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CHEMISTRY

Target : JEE (Main)

EQUIVALENT CONCEPT & TITRATIONS

EQUIVALENT CONCEPT & TITRATIONS

Contents

JEE(MAIN) SYLLABUS

Electronic concepts of oxidation and reduction, redox reactions, oxidation number, rules for assigning oxidation number, balancing of redox reactions, concept of equivalents, titration, hardness of water.

JEE(ADVANCED) SYLLABUS

Concept of oxidation and reduction, redox reactions, oxidation number, balancing redox reactions and normality, Law of Equivalence, titration, Application of redox titration, hardness of water, parts per million (PPM), Bleaching powder, Hydrogen peroxide (H_2O_2), Oleum.

Equivalent Concept & Titrations

Oxidation & Reduction

Let us do a comparative study of oxidation and reduction :

Oxidation

1. Addition of Oxygen
e.g. $2Mg + O_2 \rightarrow 2MgO$

2. Removal of Hydrogen
e.g. $H_2S + Cl_2 \rightarrow 2HCl + S$

3. Increase in positive charge
e.g. $Fe^{2+} \rightarrow Fe^{3+} + e^-$

4. Increase in oxidation number
e.g. $\overset{(+2)}{SnCl_2} \rightarrow \overset{(+4)}{SnCl_4}$

5. Removal of electron
e.g. $Sn^{2+} \rightarrow Sn^{4+} + 2e^-$

Reduction

1. Removal of Oxygen
e.g. $CuO + C \rightarrow Cu + CO$

2. Addition of Hydrogen
e.g. $S + H_2 \rightarrow H_2S$

3. Decrease in positive charge
e.g. $Fe^{3+} + e^- \rightarrow Fe^{2+}$

4. Decrease in oxidation number
e.g. $\overset{(+7)}{MnO_4^-} \rightarrow \overset{(+2)}{Mn^{2+}}$

5. Addition of electron
e.g. $Fe^{3+} + e^- \rightarrow Fe^{2+}$

Oxidation Number

- It is an imaginary or apparent charge developed over atom of an element when it goes from its elemental free state to combined state in molecules.
- It is calculated on basis of an arbitrary set of rules.
- It is a relative charge in a particular bonded state.
- In order to keep track of electron-shifts in chemical reactions involving formation of compounds, a more practical method of using oxidation number has been developed.
- In this method, it is always assumed that there is a complete transfer of electron from a less electronegative atom to a more electronegative atom.

Rules governing oxidation number

The following rules are helpful in calculating oxidation number of the elements in their different compounds. It is to be remembered that the basis of these rule is the electronegativity of the element .

- **Fluorine atom :**
Fluorine is most electronegative atom (known). It always has oxidation number equal to –1 in all its compounds

- **Oxygen atom :**
In general and as well as in its oxides , oxygen atom has oxidation number equal to –2.

In case of
(i) peroxide (e.g. H_2O_2 , Na_2O_2) is –1,
(ii) super oxide (e.g. KO_2) is –1/2
(iii) ozonide (e.g. KO_3) is –1/3
(iv) in OF_2 is + 2 & in O_2F_2 is +1

- **Hydrogen atom :**
In general, H atom has oxidation number equal to +1. But in metallic hydrides (e.g. NaH, KH), it is –1.

- **Halogen atom :**
In general, all halogen atoms (Cl, Br , I) have oxidation number equal to –1.
But if halogen atom is attached with a more electronegative atom than halogen atom, then it wil show positive oxidation numbers.

e.g. $K\overset{+5}{Cl}O_3$, $H\overset{+5}{I}O_3$, $H\overset{+7}{Cl}O_4$, $K\overset{+5}{Br}O_3$

- **Metals :**
  (a) Alkali metal (Li , Na, K, Rb, ...) always have oxidation number +1
  (b) Alkaline earth metal (Be , Mg , Ca ....) always have oxidation number +2.
  (c) Aluminium always has +3 oxidation number

Note : *Metal may have negative or zero oxidation number*

- Oxidation number of an element in free state or in allotropic forms is always zero

  e.g. $\overset{0}{O}_2, \overset{0}{S}_8, \overset{0}{P}_4, \overset{0}{O}_3$

- Sum of the oxidation numbers of atoms of all elements in a molecule is zero.
- Sum of the oxidation numbers of atoms of all elements in an ion is equal to the charge on the ion .
- If the group number of an element in modern periodic table is ***n***, then its oxidation number may vary from

  (n – 10) to ***(n – 18)*** (but it is mainly applicable for p-block elements)

  e.g. N- atom belongs to 15[th] group in the periodic table, therefore as per rule, its oxidation number may vary from

  –3 to +5 ($\overset{-3}{N}H_3, \overset{+2}{N}O, \overset{+3}{N}_2O_3, \overset{+4}{N}O_2, \overset{+5}{N}_2O_5$)

- The maximum possible oxidation number of any element in a compound is never more than the number of electrons in valence shell.(but it is mainly applicable for p-block elements)

Calculation of average oxidation number :

Solved Examples

Example-1 ***Calculate oxidation number of underlined element :***

(a) $Na_2\underline{S}_2O_3$ **(b) $Na_2\underline{S}_4O_6$**

Solution. (a) Let oxidation number of S-atom is x. Now work accordingly with the rules given before .

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

$x = +2$

(b) Let oxidation number of S-atom is x

$\therefore \quad (+1) \times 2 + (x) \times 4 + (-2) \times 6 = 0$

$x = + 2.5$

- It is important to note here that $Na_2S_2O_3$ have two S-atoms and there are four S-atom in $Na_2S_4O_6$. However none of the sulphur atoms in both the compounds have + 2 or + 2.5 oxidation number, it is the average of oxidation number, which reside on each sulphur atom. Therefore, we should work to calculate the individual oxidation number of each sulphur atom in these compounds.

Calculation of individual oxidation number

It is important to note that to calculate individual oxidation number of the element in its compound one should know the structure of the compound and use the following guidelines.

Formula :

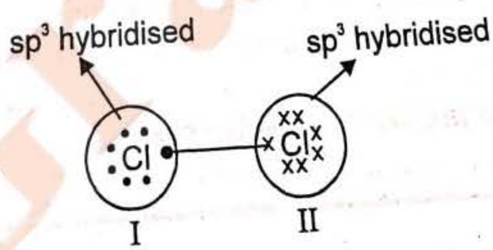
Oxidation Number = Number of electrons in the valence shell – Number of electrons taken up after bonding

Guidelines : It is based on electronegativity of elements.

1. If there is a bond between similar type of atom and each atom has same type of hybridisation, then bonded pair electrons are equally shared by each element.

Example : Calculate oxidation number of each Cl-atom in Cl_2 molecule

Structure :



Number of electrons taken up after bonding $= 7 - 7 = 0$.

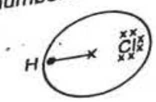
$\therefore$ oxidation number $= 7 - 7 = 0$

II : similarly, oxidation number $= 7 - 7 = 0$

2. *If there is a bond between different type of atoms :*
e.g. $A - B$ (if B is more electronegative than A)
Then after bonding, bonded pair of electrons are counted with B - atom .

Example : Calculate oxidation number of each atom in HCl molecule

Structure :



Note : Electron of H-atom is now counted with Cl-atom, because Cl-atom is more electronegative than H-atom

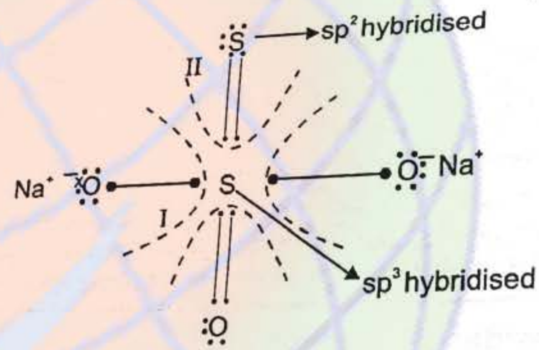
H : Number of electrons in the valence shell = 1
Number of electrons taken up after bonding = 0
Oxidation number of H $= 1 - 0 = +1$

Cl : Number of electrons in the valence shell = 7
Number of electrons taken up after bonding = 8
Oxidation number of Cl $= 7 - 8 = -1$

Solved Examples

Example-2 Calculate individual oxidation number of each S-atom in $Na_2S_2O_3$ (sodium thiosulphate) with the help of its structure .

Solution. **Structure :**



Note : ***I* (central S-atom) is sp³ hybridised (25% s-character) and *II* (terminal S-atom) is sp² hydbridised (33% s-character). Therefore, terminal sulphur atom is more electronegative than central sulphur atom. Now, the shared pair of electrons are counted with terminal S-atom.**

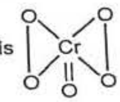
$\therefore$ *I*, S-atom : Number of electrons in the valence shell = 6
Number of electrons left after bonding = 0
Oxidation number of central S-atom $= 6 - 0 = +6$

II, S-atom : Number of electrons in the valence shell = 6
Number of electrons left after bonding = 8
Oxidation number of terminal S-atom $= 6 - 8 = -2$

Now, you can also calculate Average Oxidation number of S $= \dfrac{6 + (-2)}{2} = +2$ (as we have calculated before)

Miscellaneous Examples :

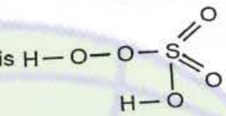
In order to determine the exact or individual oxidation number we need to take help from the structures of the molecules. Some special cases are discussed as follows:

- The structure of CrO_5 is 

From the structure, it is evident that in CrO_5 there are two peroxide linkages and one double bond. The contribution of each peroxide linkage is –2. Let the oxidation number of Cr is x.

$\therefore$ x + (–2)2 + (–2) = 0 or x = 6

$\therefore$ Oxidation number of Cr = + 6 **Ans**

- The structure of H_2SO_5 is 

From the structure, it is evident that in H_2SO_5, there is one peroxide linkage, two sulphur-oxygen double bonds and one OH group. Let the oxidation number of S = x.

$\therefore$ (+ 1) + (– 2) + x + (–2) 2+ (–2) + 1 = 0

or x + 2 – 8 = 0 or x – 6 = 0 or x = 6

$\therefore$ Oxidation number of S in H_2SO_5 is + 6 **Ans.**

Paradox of fractional oxidation number

Fractional oxidation number is the average of oxidation state of all atoms of element under examination and the structural parameters reveal that the atoms of element for whom fractional oxidation state is realised a actually present in different oxidation states. Structure of the species C_3O_2, Br_3O_8 and $S_4O_6^{2-}$ reveal the following bonding situations :

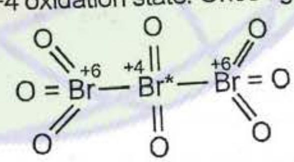
- The element marked with asterisk (*) in each species is exhibiting different oxidation number from rest of the atoms of the same element in each of the species. This reveals that in C_3O_2, two carbon atoms are present in +2 oxidation state each whereas the third one is present in zero oxidation state and the average is + 4/3. However, the realistic picture is +2 for two terminal carbons and zero for the middle carbon.

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

Structure of C_3O_2

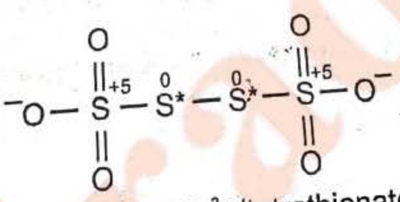
(Carbon suboxide)

- Likewise in Br_3O_8, each of the two terminal bromine atoms are present in +6 oxidation state and the middle bromine is present in +4 oxidation state. Once again the average, that is different from reality, is + 16/3.



Structure of Br_3O_8 (Tribromooctaoxide)

- In the same fashion, in the species $S_4O_6^{2-}$, average oxidation number of S is + 2.5, whereas the reality being +5,0,0 and +5 oxidation number respectively for respective sulphur atoms.



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

In general, the conclusion is that the idea of fractional oxidation state should be taken with care and the reality is revealed by the structures only.

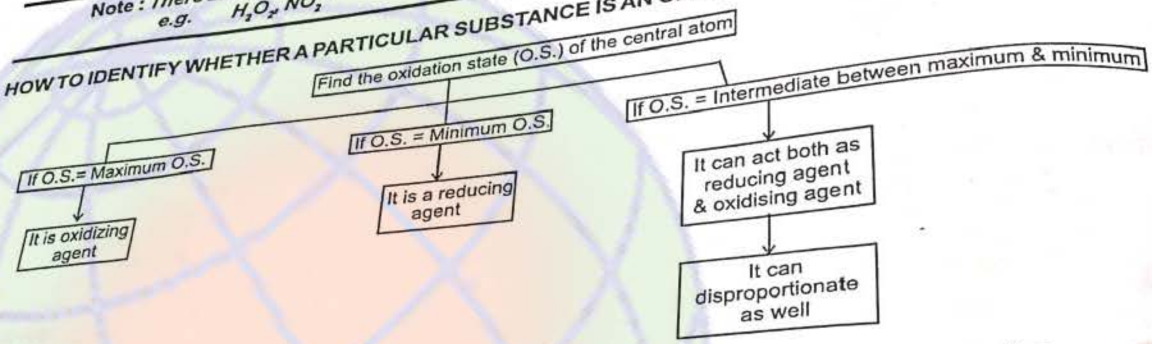
Oxidising and reducing agent

- **Oxidising agent or Oxidant :**
  Oxidising agents are those compounds which can oxidise others and reduce itself during the chemical reaction. Those reagents in which for an element, oxidation number decreases or which undergoes gain of electrons in a redox reaction are termed as oxidants.
  e.g. $KMnO_4$, $K_2Cr_2O_7$, HNO_3, conc.H_2SO_4 etc are powerful oxidising agents.

- **Reducing agent or Reductant :**
  Reducing agents are those compounds which can reduce other and oxidise itself during the chemical reaction. Those reagents in which for an element, oxidation number increases or which undergoes loss of electrons in a redox reaction are termed as reductants.
  e.g. KI, $Na_2S_2O_3$ etc are the powerful reducing agents.

Note : There are some compounds also which can work both as oxidising agent and reducing agent
e.g. H_2O_2, NO_2^-

HOW TO IDENTIFY WHETHER A PARTICULAR SUBSTANCE IS AN OXIDISING OR A REDUCING AGENT



Redox reaction

A reaction in which oxidation and reduction simultaneously take place is called a redox reaction
In all redox reactions, the total increase in oxidation number must be equal to the total decrease in oxidation number.

$$\text{e.g. } 10\overset{+2}{Fe}SO_4 + 2K\overset{+5}{Mn}O_4 + 8H_2SO_4 \longrightarrow 5\overset{+3}{Fe}_2(SO_4)_3 + 2\overset{+2}{Mn}SO_4 + K_2SO_4 + 8H_2O$$

Disproportionation Reaction :

A redox reaction in which same element present in a particular compound in a definite oxidation state is oxidized as well as reduced simultaneously is a disproportionation reaction.
Disproportionation reactions are a special type of redox reactions. One of the reactants in a disproportionation reaction always contains **an element that can exist in at least three oxidation states**. *The element in the form of reacting substance is in the intermediate oxidation state and both higher and lower oxidation states of that element are formed in the reaction. For example :*

$$2H_2\overset{-1}{O}_2(aq) \longrightarrow 2H_2\overset{-2}{O}(\ell) + \overset{0}{O}_2(g)$$

$$\overset{0}{S}_8(s) + 12OH^-(aq) \longrightarrow 4\overset{-2}{S}{}^{2-}(aq) + 2\overset{+2}{S}_2O_3^{2-}(aq) + 6H_2O(\ell)$$

$$\overset{0}{Cl}_2(g) + 2OH^-(aq) \longrightarrow \overset{+1}{Cl}O^-(aq) + \overset{-1}{Cl}{}^-(aq) + H_2O(\ell)$$

Consider the following reactions :

(a) $2KClO_3 \longrightarrow 2KCl + 3O_2$

$KClO_3$ plays a role of oxidant and reductant both. Here, Cl present in $KClO_3$ is reduced and O present in $KClO_3$ is oxidized. Since same element is not oxidized and reduced, so **it is not a disproportionation reaction,** although it looks like one.

(b) $NH_4NO_2 \longrightarrow N_2 + 2H_2O$
Nitrogen in this compound has -3 and +3 oxidation number, which is not a definite value. So it is not a disproportionation reaction. It is an example of comproportionation reaction, which is a class of redox reaction in which an element from two different oxidation state gets converted into a single oxidation state.

(c) $4K\overset{+5}{Cl}O_3 \longrightarrow 3K\overset{+7}{Cl}O_4 + K\overset{-1}{Cl}$
It is a case of disproportionation reaction and Cl atom is disproportionating.

List of some important disproportionation reactions

1. $H_2O_2 \longrightarrow H_2O + O_2$
2. $X_2 + OH^-(dil.) \longrightarrow X^- + XO^-$ (X = Cl, Br, I)
3. $X_2 + OH^-(conc.) \longrightarrow X^- + XO_3^-$

F_2 does not undergo disproportionation as it is the most electronegative element.

$F_2 + NaOH(dil.) \longrightarrow F^- + OF_2$

$F_2 + NaOH(conc.) \longrightarrow F^- + O_2$

4. $(CN)_2 + OH^- \longrightarrow CN^- + OCN^-$
5. $P_4 + OH^- \longrightarrow PH_3 + H_2PO_2^-$
6. $S_8 + OH^- \longrightarrow S^{2-} + S_2O_3^{2-}$
7. $MnO_4^{2-} \longrightarrow MnO_4^- + MnO_2$
8. $NH_2OH \longrightarrow N_2O + NH_3$
   $NH_2OH \longrightarrow N_2 + NH_3$
9. Oxyacids of Phosphorus (+1, +3 oxidation number)
   $H_3PO_2 \longrightarrow PH_3 + H_3PO_3$
   $H_3PO_3 \longrightarrow PH_3 + H_3PO_4$
10. Oxyacids of Chlorine(Halogens)(+1, +3, +5 Oxidation number)
    $ClO^- \longrightarrow Cl^- + ClO_2^-$
    $ClO_2^- \longrightarrow Cl^- + ClO_3^-$
    $ClO_3^- \longrightarrow Cl^- + ClO_4^-$
11. $HNO_2 \longrightarrow NO + HNO_3$

- Reverse of disproportionation is called **Comproportionation.** In some of the disproportionation reactions, by changing the medium (from acidic to basic or reverse), the reaction goes in backward direction and can be taken as an example of **Comproportionation reaction.**

$$I^- + IO_3^- + H^+ \longrightarrow I_2 + H_2O$$

Balancing of redox reactions

All balanced equations must satisfy two criteria.

1. **Atom balance (mass balance) :**
   There should be the same number of atoms of each kind on reactant and product side.

2. **Charge balance :**
   The sum of actual charges on both sides of the equation must be equal.
   There are two methods for balancing the redox equations :
   1. Oxidation - number change method
   2. Ion electron method or half cell method

- Since First method is not very much fruitful for the balancing of redox reactions, students are advised to use second method (Ion electron method) to balance the redox reactions

Ion electron method :
By this method redox equations are balanced in two different medium.
(a) Acidic medium (b) Basic medium

- **Balancing in acidic medium**
  Students are adviced to follow the following steps to balance the redox reactions by Ion electron method in acidic medium

Solved Examples

Example-3 Balance the following redox reaction :

$$FeSO_4 + KMnO_4 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + MnSO_4 + H_2O + K_2SO_4$$

Solution. **Step–I** Assign the oxidation number to each element present in the reaction.

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

Step II :
Now convert the reaction in Ionic form by eliminating the elements or species, which are not undergoing either oxidation or reduction.

$$Fe^{2+} + \overset{+7}{Mn}O_4^- \longrightarrow Fe^{3+} + Mn^{2+}$$

Step III :
Now identify the oxidation / reduction occuring in the reaction

undergoes reduction.

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

undergoes oxidation.

Step IV : Spilt the Ionic reaction in two half, one for oxidation and other for reduction.

$$Fe^{2+} \xrightarrow{\text{oxidation}} Fe^{3+} \quad \Big| \quad MnO_4^- \xrightarrow{\text{Reduction}} Mn^{2+}$$

Step V :
Balance the atom other than oxygen and hydrogen atom in both half reactions

$$Fe^{2+} \longrightarrow Fe^{3+} \quad \Big| \quad MnO_4^- \longrightarrow Mn^{2+}$$

Fe & Mn atoms are balanced on both side.

Step VI :
Now balance O & 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.

$Fe^{2+} \longrightarrow Fe^{3+}$ (no oxygen atom) ....(i)

$8H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4H_2O$ ....(ii)

Step VII :
Equation (i) & (ii) are balanced atomwise. Now balance both equations chargewise. To balance the charge, add electrons to the electrically positive side.

$Fe^{2+} \xrightarrow{\text{oxidation}} Fe^{3+} + e^-$ ....(1)

$5e^- + 8H^+ + MnO_4^- \xrightarrow{\text{Reduction}} Mn^{2+} + 4H_2O$ ....(2)

Step VIII :
The number of electrons gained and lost in each half -reaction are equalised by multiplying both the half reactions with a suitable factor and finally the half reactions are added to give the overall balanced reaction.

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