Chapter 11 Redox and Electrochemistry

Day - 1

OXIDATION AND REDUCTION

Redox reactions are those reactions in which oxidation and reduction takes place simultaneously

Classical view of redox reactions

- Oxidation is addition of oxygen / electronegative element to a substance or removal of hydrogen / electropositive element from a substance

$2\ Mg\ (s) + O_2\ (g) \rightarrow 2\ MgO\ (s)$
$S\ (s) + O_2\ (g) \rightarrow SO_2\ (g)$

$2\ H_2S(g) + O_2\ (g) \rightarrow 2\ S\ (s) + 2\ H_2O\ (l)$

- Reduction is removal of oxygen / electronegative element from a substance or addition of hydrogen / electropositive element to a substance

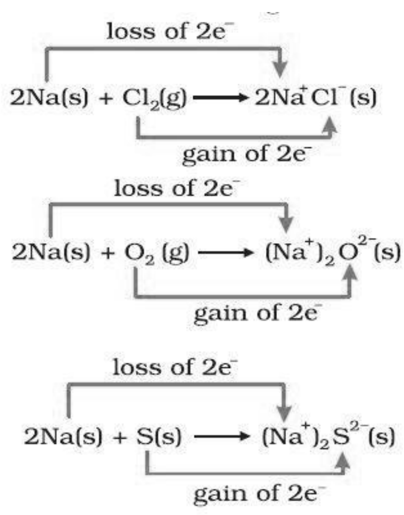
$2\ HgO\ (s) \rightarrow 2\ Hg\ (l) + O_2\ (g)$ (removal of oxygen from mercuric oxide)
$2\ FeCl_3\ (aq) + H_2\ (g) \rightarrow 2\ FeCl_2\ (aq) + 2\ HCl(aq)$ (removal of electronegative element, chlorine from ferric chloride)

Modern view of redox reactions

Redox reactions in terms of Electron transfer

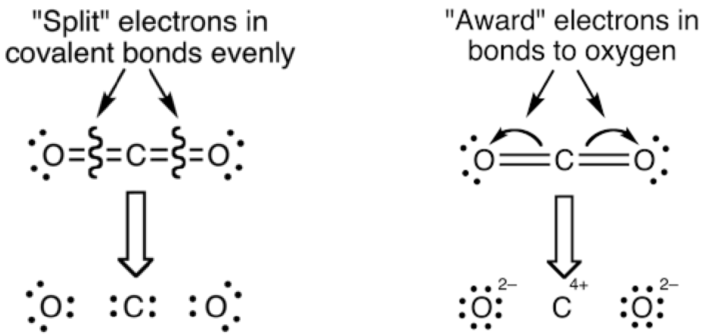
- Oxidation is defined as loss of electrons by any species
- Reduction is defined as gain of electrons by any species

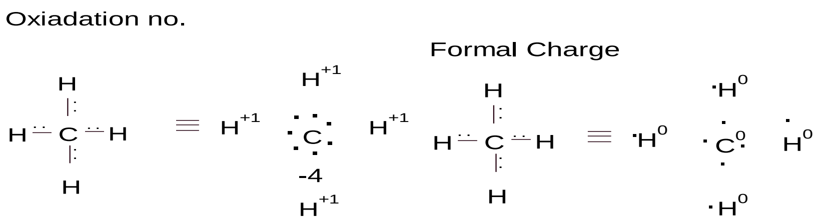
$2Na(s) + Cl_2(g) \rightarrow 2NaCl\ (s)$
$2Na(s) + ½\ O_2(g) \rightarrow Na_2O(s)$
$2Na(s) + S(s) \rightarrow Na_2S(s)$



Oxidation number: The charge remaining on an atom when all ligands are removed heterolytically in their closed form, with the electrons being transferred to the more electronegative partner (homonuclear bonds do not contribute to the oxidation number).

Formal charge: The charge remaining on an atom when all ligands are removed homolytically.

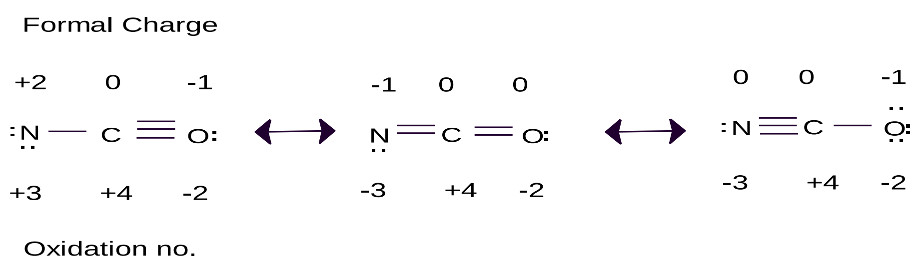




Formal Charge versus Oxidation Number

For a formal charge, bonding electrons are shared equally by the atoms.

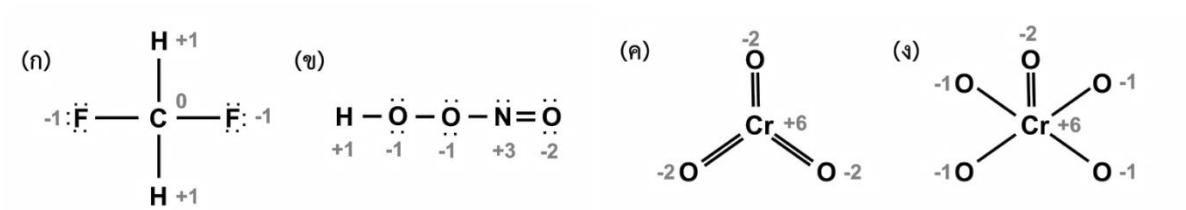
The formal charge of an atom may change between resonance forms.



For an oxidation number, bonding electrons are transferred to the more electronegative atom.

The oxidation number of an atom is the same in all resonance forms.

SOME EXAMPLES

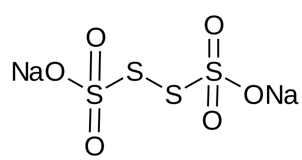


RULES FOR ASSIGNING OXIDATION NUMBER TO AN ATOM

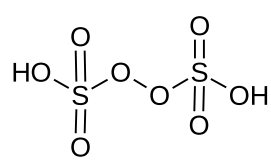
- In the free or elementary state, the oxidation number of an atom is always zero. This is irrespective of its allotropic form
- For ions composed of only one atom, the oxidation number is equal t the charge on the ion
- For neutral molecules sum of oxidation number of all atoms is equal to zero
- In a polyatomic ion, the algebraic sum of all the oxidation numbers of atoms of the ion must be equal to the charge on the ion
- Oxidation number of Hydrogen is always +1 (except in hydrides, it is -1).
- Oxidation number of oxygen in most of compounds is -2. In peroxides it is (-1). In superoxides, it is (-1/2). In OF_2 oxidation number of oxygen is +2. In O_2F_2 oxidation number of oxygen is +1
- Oxidation number of Fluorine is -1 in all its compounds

Some examples:

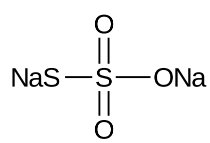
$Na_2S_4O_6$



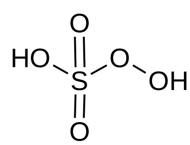
$H_2S_2O_8$



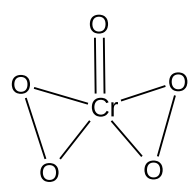
$Na_2S_2O_3$



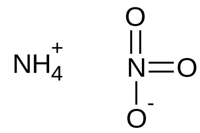
H_2SO_5



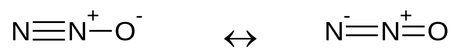
CrO_5



NH_4NO_3



N_2O



EQUIVALENT WEIGHT AND NORMALITY

Equivalent weight is the quantity of a substance that exactly reacts with or produces, directly or indirectly with 1.00797 grams (g) of hydrogen or 7.9997 g of oxygen; or, the weight of an element that is liberated in an electrolysis (chemical reaction caused by an electric current) by the passage of 96,500 coulombs of electricity.

- Equivalent weight can only be found by experiment.
- Equivalent weight of same element or component can be different and it depends upon reaction.
- Finding equation weight theoretically.

1. Eq. Wt. of element $= \frac{\text{Atomic weight}}{\text{valency}}$

$\text{ex. 1} \quad \text{Na} \Rightarrow \text{Eq. Wt.} = \frac{23}{1} = 23$

$\text{ex. 2} \quad \text{Fe} \Rightarrow \text{Eq. Wt.} = \frac{56}{2} = 28$

or $\frac{56}{3} = 18.66$

2. Equivalent weight of Acid

$\text{Eq. Wt.} = \frac{\text{molecular mass of acid}}{\text{No.of replaceble H}^+ \text{ ions}}$ or $\frac{\text{Molecular mass}}{\text{Basiaty of acid}}$

$\text{ex. 1} \quad \text{HCl} \Rightarrow \text{Eq. Wt.} = \frac{36.5}{1} = 36.5$

$\text{ex. 2} \quad H_2SO_4 \Rightarrow \text{Eq. Wt.} = \frac{98}{2} = 49$

In reaction $H_2SO_4 + NaOH \rightarrow NaHSO_4 + H_2O$

$\text{Eq. wt. of } H_2SO_4 = \frac{98}{1} = 98$

$\text{ex. 3} \quad H_3PO_4 \Rightarrow \text{Eq. Wt.} = \frac{98}{3} = 32.66$

$\text{ex. 4} \quad H_3PO_3 \Rightarrow \text{Eq. Wt.} = \frac{82}{2} = 41$

$\text{ex. 5} \quad H_3PO_2 \Rightarrow \text{Eq. Wt.} = \frac{66}{1} = 66$

3. Equivalent of Base $= \frac{\text{molecular mass of acid}}{\text{Replacable OH}^-}$ or $\frac{\text{Molecular Wt.}}{\text{Acidity of base}}$

$\text{ex. 1} \quad \text{NaOH} \Rightarrow E = \frac{40}{1} = 40$

ex. 2 $Ca(OH)_2 \Rightarrow E = \frac{74}{2} = 37$

4. Equivalent wt. of ions $= \frac{\text{ionic Mass}}{\text{charge absolute value}}$

ex. 1 $Na^+ \Rightarrow E = \frac{23}{1} = 1$

ex. 2 $SO_4^{-2} \Rightarrow E = \frac{96}{2} = 48$

ex. 3 $PO_4^{-3} \Rightarrow E = \frac{95}{3} = 31.66$

5. Equivalent of salt $= \frac{\text{Molecular Mass}}{\text{Total charge of cation or anion}}$ OR = $E_{Cation} + E_{Anion}$

ex. 1 $NaCl \Rightarrow E = \frac{58.5}{1} = 58.5$

ex. 2 $Na_2CO_3 \Rightarrow E = \frac{106}{2} = 53$

ex. 3 $Ca_3(PO_4)_2 \Rightarrow E = \frac{40\times3+31\times2+16\times8}{6} = \frac{310}{6} = 51.6$ or $E = 20 + 31.6 = 51.6$

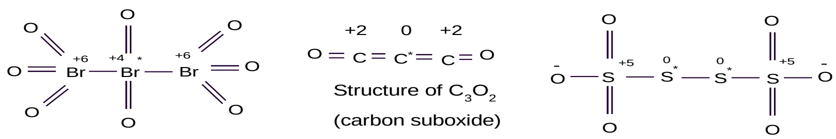
6. Equivalent in oxidizing of Reducing agent $E = \frac{\text{Formula mass}}{\text{change in Oxidation Number}}$

Species	Changes to	Medium		Reaction	CON	$E = \frac{m}{CON}$
MnO_4^-	Mn^{++}	A	O	$MnO_4^- + 8H^+ + Se^- \rightarrow Mn^{2+} + 4H_2O$	5	M/5
MnO_4^-	MnO_2	B	O	$MnO_4^- + 3H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$	3	M/3
MnO_4^-	MnO_4^{--}	N	O	$MnO_4^- + e^- \rightarrow MnO_4^{--}$	1	M
$Cr_2O_7^{--}$	Cr^{3+}	A	O	$Cr_2O_7^{--} + 14H^+ + 6e^- \rightarrow 2Cr^{+3} + 7H_2O$	6	m/6
Cl_2	Cl^-		O	$Cl_2 + 2e^- \rightarrow 2Cl^-$	2	m/2
Cu^{++}	Cu^+	A	O	$Cu^{+2} + e^- \rightarrow Cu^+$	1	m
H_2O_2	H_2O	A	O	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	2	m/2
H_2O_2	O_2	A	R	$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$	2	m/2
Fe++	Fe^{+3}		R	$Fe^{++} \rightarrow Fe^{+3} + e^-$	1	m
$S_2O_3^{--}$	$S_4O_6^{--}$		R	$2S_2O_3^{--} \rightarrow S_4O_4^{--} + 2e^-$	2 for2	m
$C_2O_4^{--}$	CO_2		R	$C_2O_4^{--} \rightarrow 2CO_2 + 2e^-$	2	m/2
As_2O_3	AsO_4^{-3}	A	R	$As_2O_3 + 5H_2O \rightarrow 2AsO_4^{-3} + 10H^+ + 4e^-$	4	m/4

The Paradox of Fractional Oxidation Number

Sometimes, we come across with certain compounds in which the oxidation number of a particular element in the compound is in fraction. Examples are:
C_3O_2 [where oxidation number of carbon is (4/3)],
Br_3O_8 [where oxidation number of bromine is (16/3)]
and $Na_2S_4O_6$ (where oxidation number of sulphur is 2.5).

We know that the idea of fractional oxidation number is unconvincing to us, because electrons are never shared/transferred in fraction. Actually this fractional oxidation state is the average oxidation state of the element under examination and the structural parameters reveal that the element for whom fractional oxidation state is realised is present in different oxidation states. Structure of the species C3O2, Br3O8 and S4O6 2– reveal the following bonding situations:



Types of Redox Reactions

Combination Reactions: Chemical reactions in which two or more substances (elements or compounds) combine to form a single substance.

0 0 +4 -2

$C(s) + O_2\ (g) \xrightarrow{\Delta} CO_2(g)$

0 0 +2 -3

$3Mg(s) + N_2\ (g) \xrightarrow{\Delta} Mg_3N_2(s)$

Decomposition Reactions: Chemical reactions in which a compound break up into two or more simple substances

+1-1 0 0

$2NaH(s) \xrightarrow{\Delta} 2Na(s) + H_2(g)$

+1 +5 -2 +1-1 0

$2KClO_3(s) \xrightarrow{\Delta} 2KCl(s) + 3O_2\ (g)$

Displacement Reactions: Reaction in which one ion(or atom)in a compound is replaced by an ion(or atom) of other element

Metal Displacement Reactions: Reactions in which a metal in a compound is displaced by another metal in the un-combined state

+2+4-2 0 0 +2 +4 -2

$CuSO_4(aq) + Zn\ (s) \xrightarrow{\Delta} Cu(s) + ZnSO_4(aq)$

+3 -2 0 +3-2 0

$CrO_3(s) + 2Al\ (s) \xrightarrow{\Delta} Al_2O_3(s) + 2Cr(s)$

Non-metal Displacement Reactions: Such reactions are mainly hydrogen displacement or oxygen displacement reactions

0 + 1 – 2 + 1 -2 + 1 0

$2Na(s) + 2H_2O(1) \rightarrow 2NaOH(aq) + H_2(g)$

0 + 1 -2 + 3 -2 0

$2Fe(s) + 3H_2O(1) \xrightarrow{\Delta} Fe_2O_3(s) + 3H_2(g)$

Disproportionation Reactions: Reactions in which an element in one oxidation state is simultaneously oxidized and reduced

0 -3 +1

$P_4(s) + 3OH^-(aq) + 3H_2O(1) \rightarrow PH_3(g) + 3H_2PO_2^-$

0 -2 +2

$S_8(s) + 12\ OH^-\ (aq) \rightarrow 4S^{2-}\ (aq) + 2S_2O_3^{2-}(aq) + 6H_2O(l)$