

Ans. (1) Representing per atom oxidation number of different elements in imbalanced equation (skeletal equation).

$\overset{+2}{Fe^{2+}}(aq) + \overset{+6}{Cr_2O_7^{2-}}(aq) + H^+(aq) \rightleftharpoons \overset{+3}{Fe^{3+}}(aq) + \overset{+3}{Cr^{3+}}(aq) + H_2O(l)$

Reducing agent Oxidizing agent

(2) Splitting of the reaction into two partial equations i.e. oxidation and reduction half reactions.

$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq)$ (Oxidation half reaction)

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

(3) Balancing the atoms other than oxygen and hydrogen in both the partial equations (by multiplying different species by appropriate numbers)-

$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq)$

$Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq)$

(4) Now, balancing oxygen (by adding sufficient number of H_2O molecules to the side deficient in oxygen)-

$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq)$

$Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

(5) Now, balancing hydrogen in acidic medium (by adding suitable number of H^+ ions to the side deficient in hydrogen) -

$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq)$

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

(6) Balancing charge in partial equations (by adding appropriate number of electrons in appropriate side)-

$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$

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

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(7) Balancing number of electrons removed in oxidation to the number of electrons gained in reduction (by multiplying partial equations by some suitable numbers) and adding the partial equations-

$$[Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-] \times 6$$
$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

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

This is balanced form of given redox reaction.

(2) Oxidation Number Change Method

The important steps involved in this method are as under-

(1) First per atom oxidation number of different elements are represented in imbalanced equation (skeletal equation). Here, it becomes clear that which element is acting like oxidizing agent and which one like reducing agent.

(2) Now, total increase in oxidation number of reducing agent and total decrease in oxidation number of oxidizing agent are represented.

(3) In this step, total increase in oxidation number of reducing agent and total decrease in oxidation number of oxidizing agent are equalized by multiplying reducing and oxidizing agents by some suitable numbers (usually cross multiplication is carried out).

(4) Now atoms other than oxygen and hydrogen are balanced in both the partial equations by multiplying different species by appropriate numbers.

(5) Now, oxygen is balanced by adding sufficient number of H_2O molecules to the side deficient in oxygen.

(6) Now, hydrogen is balanced. Here, if the reaction is occurring in acidic medium then suitable number of H^+ ions are added to the side deficient in hydrogen. But, if the reaction is occurring in basic medium then for balancing hydrogen, suitable number of H_2O molecules are added to the side deficient in hydrogen and same number of OH^- ions are added in opposite side.

Thus, balanced form of given redox reaction gets obtained.

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Q. Balance following redox reaction using oxidation number change method-

$Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) + H^+(aq) \rightleftharpoons Fe^{3+}(aq) + Cr^{3+}(aq) + H_2O(l)$

Ans.- (1) Representing per atom oxidation number of different elements in imbalanced equation (skeletal equation).

$$\overset{+2}{Fe^{2+}}(aq) + \overset{+6}{Cr_2O_7^{2-}}(aq) + H^+(aq) \rightleftharpoons \overset{+3}{Fe^{3+}}(aq) + \overset{+3}{Cr^{3+}}(aq) + H_2O(l)$$

Reducing agent — Oxidizing agent

(2) Representing total increase in oxidation number of reducing agent and total decrease in oxidation number of oxidizing agent-

Total increase in O.No. of reducing agent = 1

$Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) + H^+(aq) \rightleftharpoons Fe^{3+}(aq) + Cr^{3+}(aq) + H_2O(l)$

Total decrease in O.No. of oxidizing agent = $2\times3 = 6$

(3) Equating total increase in oxidation number of reducing agent to the total decrease in oxidation number of oxidizing agent (by multiplying reducing and oxidizing agents by some suitable numbers)-

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

(4) Balancing the atoms other than oxygen and hydrogen in both the partial equations (by multiplying different species by appropriate numbers)

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

(5) Now, balancing oxygen (by adding sufficient number of H_2O molecules to the side deficient in oxygen)-

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

(6) Now, balancing hydrogen in acidic medium (by adding suitable number of H^+ ions to the side deficient in hydrogen)-

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

This is balanced form of given redox reaction.

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