OXIDATION STATE OR NUMBER (ON)

I. Rules

A. Algebraic sum of ON's of all atoms in a formula is zero for a neutral compound or equals the charge on the ion for an ion

B. ON for an atom of any **uncombined** element is zero (O_2, Na, S_8)

C. Good metals (alkali and alkaline earth) **always** have their ON = group number (GN); Group 3 usually have ON = +3 but +1 also known

D. Fluorine ON = -1 always. Other halogens usually have ON = -1 except in compounds with oxygen or other halogens when the oxidation number can be positive.

E. Hydrogen has ON = 1 except in metal hydrides when the oxidation number is negative.

F. Oxygen usually has ON = -2 except in compounds with fluorine when the oxidation number can be positive and in compounds containing the O-O bond. For peroxides ON = -1 and for superoxides ON = -1/2.

II. Generalizations

A. Maximum oxidation number possible = GN (GN - 2 next most common)

B. For nonmetalas and metalloids (group 4 and greater) minimum oxidation number = GN - 8

C. More electronegative element **always** has a negative ON where electronegativity increases across a period (L -> R) and up a group; S ≈ I < Br < N < Cl < O < F

D. Total ON is conserved in a chemical reaction (allows one to balance redox reactions since oxidations and reductions must exactly compensate each other)

III. Uses

A. Determining oxidation numbers

1. peroxide, O_2^{2-}: 2 ON(O) = -2 => ON(O) = -1
2. superoxide, O_2^-: 2 ON(O) = -1 => ON(O) = -1/2
3. $K_2Cr_2O_7$: 2 ON(K) + 2 ON(Cr) + 7 ON(O) = 2(+1) + 2 ON(Cr) + 7(-2) = 0 => ON(Cr) = +6
4. OF_2: ON(O) + 2 ON(F) = ON(O) + 2(-1) = 0 => ON(O) = +2
5. $Na_2H_3IO_6$: 2 ON(Na) + 3 ON(H) + ON(I) + 6 ON(O) = 2(+1) + 3(+1) + ON(I) + 6(-2) = 0 => ON(I) = +7
6. $BaFeO_4$: ON(Ba) + ON(Fe) + 4 ON(O) = 2 + ON(Fe) - 8 => ON(Fe) = +6
7. UO_2^{2+}: ON(U) + 2 ON(O) = ON(U) - 4 = 2 => ON(U) = +6

B. Nomenclature

1. metal ions and compounds named by putting ON in parentheses as a roman numeral - exceptions: Group 1 and 2, Al (understood to be +3), Zn and Cd (both known to be +2), and Ag (+1)
   a) Fe^{3+} is iron(III) ion so $FeCl_3$ is iron(III) chloride
   b) Mn_2O_7 is manganese(VII) oxide
   c) mercury(I) fluoride is Hg_2F_2

d) zinc nitride: Zn_3N_2 but iron(II) nitride: Fe_3N_2

2. all monatomic anions of nonmetals and metalloids named by adding suffix ide to root of element name; charge = GN - 8; have octet of electrons
   a) Group 7: F^-, Cl^-, Br^-, I^-
   b) Group 6: O^{2-}, S^{2-}, Se^{2-} (selenide), Te^{2-} (telluride)
   c) Group 5: N^{3-}, P^{3-}, As^{3-} (arsenide), Sb^{3-} (antimonide)
   d) Group 4: C^{4-} (carbide), Si^{4-} (silicide), Ge^{4-} (germanide), Sn^{4-} (stannide)
   e) other: H^- (hydride), OH^- (hydroxide), CN^- (cyanide), N_3^- (azide)
3. oxoanions/oxoacides - anion has oxygen combined with another element; when only one oxidation state exists suffix ate/ic is used; with two oxidation states higher uses ate/ic and lower uses ite/ous suffix; when four different oxidation states exist for the element combined with oxygen the highest uses the prefix per and the lowest the prefix hypo - within a group the higher the oxidation number the more oxygen atoms

a) Group 7 halogens	XO_4^- (per...ate/per... ic) XO_3^- (...ate/...ic) XO_2^- (...ite/...ous) XO^- (hypo...ite/hypo...ous)
b) Group 6 S, Se, Te	XO_4^{2-} (...ate/... ic) - sulf...; selen...; tellur... XO_3^{2-} (...ite/...ous)
c) Group 5 P, As, Sb	XO_4^{3-} (...ate/... ic) - phosph...; arsen...; antimon...
d) Group 4 Si, Ge	XO_4^{4-} (...ate/... ic) - silic...; german...

e) exceptions - 2nd period elements too small for more than three covalently bonded oxygen atoms

CO_3^{2-} (carbonate/carbonic acid)
NO_3^- (nitrate/nitric acid)
NO_2^- (nitrite/nitrous acid)

f) other - transition elements

MnO_4^- (permanganate)
CrO_4^{2-} (chromate)
$Cr_2O_7^{2-}$ (dichromate)

C. Predicting likely formulas of binary compounds (ionic as well as covalent)

1. choose less electronegative element to play the role of the "cation" with ON = GN (ON = GN - 2 also common)
2. choose more electronegative element to be the "anion" with ON = GN - 8
3. examples

a) 5th period oxides (all actually exist):

Rb_2O SrO In_2O_3 SnO_2 Sb_2O_5 TeO_3 I_2O_7 XeO_4

b) binary compounds with nitrogen (again all exist):

Li_3N Ba_3N_2 BN Ge_3N_4 P_3N_5 N_2O_5 NCl_3^*

c) binary compounds with fluorine (all exist)

CsF BeF_2 AlF_3 PbF_4 AsF_5 SF_6 IF_7 XeF_6^*

*ON = GN - 2; NCl_5 and XeF_8 do not exist

D. Estimating relative strengths of oxoacids (and acidic oxides)

1. same element, different number of lone oxygens (only bonded to one atom)
   a) H_2SO_3 (SO_2), ON = 4 < H_2SO_4 (SO_3), ON = 6
   b) HNO_2 (N_2O_3), ON = 3 < HNO_3 (N_2O_5), ON = 5
   c) $HClO$ (Cl_2O), ON = 1 < $HClO_2$ (Cl_2O_3), ON = 3 < $HClO_3$ (Cl_2O_5), ON = 5 < $HClO_4$ (Cl_2O_7), ON = 7
2. different elements, different number of lone oxygens
   a) H_3PO_4, ON = 5 < H_2SO_4, ON = 6 < $HClO_4$, ON = 7
   b) H_2SO_3, ON = 4 < HNO_3, ON = 5

E. Redox reactions

1. best way to balance these reactions (easy! will do in CHEM 118) - can you imagine trying to get these coefficients by inspection:

$$258OH^- + Fe(CN)_6^{4-} + 61Ce^{4+} \rightarrow Fe(OH)_3 + 61Ce(OH)_3 + 6CO_3^{2-} + 6NO_3^- + 36H_2O$$

2. determine what is oxidized/reduced, number of electrons transferred
   a) assign oxidation numbers and determine what is oxidized/reduced
   b) using stoichiometric coefficients, determine number of electrons transferred
      1) $2\ Na(ON = 0)\ +\ Cl_2(ON = 0)\ \rightarrow\ 2\ Na(ON = 1)Cl(ON = -1)$

         OX: Na (0 -> 1); RED: Cl (0 -> -1); 2 mol electrons transferred
      2) $C(ON = -4)H_4(ON = 1)\ +\ 2\ O_2(ON = 0)\ \rightarrow$
         $C(ON = 4)O_2(ON = -2)\ +\ 2\ H_2(ON = 1)O(ON = -2)$

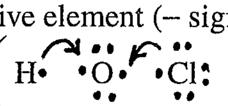
         OX: C (-4 -> 4); RED: O (0 -> -2); 8 mol electrons transferred

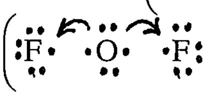
IV. Comments

A. ON's are a formal way to keep track of electrons in a redox reaction - can be fractions

B. ON are assigned based upon a molecular or ionic formula - structure need not be given

C. The rules for determining ON's are equivalent to **imagining** that all bonds are ionic => one **imagines** that every element in the formula exists as the neutral atom - the "molecule" or "ion" is formed by transfer of valence electrons from the less electronegative element (+ sign) to the more electronegative element (– sign) as in ionic compounds

$H(ON = 1)Cl(ON = 1)O(ON = -1)$ => ( = H^+ O^{2-} Cl^+)

$O(ON = 2)F_2(ON = -1)$ => ( = F^- O^{2+} F^-)