Unit 8, Lesson 02: Introduction to Oxidation Numbers

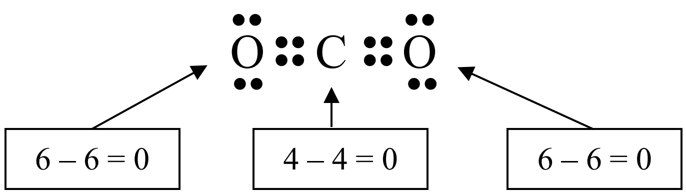
These youtube videos by Tyler DeWitt are excellent. Before reading the notes, please watch:
1. How to Calculate Oxidation Numbers Introduction
2. How to Calculate Oxidation Numbers Practice Problems

Background
Many (but not all) chemical reactions occur when electrons are gained, lost or shared by atoms, so it is critical to be able to follow the movement of electrons during reactions.

Earlier in this course, we calculated the formal charges (FC) on the atoms in molecules to determine how the electrons (and therefore the charges) were distributed in a molecule. We used FC to predict the stability of a molecule. In this method, the electrons in bonds are assumed to be ***equally*** shared between both bonded atoms, regardless of the electronegativities of the bonded atoms. That is, all bonds are considered to be entirely covalent.

To calculate formal charge (FC):
FC = (# of valence electrons in the unbonded atom) – (# of electrons around the bonded atom when the bonding electrons are divided equally between the bonded atoms)

eg. for CO_2



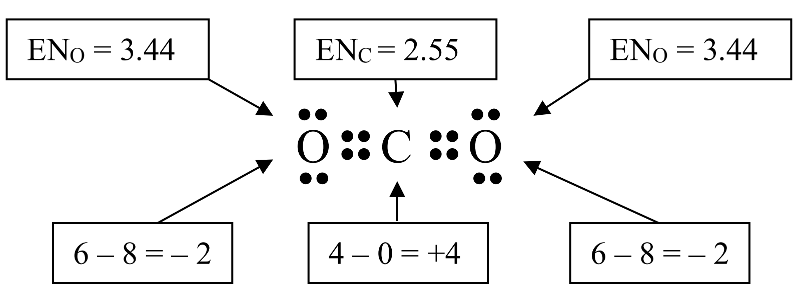
Another way of determining where the electrons are found in a molecule is called 'oxidation numbers' or 'oxidation states'. Some of the possible oxidation states of each element are written above each element's symbol on your Periodic Table. Oxidation numbers are hypothetical. They are used as a tracking system to follow the movement of electrons during chemical reactions. Oxidation numbers are ideally suited for use in redox reactions and electrochemistry, so this is the system we will use in this unit.

During redox reactions, the oxidation numbers of the atoms change.
- If the oxidation numbers don't change, then the reaction is NOT a redox reaction.
- If the oxidation number of an atom or ion increases, the atom or ion has been oxidized.
- If the oxidation number of an atom or ion decreases (reduces), then the atom or ion has been reduced.

To determine an element's oxidation number in a certain compound, the electrons in bonds are assumed to be ***unequally*** shared between bonded atoms. In fact, the bonded electrons are assigned entirely to the atom with higher electronegativity. That is, all bonds except those with $\Delta EN = 0.00$ are considered to be entirely ionic.

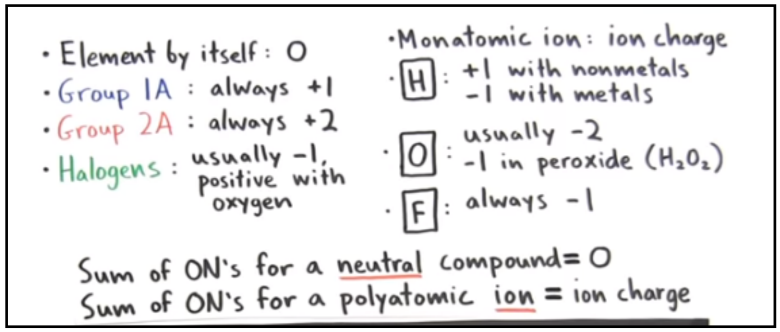
To calculate oxidation number (or oxidation state):
Oxidation number = (# of valence electrons in the unbonded atom) – (# of electrons around the bonded atom when the bonding electrons are assigned to the bonded atom with higher EN)

eg. for CO_2



Rather than drawing molecules and doing calculations, it is faster and easier to memorize a set of rules for assigning oxidation numbers. In a bond, the atom with the highest electronegativity is assigned a negative oxidation number, because the electrons will spend more time closer to this atom, giving it a negative charge. The less electronegative atom is assigned a positive oxidation number.

The rules for assigning oxidation numbers in Tyler DeWitt's videos are shown to the right:



Here is a summary of the rules for assigning oxidation numbers re-written in priority sequence, with examples:

1. The oxidation number for any pure element is zero.
   eg. Zn (s), N_2 (g), P_4 (s), He (g), O_2 (g), O_3 (g), S (s), S_8 (s), Au (s), Hg (ℓ)

2. For monoatomic (single atom) ions, the oxidation number is equal to the charge on the ion.
   eg. oxidation number of Cl^{1-} is –1 oxidation number of Ca^{2+} is +2
   oxidation number of Pb^{4+} is +4 oxidation number of P^{3-} is –3

3. The oxidation number of fluorine in a compound is ALWAYS –1.

4. The oxidation number of hydrogen is +1, except when it is bonded to a metal, creating a metal hydride such as NaH, LiH, or CaH_2. In metal hydrides, because hydrogen has the higher electronegativity, it is assigned an oxidation number of –1.

5. The oxidation number of oxygen is usually –2, except:

a) in peroxides such as Na_2O_2, H_2O_2, K_2O_2. In peroxides, oxygen's oxidation number is –1
b) in OF_2. Because fluorine's oxidation number in compounds is always –1, oxygen must be +2

6. The sum of the oxidation numbers of all of the atoms in a compound must equal the overall charge for the compound

a) if the compound is neutral overall (uncharged) then the sum of the oxidation number is zero
b) if the formula is for an ion, then the sum of the oxidation numbers is equal to the charge of the ion

Examples: Find the oxidation numbers of the elements in the following compounds. I use algebra:

a) $NiCl_2$ We have a rule for chlorine, but no rule for nickel, so solve for nickel
$1\,(\text{Ni}) + 2\,(\text{C}\ell) = 0$
$1\,(\text{Ni}) + 2\,(-1) = 0$ rearrange, and
$1\,(\text{Ni}) = +2$

b) $K_2Cr_2O_7$ We have a rule for potassium and oxygen, but no rule for chromium, so solve for Cr:
$2\,(\text{K}) + 2\,(\text{Cr}) + 7\,(\text{O}) = 0$
$2\,(+1) + 2\,(\text{Cr}) + 7\,(-2) = 0$ rearrange, and
$2\,(\text{Cr}) = +12$ divide by two, and
$\text{Cr} = +6$

c) MnO_4^{1-} We have a rule for oxygen but no rule for manganese, so solve for Mn:
$1\,(\text{Mn}) + 4\,(\text{O}) = -1$
$1\,(\text{Mn}) + 4\,(-2) = -2$ rearrange, and is Mn is +6

Use oxidation numbers to identify the oxidizing and reducing agents in the following unbalanced reactions. The first question is done for you as an example:

0 +2 Mg ox'n number increases ∴ oxidized

∴ Mg is the reducing agent

1. $Mg\ (s) \quad + \quad N_2\ (g) \quad \rightarrow \quad Mg_3N_2\ (s)$

0 –3 N_2 ox'n number decreases ∴ reduced

∴ N_2 is the oxidizing agent

2. $KC\ell O_3\ (s) \quad \rightarrow \quad KC\ell\ (s) \quad + \quad O_2\ (g)$

3. $C_2H_4\ (g) \quad + \quad O_2\ (g) \quad \rightarrow \quad CO_2\ (g) \quad + \quad H_2O\ (g)$

4. $Cu(NO_3)_2\ (aq) \quad + \quad Na_2CO_3\ (aq) \quad \rightarrow \quad NaNO_3\ (aq) \quad + \quad CuCO_3\ (aq)$

5. $H_2O_2\ (l) \quad \rightarrow \quad O_2\ (g) \quad + \quad H_2O\ (l)$

Unit 8, Lesson 02: Practice with Oxidation Numbers

1. Find the oxidation numbers of the elements in **bold** print.

a) H**Cℓ**O
b) K**Cℓ**O_3
c) **Mn**O_2
d) **Pb**SO_4
e) Na**I**O_4
f) **Cℓ**O_4^{1-}
g) Na_2**O_2**
h) K_2**S**O_4
i) **N**H_4^{1+}

2. State whether each of the following changes is an oxidation or a reduction.

a) MnO_4^{1-} becomes MnO_4^{2-} ____________
b) N_2 becomes NH_3 ____________
c) O^{2-} becomes O_2 ____________
d) P_4O_6 becomes P_4O_{10} ____________
e) NH_3 becomes N_2O ____________
f) SO_4^{2-} becomes $S_2O_3^{2-}$ ____________

3. Identify the oxidizing and reducing agents in the following unbalanced reactions:

a) $I_2 + H_2S \rightarrow HI + S$

b) $Zn + HNO_3 \rightarrow Zn(NO_3)_2 + NO_2 + H_2O$

c) $Ag_2O + NH_3 \rightarrow Ag + H_2O + N_2$

d) $H_2O + C\ell O_3^{1-} + SO_2 \rightarrow SO_4^{2-} + HC\ell$

e) $K_2Cr_2O_7 + HBr \rightarrow KBr + CrBr_3 + H_2O + Br_2$

f) $SnC\ell_2 + PbC\ell_4 \rightarrow SnC\ell_4 + PbC\ell_2$

g) $Sb + C\ell_2 \rightarrow SbC\ell_3$

h) $NaI + H_2SO_4 \rightarrow H_2S + I_2 + Na_2SO_4 + H_2O$