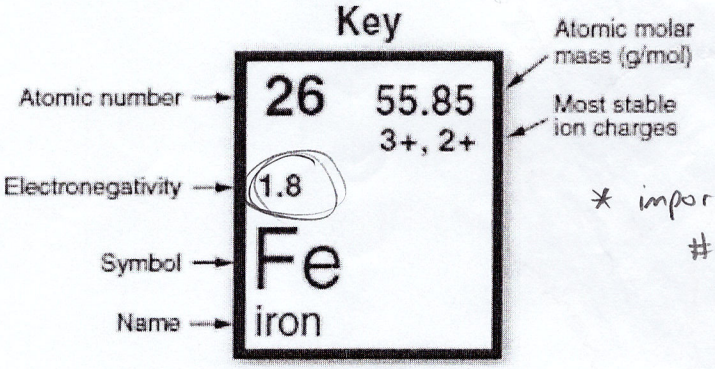
Oxidation Numbers

- To help us identify what atoms/ions are being oxidized and reduced, the concept of *oxidation numbers* was developed
- **Oxidation numbers** is a concept developed to provide a way to keep track of electron transfer in redox reactions according to a set of certain rules
    - Oxidation numbers do **NOT** represent the actual charges on ions, but was a method designed to "book-keep" the transfer of electrons

- General rules for assigning oxidization numbers

RULES	EXAMPLES
1. A pure element in *atom* form has an oxidation number of 0.	Na in $Na_{(s)}$, Br in $Br_{2((l)}$ and P in $P_{4(s)}$ all have an oxidation number of 0.
2. Group 1 metals always have an oxidation number of +1 when in *ion* form.	In the compound $NaCl_{(aq)}$, the oxidation number of the sodium ion ($Na^{+}_{(aq)}$) is +1.
3. Groups 2 metals always have an oxidation number of +2 when in *ion* form.	In the compound, $Ca(OH)_{2(aq)}$, the oxidation number of the calcium ion ($Ca^{2+}_{(aq)}$) is +2.
4. In general, most metals will have an oxidation equal to their charge when in ion form	In the compound, $ZnSO_{4(aq)}$, the oxidation number of the zinc ion ($Zn^{2+}_{(aq)}$) is +2.
5. The oxidation number of oxygen *ion* is usually -2 (exceptions include peroxides (H_2O_2) and the compound OF_2)	The oxidation number of O in Li_2O and KNO_3 is -2.
6. Hydrogen *ions* usually have an oxidation number of +1 (exceptions include metal hydrides where it has an -1 oxidation number)	The oxidation number of H in H_2O and CH_4 is +1.
7. Fluorine *ions* always have an oxidation number of -1.	The oxidation number of F in MgF_2 is -1.
8. Chlorine usually has an oxidation number of -1 (exceptions are in compounds with oxygen and fluorine).	The oxidation number of Cl in NaCl is -1.
9. 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	The oxidation number of N in CN^- is -3. The oxidation number of S in CS_2 is -2.



* important for rule #8!

- For all other ions that do not fall under the rules listed in the above table, you will need to calculate the oxidation numbers.
  - The sum of all oxidation numbers of all the atoms in a neutral compound is zero.
  - The sum of all oxidation numbers of all the atoms in a polyatomic ion equals the charge on the ion.

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

*mole coefficient out in front doesn't effect oxidation #'s!

a. CH_4

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

$x + 4 = 0$

$x = -4$

∴ C: -4, H: +1

b. MnO_4^-

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

$x - 8 = -1$

$x = +7$

∴ Mn: +7, O: -2

c. HNO_3

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

$1 + x - 6 = 0$

$x - 5 = 0$

$x = 5$

H: +1, N: +5, O: -2

d. $SiBr_4$ * molecular compound! ∴ use electronegativities

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

$x - 4 = 0$

$x = 4$

∴ Si: +4, Br: -1

e. Na_2SO_4

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

$2 + x - 8 = 0$

$x - 6 = 0$

$x = 6$

∴ Na: +1, S: +6, O: -2

f. $(NH_4)_2SO_4$

$2(x) + 8(+1) + (1)(y) + 4(-2) = 0$

??

look at separate ions.

SO_4^{2-}

∴ $1(x) + 4(-2) = -2$

$x - 8 = -2$

$x = 6$

∴ O: -2, S: +6

NH_4^{+1}

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

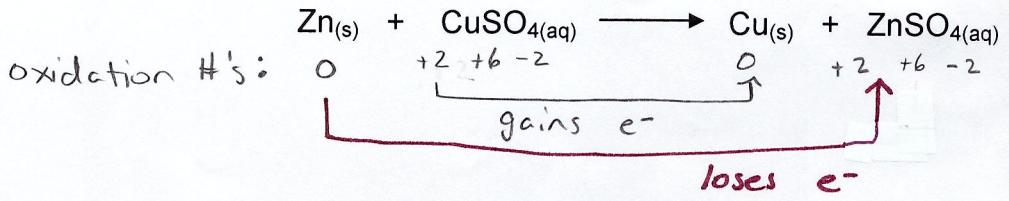
$x + 4 = +1$

$x = -3$

∴ N: -3, H: +1

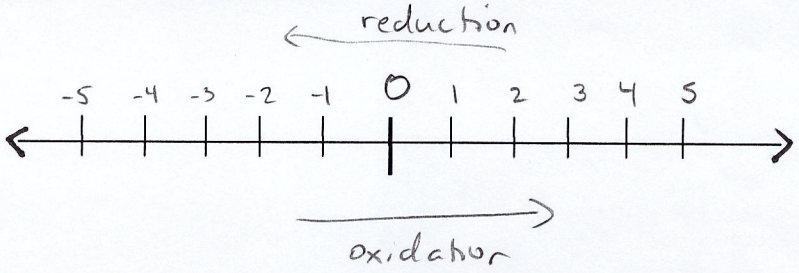
****Now try pg. 457 # 7-10****

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



∴ Zn is oxidized, and Zn is reducing agent
Cu^{2+} is reduced, and $CuSO_4$ is oxidizing agent.

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

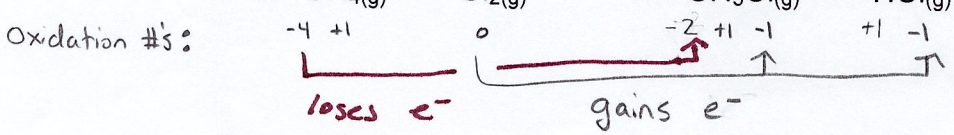


- When a reaction contains no elements that have a change in oxidation numbers, then no electron transfer has occurred. This means the reaction is not a redox reaction.

EXAMPLES:

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

a. $CH_{4(g)} + Cl_{2(g)} \longrightarrow CH_3Cl_{(g)} + HCl_{(g)}$



∴ Cl is reduced, Cl_2 is oxidizing agent
C is oxidized, CH_4 is reducing agent.

* mole ratios do <u>not</u> effect oxidation #'s

b. The combustion of propane (C_3H_8) in an open system. → $H_2O_{(g)}$

3(0) + 8(+1) = 0 ; 1(0) + 2(-2) = 0

$$C_3H_8 + 5O_{2(g)} \longrightarrow 4H_2O_{(g)} + 3CO_{2(g)}$$

Oxidation #'s: $-\frac{8}{3}$ +1 | 0 | +1 -2 | +4 -2

loses e^- (becomes more "+")

gains e^- (becomes more "-")

∴ C is being oxidized, C_3H_8 is reducing agent

O is being reduced, $O_{2(g)}$ is oxidizing agent

1(+2) + 1(x) + 3(-2) = 0 ; 1(x) + 2(-2) = 0

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

oxidation #'s: +2 +4 -2 | +1 -1 | +2 -1 | +1 -2 | +4 -2

↑ group 2 element

no change in any oxidation #'s

∴ not a redox rxn!

*****Now try pg. 461 #11-14 (#11: don't worry about the "disproportionation" part) and Practice Problems*****

Practice Problems

For each of the redox reactions, assign each element its oxidation number to identify what is being oxidized, what is being reduced, the oxidizing agent, and the reducing agent. (Don't worry about the reactions being balanced).

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

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

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

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

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

SOLUTIONS

Practice Problems

For each of the redox reactions, assign each element its oxidation number to identify what is being oxidized, what is being reduced, the oxidizing agent, and the reducing agent. (Don't worry about the reactions being balanced).

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

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

   As is oxidized, $As_2O_3^-$ is reducing agent

   I is reduced, IO_3^- is oxidizing agent

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

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

   Cu is reduced, CuO is oxidizing agent

   N is oxidized, NH_3 is reducing agent

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

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

   Se is oxidized, H_2Se is reducing agent

   Mn is reduced, MnO_4^- is oxidizing agent

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

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

   Pb is reduced, PbO_2 is oxidizing agent

   Pb is oxidized, Pb is reducing agent.

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

   exception to rule!

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

   Cl is reduced, Cl_2 is oxidizing agent

   Cl is oxidized, Cl_2 is reducing agent as well!