Oxidation Numbers

* To help us identify what atoms/ions are being oxidized and reduced, the concept of *oxidation numbers* was developed

* **Oxidation numbers** provide a way to keep track of electron transfer during redox reactions according to a set of certain rules
  - Oxidation numbers do **NOT** represent the actual charges on ions, but are numbers designed to "book-keep" the electron transfer during redox reactions

* General rules for assigning oxidization numbers

Need to memorize!

1. A pure element in *atom* form has an oxidation number of 0. see example #1
2. Group 1 metals always have an oxidation number of +1 (ie. their common charge) when in *ion* form and groups 2 metals always have an oxidation number of +2 (ie. their common charge) when in *ion* form. see example #5
3. In general, most metals will have an oxidation number equal to their charge when in *ion* form. see example #2
4. The oxidation number of oxygen *ions* is usually -2 (exceptions include peroxides (H_2O_2) and the compound OF_2) see examples #4, 5, & 6
5. Hydrogen *ions* usually have an oxidation number of +1 (exceptions include metal hydrides where it has an -1 oxidation number). see examples #3 & 6

hydrogen acts as the anion ie. LiH
cations written first
anions written second

6. Fluorine *ions* always have an oxidation number of -1.
7. Chlorine *ions* usually has an oxidation number of -1 (exceptions are in compounds with oxygen and fluorine). see example #2

* For all other ions that do not fall under the rules listed above, the oxidation numbers need to be calculate based on the two following principles.
  - The sum of all oxidation numbers of all the elements in a neutral compound is zero. see examples #3 & 5
  - The sum of all oxidation numbers of all the elements in a polyatomic ion equals the charge on the ion. see examples #4 & 6

EXAMPLES: Determine the oxidation numbers of each element in the following compounds.

1. $Br_{2(l)}$

atom form

∴ oxidation # for Br is 0

2. $ZnCl_{2(aq)}$

both elements in ion form

∴ Cl has a −1 oxidation #

Zn has a +2 oxidation #

3. $CH_{4(g)}$

$x \quad +1$

$(x)(1) + (+1)(4) = 0$

$x + 4 = 0$

$x = -4$

∴ H has a +1 oxidation #

C has a −4 oxidation #

4. $MnO_4^-{}_{(aq)}$

$x \quad -2$

$1(x) + 4(-2) = -1$

$x - 8 = -1$

$x = +7$

∴ Mn has a +7 oxidation #

O has a −2 oxidation #

5. $Ba(NO_3)_{2(aq)}$

$+2 \quad x \quad -2$

$1(+2) + 2(x) + 6(-2) = 0$

$2 + 2x - 12 = 0$

$2x - 10 = 0$

$2x = +10$

$x = +5$

∴ Ba: +2

N: +5

O: −2

6. $(NH_4)_2SO_{4(aq)}$

$x \; +1 \quad y \; -2$

2 unknown oxidation #'s ∴ break compound into its separate ions

NH_4^+ & SO_4^{2-}

NH_4^+: $x \quad +1$

$1(x) + 4(+1) = +1$

$x + 4 = +1$

$x = -3$

∴ N: −3

H: +1

SO_4^{2-}: $y \quad -2$

$1(y) + 4(-2) = -2$

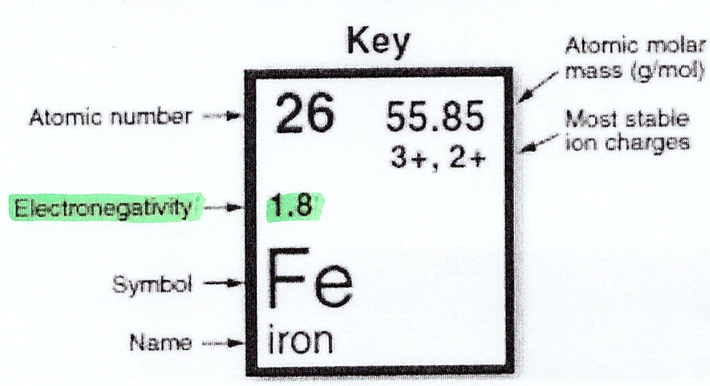
$y - 8 = -2$

$y = +6$

∴ S: +6

O: −2

- In *molecular compounds* without hydrogen, oxygen, fluorine, or chlorine, the more electronegative element is assigned an oxidation number of its negative charge as it would appear if it was in ionic compounds.



<u>EXAMPLES:</u> Determine the oxidation numbers of each element in the compound $SiBr_{4(l)}$.

molecular compound with no elements that have set rules ∴ use electronegativities.

Br is more electronegative ∴ it's oxidation # is its common charge of −1

$\underset{x}{Si}\underset{-1}{Br_{4(l)}}$

$1(x) + 4(-1) = 0$

$x - 4 = 0$

$x = +4$

∴ $\boxed{\begin{array}{l} Si: +4 \\ Br: -1 \end{array}}$

****Now try pg. 457 # 7-10****

- Consider the balanced equation for a reaction between zinc and copper(II) sulphate

decrease in oxidation #
∴ gains e^-

$$Zn_{(s)} + CuSO_{4(aq)} \rightarrow Cu_{(s)} + ZnSO_{4(aq)}$$

oxidation #'s: $Zn_{(s)}$: 0; $CuSO_{4(aq)}$: +2 +6 −2; $Cu_{(s)}$: 0; $ZnSO_{4(aq)}$: +2 +6 −2

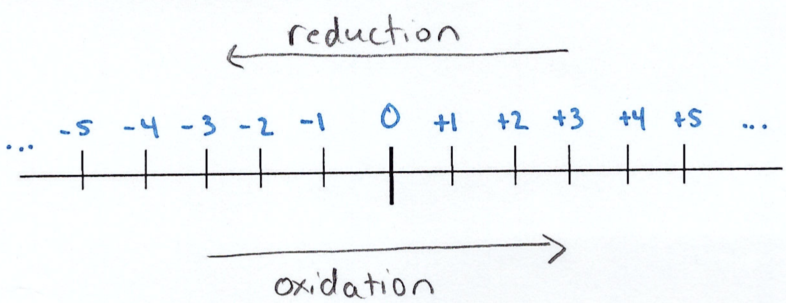
increase in oxidation #
∴ loses e^-

Zn is oxidized, ∴ $Zn_{(s)}$ is reducing agent

Cu^{2+} is reduced, ∴ $CuSO_{4(aq)}$ is oxidizing agent

- * When an ***element*** has an <u>*increase*</u> (a change to a more positive value) in the oxidation number, the **element/molecule** is undergoing <u>*oxidation*</u> (ie. the entire **molecule** is the <u>*reducing agent*</u>)

- * When an ***element*** has a <u>*decrease*</u> (a change to a more negative value) in the oxidation number, the **element/molecule** is undergoing <u>*reduction*</u> (ie. the entire **molecule** is the <u>*oxidizing agent*</u>)



- When a reaction contains no elements that have a change in oxidation numbers, then no electron transfer has occurred. This means the reaction is not a redox reaction.
  - * All double replacement reaction are examples of reactions that are **not** redox reactions.

quick rules!

ie. $AgNO_{3(aq)} + NaCl_{(aq)} \longrightarrow AgCl_{(s)} + NaNO_{3(aq)}$

  - * All single replacement reactions are examples of redox reactions.

ie. $Fe_{(s)} + Cu(NO_3)_{2(aq)} \longrightarrow Cu_{(s)} + Fe(NO_3)_{2(aq)}$

- In most redox reactions, atoms of one element are oxidized and atoms of a different element are reduced

* - It is possible for some atoms of one element to undergo oxidation and other atoms of the *same* element to undergo reduction in a single reaction
  - This type of redox reaction is called **disproportionation**
  - Consider the following copper atoms and ions in the following equation

loses e^- ∴ oxidized

$$\underset{+1\ \ -2}{Cu_2O_{(aq)}} + \underset{+1\ +6\ -2}{H_2SO_{4(aq)}} \rightarrow \underset{0}{Cu_{(s)}} + \underset{+2\ +6\ -2}{CuSO_{4(aq)}} + \underset{+1\ -2}{H_2O_{(l)}}$$

gains e^- ∴ reduced

$Cu_2O_{(aq)}$ is both oxidized & reduced!

EXAMPLES:

1. Determine whether each of the following reaction is a redox reaction. If so, identify the oxidizing and the reducing agent.

$\nearrow H_2O_{(g)}$

   a. The combustion of propane (C_3H_8) in an open system.

$3(x) + 8(+1) = 0$
$3x + 8 = 0$
$3x = -8$
$x = -8/3$

gains e^- ∴ reduced

$$\underset{-8/3\ \ +1}{C_3H_{8(g)}} + \underset{0}{5O_{2(g)}} \longrightarrow \underset{+4\ \ -2}{3CO_{2(g)}} + \underset{+1\ \ -2}{4H_2O_{(g)}}$$

Oxidation #'s

* balancing coefficients don't effect

loses e^- ∴ oxidized

$C_3H_{8(g)}$ is the reducing agent.

$O_{2(g)}$ is the oxidizing agent

$1(+2) + 1(x) + 3(-2) = 0$
$2 + x - 6 = 0$
$x - 4 = 0$
$x = +4$

$(x) + 2(-2) = 0$
$x - 4 = 0$
$x = +4$

b. $CaCO_{3(s)} + 2HCl_{(aq)} \rightarrow CaCl_{2(aq)} + H_2O_{(l)} + CO_{2(g)}$

Oxidation #'s: $CaCO_3$: +2 +4 −2; HCl: +1 −1; $CaCl_2$: +2 −2; H_2O: +1 −2; CO_2: −2

no change in any oxidation #'s
∴ not a redox rxn

$1(+1) + 1(x) + 2(-2) = 0$
$1 + x - 4 = 0$
$x = +3$

$1(+1) + 1(x) + 3(-2) = 0$
$1 + x - 6 = 0$
$x = +5$

c. $HNO_{2(aq)} \rightarrow HNO_{3(aq)} + NO_{(g)} + H_2O_{(l)}$

Oxidation #'s: HNO_2: +1 +3 −2; HNO_3: +1 +5 −2; NO: +2 −2; H_2O: +1 −2

oxidation

reduction

$HNO_{2(aq)}$ is both the oxidizing agent
& the reducing agent

This is an example of disproportionation.

Now try pg. 461 #11 and Practice Problems

Practice Problems

For each of the redox reactions; assign oxidation numbers to each element, identify what element is oxidized, what element is reduced, the oxidizing agent, and the reducing agent. Identify any disproportionation reactions.

1. $3\ AsO_3^{3-}{}_{(aq)} + IO_3^{-}{}_{(aq)} \rightarrow 3\ AsO_4^{3-}{}_{(aq)} + I^{-}{}_{(aq)}$

2. $3\ CuO_{(s)} + 2\ NH_{3(g)} \rightarrow N_{2(g)} + 3\ H_2O_{(l)} + 3\ Cu_{(s)}$

3. $2\ MnO_4^{-}{}_{(aq)} + 5\ H_2Se_{(g)} + 6\ H^{+}{}_{(aq)} \rightarrow 5\ Se_{(s)} + 2\ Mn^{2+}{}_{(aq)} + 8\ H_2O_{(l)}$

4. $PbO_{2(s)} + Pb_{(s)} + 2\ H_2SO_{4(aq)} \rightarrow 2\ PbSO_{4(s)} + 2\ H_2O_{(l)}$

5. $6\ Cl_{2(g)} + 12\ OH^{-}{}_{(aq)} \rightarrow 2\ ClO_3^{-}{}_{(aq)} + 10\ Cl^{-}{}_{(aq)} + 6\ H_2O_{(l)}$

Answers

1. $3\ AsO_3^{3-}{}_{(aq)} + IO_3^{-}{}_{(aq)} \rightarrow 3\ AsO_4^{3-}{}_{(aq)} + I^{-}{}_{(aq)}$

   +3 -2   +5 -2   +5 -2   -1

   As is oxidized, therefore $AsO_3^{3-}{}_{(aq)}$ is the reducing agent.
   I is reduced, therefore IO_3^- is the oxidizing agent.

2. $3\ CuO_{(s)} + 2\ NH_{3(g)} \rightarrow N_{2(g)} + 3\ H_2O_{(l)} + 3\ Cu_{(s)}$

   +2 -2   -3 +1   0   +1 -2   0

   Cu is reduced, therefore $CuO_{(s)}$ is the oxidizing agent.
   N is oxidized, therefore $NH_{3(g)}$ is the reducing agent.

3. $2\ MnO_4^{-}{}_{(aq)} + 5\ H_2Se_{(g)} + 6\ H^{+}{}_{(aq)} \rightarrow 5\ Se_{(s)} + 2\ Mn^{2+}{}_{(aq)} + 8\ H_2O_{(l)}$

   +7 -2   +1 -2   +1   0   +2   +1 -2

   Se is oxidized, therefore $H_2Se_{(g)}$ is the reducing agent.
   Mn is reduced, therefore $MnO_4^{-}{}_{(aq)}$ is the oxidizing agent.

4. $PbO_{2(s)} + Pb_{(s)} + 2\ H_2SO_{4(aq)} \rightarrow 2\ PbSO_{4(s)} + 2\ H_2O_{(l)}$

   +4 -2   0   +1 +6 -2   +2 +6 -2   +1 -2

   Pb is reduced, therefore $PbO_{2(s)}$ is the oxidizing agent.
   Pb is oxidized, therefore $Pb_{(s)}$ is the reducing agent.

5. $6\ Cl_{2(g)} + 12\ OH^{-}{}_{(aq)} \rightarrow 2\ ClO_3^{-}{}_{(aq)} + 10\ Cl^{-}{}_{(aq)} + 6\ H_2O_{(l)}$

   0   -2 +1   +5 -2   -1   +1 -2

   Cl is reduced, therefore $Cl_{2(g)}$ is the oxidizing agent.
   Cl is oxidized, therefore $Cl_{2(g)}$ is also the reducing agent.
   This is an example of a ***disproportionation*** reaction.