Oxidation Number

Any element in nature exists in two forms; free form also known as the elemental form and combined form (molecules, compounds and ions). If it exists in a free form, it has no charge and if it exists in a combined form, it has a charge. This charge is known as the oxidation number. Therefore, **Oxidation number** also called as **oxidation state** is **the charge on an atom in a molecule or a compound**. The oxidation numbers, positive or negative, are assigned to elements (atoms) in compounds based on certain rules, which are:

First, you got to know how to recognize an elemental form by its symbol. All elemental forms (except few mentioned below) carry the same symbols as atomic symbols. For example, Cu, Fe, Au, and Ag are the elemental symbols as well as atomic symbols. Exceptions to this are the following elements, which have different symbols for elements and atoms:

Element	Elemental symbol	Atomic symbol
Hydrogen	H_2	H
Nitrogen	N_2	N
Oxygen	O_2	O
Fluorine	F_2	F
Chlorine	Cl_2	Cl
Bromine	Br_2	Br
Iodine	I_2	I
Phosphorous	P_4	P
Sulfur	S_8	S

Rules

- In free elemental states, atoms are assigned zero oxidation numbers. Why? We do not know the charges when the elements are created by the nature (most elements are nature-made and few of them are man-made).

- All alkali metals (Group IA) have oxidation number of +1, all alkaline earth metals (Group IIA) have the oxidation number of +2, Halogens (VIIIA) most commonly have the oxidation number of -1(Fluorine always has -1 but other halogens might change when they combine with a more electronegative halogen or oxygen).

- Hydrogen most commonly has the oxidation number of +1 when it bonded to nonmetals (H_2S, H_2O, HCl, etc) except in hydrides (bonded to metals, like NaH, LiH, CaH_2) where it has -1.

- Oxygen most commonly carries oxidation number of -2 (CaO, CO_2) except in peroxides (H_2O_2), where it carries -1.

- The sum of the oxidation states of all the elements in molecules or ions must be equal to the charges on the molecules or ions:
    - Neutral molecules do not carry any charges and hence the sum of the oxidation numbers in these molecules must be zero.
    - In polyatomic ions, the sum of the oxidation numbers must be equal to the net charge of the ions.

Assigning the Oxidation Number

First assign the oxidation number to more a common or a familiar element(s) based on the above first four rules and then predict the oxidation number on a less common or not so familiar element based on the last rule.

Example

Assign the oxidation numbers to all the elements in the following compounds or ions: (a) BaO_2, (b) Li_2O, (c) $Cr_2O_7^{2-}$, (d) NH_4^+, (e) $Ca_3(PO_4)_2$.

Answer

(a) Ba belongs to Group IIA and hence has the oxidation number of +2. BaO_2 is a neutral compound and hence by the last rule, it must carry -1 oxidation number.

$(1 \times Ba) + (2 \times O) = 0$
$(1 \times (+2)) + (2 \times O) = 0$
$+2 + (2 \times O) = 0$
or $O = -1$

(b) Li is an alkali metal and has +1 oxidation number. By the last rule, O must carry -2 oxidation number.

$(2 \times Li) + (1 \times O) = 0$
$(2 \times (+1)) + (1 \times O) = 0$
$+2 + (1 \times O) = 0$
or $O = -2$

(c) This is a polyatomic ion. Between two elements, O is more common than Cr. Hence, first assign the oxidation number to O and then predict the oxidation number on Cr. The O generally carries -2 oxidation number and there are seven O atoms, hence the total oxidation number on seven O atoms is -14. The sum of the oxidation numbers should add up to -2, the charge on the polyatomic ion:

$(2 \times Cr) + (7 \times O) = -2$

(2 x Cr) + (7 x (-2)) =-2
(2 x Cr) -14 = -2
2 x Cr = +12
or Cr = +6

(d) This is also a polyatomic ion with +1 charge. The H carries +1 oxidation number and hence

(1 x N) + (4 x H) = +1
(1 x N) + (4 x (+1)) = +1
(1 x N) +4 = +1
or N = -3

(e) In this compound, Ca carries +2 oxidation number and O carries -2. The most uncommon element here is P and hence the oxidation number on that is calculated as follows.

(3 x Ca) + (2 x P) + (8 x O) = 0
(3 x (+2)) + (2 x P) + (8 x (-2)) = 0
+6 + (2 x P) – 16 = 0
Or P = +5