Oxidation number or Oxidation state.

(1) **Definition:** Charge on an atom produced by donating or accepting electrons is called **oxidation number** or **oxidation state.** It is the number of effective charges on an atom.

(2) **Valency and oxidation number:** Valency and oxidation number concepts are different. In some cases (mainly in the case of electrovalent compounds), valency and oxidation number are the same but in other cases they may have different values. Points of difference between the two have been tabulated below

Valency	**Oxidation number**
It is the combining capacity of the element. No plus or minus sign is attached to it.	O.N. is the charge (real or imaginary) present on the atom of the element when it is in combination. It may have plus or minus sign.
Valency of an element is usually fixed.	O.N. of an element may have different values. It depends on the nature of compound in which it is present.
Valency is always a whole number.	O.N. of the element may be a whole number or fractional.
Valency of the element is never zero except of noble gases.	O.N. of the element may be zero.

(3) **Oxidation number and Nomenclature**

(i) When an element forms two monoatomic cations (representing different oxidation states), the two ions are distinguished by using the ending-ous and ic. The suffix – ous is used for the action with lower oxidation state and the suffix – ic is used for the action with higher oxidation state. For example: Cu^{+} (oxidation number +1) cuprous: Cu^{2+} (oxidation number +2) cupric

(ii) **Albert Stock** proposed a new system known as Stock system. In this system, the oxidation states are indicated by Roman numeral written in parentheses immediately after the name of the element. For example,

Cu_2O	Copper (I) oxide	SnO	Tin (II) oxide
$FeCl_2$	Iron (II) chloride	Mn_2O_7	Manganese (VII) oxide
$K_2Cr_2O_7$	Potassium dichromate (VI)	Na_2CrO_4	Sodium chromate (VI)
V_2O_5	Vanadium (V) oxide	CuO	Copper (II) oxide
SnO_2	Tin (IV) oxide	$FeCl_3$	Iron (III) chloride

Note**:** Stock system is not used for non-metals.

(4) **Rules for the determination of oxidation number of an atom**

The following rules are followed in ascertaining the oxidation number of an atom,

(i) If there is a covalent bond between two same atoms then oxidation numbers of these two atoms will be zero. Bonded electrons are symmetrically distributed between two atoms. Bonded atoms do not acquire any charge. So oxidation numbers of these two atoms are zero.

$$A{:}\,A \text{ or } A - A \rightarrow A^{*} + A^{*}$$

For e.g. Oxidation number of Cl in Cl_2, O in O_2 and N and N_2 is zero.

(ii) If covalent bond is between two different atoms then electrons are counted towards more electronegative atom. Thus oxidation number of more electronegative atom is negative and oxidation number of less electronegative atom is positive. Total number of charges on any element depends on number of bonds.

$$A - B \rightarrow A^{+} + B{:}^{-}$$

$$A - B \rightarrow A^{+2} + {:}\,B\,{:}^{-2}$$

The oxidation number of less electronegative element (A) is + 1 and + 2 respectively.

(iii) If there is a coordinate bond between two atoms then oxidation number of donor atom will be + 2 and of acceptor atom will be – 2.

$$A \rightarrow B \rightarrow A^{2+} + B^{-2}$$

(iv) The oxidation number of all the atoms of different elements in their respective elementary states is taken to be zero. For example, in $N_2, Cl_2, H_2, P_4, S_8, O_2, Br_2, Na, Fe, Ag$ etc. the oxidation number of each atom is zero.

(v) The oxidation number of a monoatomic ion is the same as the charge on it. For example, oxidation numbers of Na^+, Mg^{2+} and Al^{3+} ions are + 1, + 2 and + 3 respectively while those of Cl^-, S^{2-} and N^{3-} ions are –1, –2 and –3 respectively.

(vi) The oxidation number of hydrogen is + 1 when combined with non-metals and is –1 when combined with active metals called metal hydrides such as LiH, KH, MgH_2, CaH_2 etc.

(vii) The oxidation number of oxygen is – 2 in most of its compounds, except in peroxides like H_2O_2, BaO_2 etc. where it is –1. Another interesting exception is found in the compound OF_2 (oxygen difluoride) where the oxidation number of oxygen is + 2. This is due to the fact that fluorine being the most electronegative element known has always an oxidation number of –1.

(viii) In compounds formed by union of metals with non-metals, the metal atoms will have positive oxidation numbers and the non-metals will have negative oxidation numbers. For example,

(a) The oxidation number of alkali metals (Li, Na, K etc.) is always +1 and those of alkaline earth metals (Be, Mg, Ca etc.) is + 2.

(b) The oxidation number of halogens (F, Cl, Br, I) is always –1 in metal halides such as KF, $AlCl_3$, $MgBr_2$, CdI_2. Etc.

(ix) In compounds formed by the union of different elements, the more electronegative atom will have negative oxidation number whereas the less electronegative atom will have positive oxidation number. For example,

(a) N is given an oxidation number of –3 when it is bonded to less electronegative atom as in NH_3 and NI_3, but is given an oxidation number of + 3 when it is bonded to more electronegative atoms as in NCl_3.

(b) Since fluorine is the most electronegative element known so its oxidation number is always –1 in its compounds i.e. oxides, interhalogen compounds etc.

(c) In interhalogen compounds of Cl, Br, and I; the more electronegative of the two halogens gets the oxidation number of –1. For example, in $BrCl_3$, the oxidation number of Cl is –1 while that of Br is +3.

(x) For neutral molecule, the sum of the oxidation numbers of all the atoms is equal to zero. For example, in NH_3 the sum of the oxidation numbers of nitrogen atom and 3 hydrogen atoms is equal to zero. For a complex ion, the sum of the oxidation numbers of all the atoms is equal to charge on the ion. For example, in SO_4^{2-} ion, the sum of the oxidation numbers of sulphur atom and 4 oxygen atoms must be equal to –2.

(xi) It may be noted that oxidation number is also frequently called as oxidation state. For example, in H_2O, the oxidation state of hydrogen is +1 and the oxidation state of oxygen is – 2. This means that oxidation number gives the oxidation state of an element in a compound.

(xii) In the case of representative elements, the highest oxidation number of an element is the same as its group number while highest negative oxidation number is equal to (8 – Group number) with negative

sign with a few exceptions. The most common oxidation states of the representative elements are shown in the following table,

Group	**Outer shell configuration**	**Common oxidation numbers (states) except zero in free state**
I A	ns^1	+1
II A	ns^2	+2
III A	ns^2np^1	+3, +1
IV A	ns^2np^2	+4,+3,+2,+1, –1, –2, –3, –4
V A	ns^2np^3	+5,+3,+1, –1, –3
VI A	ns^2np^4	+6,+4,+2,–2
VII A	ns^2np^5	+7,+5,+3, +1, –1

(xiii) Transition metals exhibit a large number of oxidation states due to involvement of (n –1) d electron besides ns electron.

(xiv) Oxidation number of a metal in carbonyl complex is always zero, e.g. Ni has zero oxidation state in $[Ni(CO)_4]$.

(xv) Those compounds which have only C, H and O the oxidation number of carbon can be calculated by following formula,

$$\boxed{\text{Oxidation number of 'C'} = \frac{(n_O \times 2 - n_H)}{n_C}}$$

Where, n_O is the number of oxygen atom, n_H is the number of hydrogen atom, n_C is the number of carbon atom.

For example, (a) $\overset{*}{C}H_3OH$; $n_H = 4, n_C = 1, n_O = 1$

Oxidation number of 'C' = $\frac{(1 \times 2 - 4)}{1} = -2$

(b) $HC\overset{*}{O}OH$; $n_H = 2,\ n_O = 2, n_c = 1$

Oxidation number of carbon = $\frac{(2 \times 2 - 2)}{1} = +2$

(5) **Procedure for calculation of oxidation number:** By applying the above rules, we can calculate the oxidation numbers of elements in the molecules/ions by the following steps.

(i) Write down the formula of the given molecule/ion leaving some space between the atoms.

(ii) Write oxidation number on the top of each atom. In case of the atom whose oxidation number has to be calculated write x.

(iii) Beneath the formula, write down the total oxidation numbers of each element. For this purpose, multiply the oxidation numbers of each atom with the number of atoms of that kind in the molecule/ion. Write the product in a bracket.

(iv) Equate the sum of the oxidation numbers to zero for neutral molecule and equal to charge on the ion.

(v) Solve for the value of x.

Oxidation number of some elements in compounds, ions or chemical species

Element	Oxidation Number	Compounds, ions or chemical species
Sulphur (s)	– 2	H_2S, ZnS, NaHS, $(SnS_3)^{2-}$, BaS, CS_2
	0	S, S_4, S_8, SCN^-
	+ 1	S_2, F_2, S_2Cl_2
	+ 4	SO_2, H_2SO_3, $(SO_3)^{2-}$, $SOCl_2$, $NaHSO_3$, $Ca[HSO_3]_2$, $[HSO_3]^-$, SF_4
	+ 6	H_2SO_4, $(SO_4)^{2-}$, $[HSO_4]^-$, $BaSO_4$, $KHSO_4$, SO_3, SF_6, $H_2S_2O_7$, $(S_2O_7)^{2-}$
Nitrogen (N)	– 3	NH_3, $(NH_4)^+$, AlN, Mg_3N_2, $(N)^{3-}$, Ca_3N_2, CN^-
	– 2	N_2H_4, $(N_2H_5)^+$
	– 1	NH_2OH
	–1/3	NaN_3, N_3H
	0	N_2
	+ 1	N_2O
	+ 2	NO
	+ 3	HNO_2, $(NO_2)^-$, $NaNO_2$, N_2O_3, NF_3
	+ 4	NO_2
	+ 5	HNO_3, $(NO_3)^-$, KNO_3, N_2O_5
Chlorine	– 1	HCl, NaCl, $CaCl_2$, $AlCl_3$, ICl, ICl_5, $SOCl_2$, CrO_2Cl_2, KCl, K_2PtCl_6, $HAuCl_4$, CCl_4
(Cl)	0	Cl, Cl_2
	+ 1	HOCl, NaOCl, $(OCl)^-$, Cl_2O
	+ 3	$KClO_2$, $(ClO_2)^-$, $HClO_2$
	+ 4	ClO_2
	+ 5	$(ClO_3)^-$, $KClO_3$, $NaClO_3$, $HClO_3$
	+ 7	$HClO_4$, Cl_2O_7, $KClO_4$, $(ClO_4)^-$
Hydrogen	– 1	NaH, CaH_2, $LiAlH_4$, LiH
(H)	+ 1	NH_3, PH_3, HF

Phosphorus	– 3	PH_3, $(PH_4)^+$, Ca_3P_2
(P)	0	P_4
	+ 1	H_3PO_2, KH_2PO_2, $BaH_4P_2O_4$
	+ 3	PI_3, PBr_3, PCl_3, P_2O_3, H_3PO_3
	+ 5	$(PO_4)^{3-}$, H_3PO_4, $Ca_3(PO_4)_2$, $H_4P_2O_7$, P_4O_{10}, PCl_5, $(P_2O_7)^{4-}$, $Mg_2P_2O_7$, ATP
Oxygen	– 2	H_2O, PbO_2, $(CO_3)^{2-}$, $(PO_4)^{2-}$, SO_2, $(C_2O_4)^{2-}$, HOCl, $(OH)^-$, $(O)^{2-}$
(O)	– 1	Na_2O_2, BaO_2, H_2O_2, $(O_2)^{2-}$, Peroxides
	– 1/2	KO_2
	0	O, O_2, O_3
	+ 1	O_2F_2
	+ 2	OF_2
Carbon	– 4	CH_4
(C)	– 3	C_2H_6
	– 2	CH_3Cl, C_2H_4
	– 1	CaC_2, C_2H_2
	0	Diamond, Graphite, $C_6H_{12}O_6$, $C_2H_4O_2$, HCHO, CH_2Cl_2
	+ 2	CO, $CHCl_3$, HCN
	+ 3	$H_2C_2O_4$, $(C_2O_4)^{2-}$
	+ 4	CO_2, H_2CO_3, $(HCO_3)^-$, CCl_4, Na_2CO_3, Ca_2CO_3, CS_2, CF_4, $(CO_3)^{-2}$
Chromium	+ 3	$Cr_2(SO_4)_3$, $CrCl_3$, Cr_2O_3, $[Cr(H_2O)_4Cl_3]$
(Cr)	+ 6	K_2CrO_4, $(CrO_4)^{2-}$, $K_2Cr_2O_7$, $(Cr_2O_7)^{2-}$, $KCrO_3Cl$, CrO_2Cl_2, $Na_2Cr_3O_{10}$, CrO_3
Manganese	+ 2	MnO, $MnSO_4$, $MnCl_2$, $Mn(OH)_2$
(Mn)	+ 8/3	Mn_3O_4
	+ 3	$Mn(OH)_3$
	+ 4	MnO_2, K_2MnO_3

	+ 6	K_2MnO_4, $(MnO_4)^{2-}$
	+ 7	$KMnO_4$, $(MnO_4)^-$, $HMnO_4$
Silicon	– 4	SiH_4, Mg_2Si
(Si)	+ 4	SiO_2, K_2SiO_3, $SiCl_4$
Iron (Fe)	$+\frac{8}{3}$	Fe_3O_4
	+ 2	$FeSO_4$ (Ferrous ammonium sulphate), $K_4Fe(CN)_6$, $FeCl_2$
	+ 3	$K_3[Fe(CN)_6]$, $FeCl_3$
Iodine (I)	+ 7	$H_4IO_6^-$, KIO_4
Osmium (Os)	+ 8	OsO_4
Xenon (Xe)	+ 6	XeO_3, XeF_6

(6) **Exceptional cases of evaluation of oxidation numbers:** The rules described earlier are usually helpful in determination of the oxidation number of a specific atom in simple molecules but these rules fail in the following cases. In these cases, the oxidation numbers are evaluated using the concepts of chemical bonding involved.

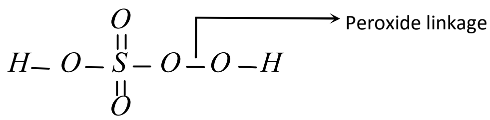
Type I. In molecules containing peroxide linkage in addition to element-oxygen bonds. For example,

(i) **Oxidation number of S in H_2SO_5**(Permonosulphuric acid or Caro's acid).

By usual method; H_2SO_5

$2 \times 1 + x + 5 \times (-2) = 0$ or $x = +8$

But this cannot be true as maximum oxidation number for S cannot exceed + 6. Since S has only 6 electrons in its valence shell. This exceptional value is due to the fact that two oxygen atoms in H_2SO_5 shows peroxide linkage as shown below,



Therefore the evaluation of o.n. of sulphur here should be made as follows,

2 × (+1) + x + 3 × (–2) + 2 × (–1)

(For H) (For S) (For O) (For O–O)

or 2 + x – 6 – 2 = 0 or x = + 6.

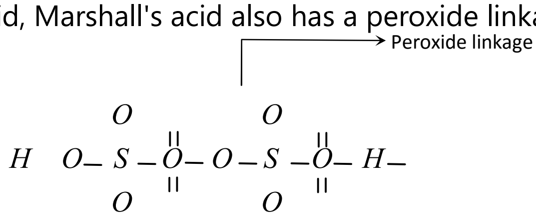
(ii) **Oxidation number of S in $H_2S_2O_8$**(Peroxidisulphuric acid or Marshall's acid)

By usual method; $H_2S_2O_8$

1 × 2 + 2x + 8 (–2) = 0

2x = + 16 – 2 = 14 or x = + 7

Similarly Caro's acid, Marshall's acid also has a peroxide linkage so that in which S shows +6 oxidation state.



Therefore the evaluation of oxidation state of sulphur should be made as follow,

2 × (+1) + 2 × (x) + 6 × (–2) + 2 × (–1) = 0

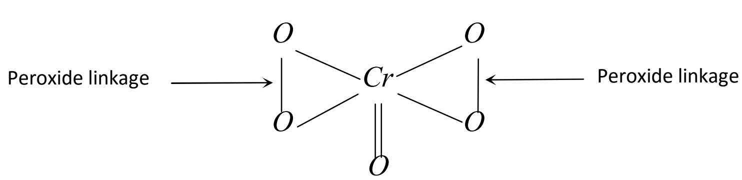
(for H) (for S) (for O) (for O–O)

or 2 + 2x – 12 – 2 = 0 or x = + 6.

(iii) **Oxidation number of Cr in CrO_5** (Blue perchromate)

By usual method CrO_5; x – 10 = 0 or x = + 10

This cannot be true as maximum o.n. of Cr cannot be more than + 6. Since Cr has only five electrons in 3d orbitals and one electron in 4s orbital. This exceptional value is due to the fact that four oxygen atoms in CrO_5 are in peroxide linkage. The chemical structure of CrO_5 is



Therefore, the evaluation of o.n. of Cr should be made as follows

x + 1 × (– 2) + 4 (–1) = 0

(For Cr) (For O) (For O–O)

or x – 2 – 4 = 0 or x = + 6.

Type II. In molecules containing covalent and coordinate bonds, following rules are used for evaluating the oxidation numbers of atoms.

(i) For each covalent bond between dissimilar atoms the less electronegative element is assigned the oxidation number of + 1 while the atom of the more electronegative element is assigned the oxidation number
of –1.

(ii) In case of a coordinate-covalent bond between similar or dissimilar atoms but the donor atom is less electronegative than the acceptor atom, an oxidation number of +2 is assigned to the donor atom and an oxidation number of –2 is assigned to the acceptor atom.

Conversely, if the donor atom is more electronegative than the acceptor atom, the contribution of the coordinate bond is neglected.

Example:

(a) Oxidation number of C in $HC \equiv N$ and $HN \overset{\rightarrow}{=} C$

The evaluation of oxidation number of C cannot be made directly by usual rules since no standard rule exists for oxidation numbers of N and C.

In such cases, evaluation of oxidation number should be made using indirect concept or by the original concepts of chemical bonding.

(b) Oxidation number of carbon in $H - N \overset{\rightarrow}{=} C$

The contribution of coordinate bond is neglected since the bond is directed from a more electronegative N atom (donor) to a less electronegative carbon atom (acceptor).

Therefore the oxidation number of N in $HN \overset{\rightarrow}{=} C$ remains – 3 as it has three covalent bonds.

1 × (+ 1) + 1 × (– 3) + x = 0

(For H) (For N) (For C)

or 1 + x – 3 = 0 or x = + 2.

(c) Oxidation number of carbon in $HC \equiv N$

In $HC \equiv N$, N is more electronegative than carbon, each bond gives an oxidation number of –1 to N. There are three covalent bonds, the oxidation number of N is $HC \equiv N$ is taken as – 3

Now $HC \equiv N$ $\therefore$ +1 + x – 3 = 0 $\Rightarrow$ x = + 2

Type III. In a molecule containing two or more atoms of same or different elements in different oxidation states.

(i) **Oxidation number of S in $Na_2S_2O_3$**

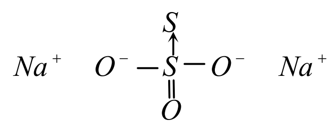
By usual method $Na_2S_2O_3$

$\therefore \quad 2 \times (+1) + 2 \times x + 3(-2) = 0$ or $2 + 2x - 6 = 0$ or $x = 2$.

But this is unacceptable as the two sulphur atoms in $Na_2S_2O_3$ cannot have the same oxidation number because on treatment with dil. H_2SO_4, one sulphur atom is precipitated while the other is oxidized to SO_2.

$$Na_2S_2O_3 + H_2SO_4 \rightarrow Na_2SO_4 + SO_2 + S + H_2O$$

In this case, the oxidation number of sulphur is evaluated from concepts of chemical bonding. The chemical structure of $Na_2S_2O_3$ is



Due to the presence of a co-ordinate bond between two sulphur atoms, the acceptor sulphur atom has oxidation number of – 2 whereas the other S atom gets oxidation number of + 2.

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

(For Na) (For O) (For S) (For coordinated S)

or $+2 - 6 + x - 2 = 0$ or $x = +6$

Thus two sulphur atoms in $Na_2S_2O_3$ have oxidation number of – 2 and +6.

(ii) **Oxidation number of chlorine in $CaOCl_2$**(bleaching powder)

In bleaching powder, Ca (OCl) Cl, the two Cl atoms are in different oxidation states i.e., one Cl^- having oxidation number of –1 and the other as OCl^- having oxidation number of +1.

(iii) **Oxidation number of N in NH_4NO_3**

By usual method $N_2H_4O_3$; $2x + 4 \times (+1) + 3 \times (-1) = 0$

$$2x + 4 - 3 = 0 \quad \text{or} \quad 2x = +1 \qquad \text{(wrong)}$$

No doubt NH_4NO_3 has two nitrogen atoms but one N has negative oxidation number (attached to H) and the other has positive oxidation number (attached to O). Hence the evaluation should be made separately for NH_4^+ and NO_3^-

NH_4^+ $\quad x + 4 \times (+1) = +1$ or $x = -3$

NO_3^- $\quad x + 3(-2) = -1$ or $x = +5$.

(iv) **Oxidation number of Fe in Fe_3O_4**

In Fe_3O_4, Fe atoms are in two different oxidation states. Fe_3O_4 can be considered as an equimolar mixture of FeO (iron (II) oxide) and Fe_2O_3 (iron (III) oxide). Thus in one molecule of Fe_3O_4, two Fe atoms are in + 3 oxidation state and one Fe atom is in + 2 oxidation state.

(v) **Oxidation number of S in sodium tetrathionate ($Na_2S_4O_6$).** Its structure can be represented as follows:

The two S-atoms which are linked to each other have oxidation number of zero. The oxidation number of other S-atoms can be calculated as follows

Let oxidation number of S = x.

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

(For S) (For S–S) (For O)

$x = +5$.