Oxidation number (ON)

In a covalent bond, the electrons (always 2 in number) are not shared equally. This depends on the difference in electronegativity between the two atoms forming the bond. Oxidation numbers refer to the number of charges an atom in a molecule would have if all the bonds were broken.

Example: $H{-}O{-}H \longrightarrow H^{+} \quad O^{2-} \quad H^{+}$

- It is a way to keep track of the electrons in an oxidation−reduction reaction (redox).
- The term "oxidation state" is mostly used for ionic compounds where the species have a real charge.
- A compound (molecule or ion) is said to be **oxidized** if its **oxidation number increases** in a reaction.
- On the other hand, if a compound is **reduced,** its **oxidation number decreases** in a reaction.

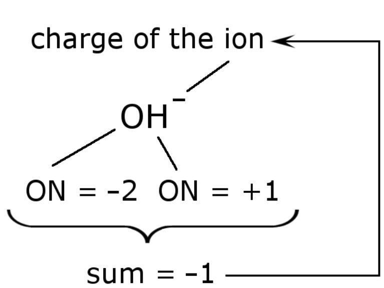
$$\overset{(+3)}{Fe^{3+}} + e^{-} \longrightarrow \overset{(+2)}{Fe^{2+}}$$

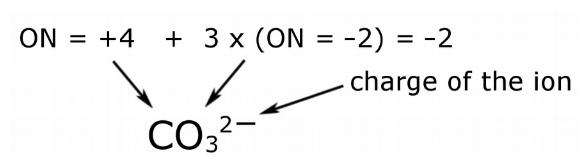
ON decreases
reduction

species	Oxidation number	example	exception
pure elements	0	O_2, Li, Cu, F_2	
single ions	valence	$Fe^{3+} = +3$, $S^{2-} = -2$	
F in compounds	−1	HF, SF_6	
O in compounds	−2	H_2O, CO, NO_2	peroxide H_2O_2: ON = −1
H in compounds	+1	H_2O, HF	Hydride MH: ON = −1
Cl, Br, I in compounds	−1	HCl, CH_3Cl	ON variable if O and F are present.

> The sum of all the ON of the atoms present in a compound = 0.
>
> The sum of all the ON of the atoms in an ion = charge of the ion.

Example:





Exercises

Find the oxidation number of the underlined atom in each of the following compounds:

a. $\underline{C}O$

b. $Li_3\underline{N}$

c. $\underline{NaH}$

d. $\underline{N}_2O_4$

e. $\underline{N}O_2$

f. $\underline{Ni}(OH)_2$

g. $H\underline{Cl}O_4$

h. $\underline{N}H_4^+$

I. $\underline{Si}F_2O$

j. $\underline{Ir}O_4^+$

k. $\underline{Cl}O_2^-$

l. $\underline{U}O_2^{2+}$

m. $[\underline{Fe}(CN)_6]^{3-}$ *(see hint)*

n. $(NH_4)_2\underline{S}O_3$

o. $\underline{Fe}_3O_4$

Hint: *$[\underline{Fe}(CN)_6]^{3-}$* *None of these atoms in this ion are listed in the oxidation number determination table. However, the "CN" group is the cyanide ion “CN^-”, with a charge of −1.*

$\underline{Fe}_3O_4$ *A fractional oxidation number is possible since this compound contains both Fe^{2+} and Fe^{3+} ions but in different proportions.*

For each of the following reaction (half-reaction), use the change of the oxidation number to indicate if the reaction is a reduction or an oxidation.

p. $H_2 \rightarrow 2H^+$

q. $V^{5+} \rightarrow V^{3+}$

r. $SF_6 \rightarrow SF_3$

s. $NO_3^- \rightarrow NO_2$

t. $S_2O_3^{2-} \rightarrow SO_4^{2-}$

Answers:

a. C = +2

b. N = −3

c. H = −1

d. N = +4

e. N = +4

f. Ni = +2

g. Cl = +7

h. N = −3

I. Si = +4

j. Ir = +9

k. Cl = +3

l. U = +6

m. Fe = +3

n. S = +4

o. Fe = +8/3 or $+2.\overline{6}$

p. oxidation: ON(H) $0 \rightarrow +1$

q. reduction: ON(V) $+5 \rightarrow +3$

r. reduction: ON(S) $+6 \rightarrow +3$, ON(F) unchanged.

s. reduction: ON(N) $+5 \rightarrow +4$, ON(O) unchanged.

t. oxidation: ON(S) $+2 \rightarrow +6$, ON(O) unchanged.

Recognizing a redox reaction

In a redox reaction, the oxidation number of the atoms changes.

Any chemical reaction involving an **element** (e.g. H_2, Fe) is a redox reaction:

$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

$C(s) + O_2(g) \longrightarrow CO_2(g)$ no metal, no charges, still it is a redox reaction.

All **combustion** reactions are redox reactions (since the element O_2 is involved).

$CH_4 + 2O_2 \longrightarrow 2H_2O + CO_2$

The ON of the carbon changes from (−4) in CH_4 to (+4) in CO_2.

Therefore the carbon is oxidized and the oxygen is reduced.

The following reactions are **not oxidation−reduction** reactions since there is **no change of the ON** anywhere.

Precipitation:

$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$

Acid base:

$Ba(OH)_2(aq) + 2HBr(aq) \longrightarrow 2H_2O(l) + BaBr_2(aq)$

However, a precipitation reaction can also involve the presence of a redox reactions

$2CuCl_2(aq) + 4I^-(aq) \longrightarrow 2CuI(s) + I_2(aq) + 4Cl^-(aq)$

Type of chemical reaction − Exercise

For each of the following, identify the type of chemical reactions

P = precipitation, **N** = Neutralization (acid−base), **RedOx** = Reduction−Oxidation

		Type
a.	$Ba(OH)_2(aq) + 2HClO_3(aq) \longrightarrow Ba(ClO_3)_2(aq) + H_2O(\ell)$	
b.	$SiCl_4(aq) + 2Mg(s) \longrightarrow 2MgCl_2(aq) + Si(s)$	
c.	$CaCl_2(aq) + Na_2SO_4(aq) \longrightarrow NaCl(aq) + CaSO_4(s)$	
d.	$CH_4(g) + H_2O(\ell) \longrightarrow CO(g) + 3H_2(g)$	
e.	$CO_3^{2-}(aq) + 2HI(aq) \longrightarrow CO_2(g) + H_2O(\ell) + 2I^-(aq)$	
f.	$AgCH_3COO(aq) + NH_4Br(aq) \longrightarrow AgBr(s) + NH_4CH_3COO(aq)$	
g.	$2PbS(s) + 3O_2(g) \longrightarrow 2PbO(s) + 2SO_2(g)$	
h.	$HCl(aq) + NH_3(g) \longrightarrow NH_4Cl(aq)$	
i.	$Ca(OH)_2(aq) + H_2SO_4(aq) \longrightarrow CaSO_4(s) + 2H_2O(\ell)$	
j.	$CuCl_2(aq) + CrCl_2(aq) \longrightarrow CuCl(s) + CrCl_3(aq)$	

Answers and explanations

a. (N) OH^- from $Ba(OH)_2$ and H^+ from $HClO_3$ react together to form a salt and water

b. (RedOx) solid metal present as a reactant or a product = Redox. Here Mg and Si (metalloid)

c. (P) without any change of the O.N*, an insoluble product is formed, $CaSO_4(s)$ solutions.

d. (RedOx) change of the oxidation number of the carbon from CH_4 (−4) to CO_2 (+4).

e. (N) CO_3^{2-} is a base and HI is an acid. H_2CO_3 is formed but unstable and gives $CO_2(g) + H_2O(\ell)$.

f. (P) an insoluble product is formed, AgBr(s), from aqueous solutions.

g. (RedOx) change of the oxidation number of the sulfur from −2 to +2 and the oxygen from 0 to −2.

h. (N) no change in oxidation state an no precipitate. NH_3 = base, HCl = acid.

i. (N and P) acid−base reaction AND formation of an insoluble compound in aqueous solution.

j. (Redox and P) Cu and Cr are both changing their oxidation state AND CuCl(s): insoluble is formed.

Note* oxidation number (O.N.) and oxidation state are similar concepts. However, oxidation state is mainly for ionic compounds when an actual charge is present on an atom. For a covalent compound, the term oxidation number is more appropriate.