Rules and Clues for Determining Oxidation Number (States)

For Atoms in Molecules and Polyatomic Ions

1. The whole notion of an oxidation state or number for an atom is based on the assumption that bonding between atoms in compounds is purely ionic. The sense of electron transfer that occurs when a bond is formed is usually determined solely by the relative electronegativities of the atoms involved. Whichever atom has the higher electronegativity formally gains an electron from the bond while the atom with the lower electronegativity loses an electron. Consider H₂O being made from 2 H atoms and an O atom.

2. It is possible to “add up” the oxidation state contributions (i.e. the contributions due to each bond) for each atom to determine its overall oxidation state. Consider the acetate ion as an example (below). Bonds between like atoms (N-N, O-O, C-C) count “0” toward the oxidation state of both atoms.

A very important and useful rule concerning oxidation states of atoms in molecules is the following:

The sum of the individual atomic oxidation states must add up to the overall charge on the molecule or ion.

When dealing with polyatomic ions, generally the oxidation state of the central atom(s) is frequently determined in the last step so that the sum of atomic oxidation states is equal to the overall charge on the ion.

3. Since the oxidation states are based on relative electronegativities, you must have an idea of the ordering of elemental electronegativities:

\[
F > O > N \sim Cl > I \geq S \geq C > H > \text{all transition metals} > \text{alkaline earths (Be, Mg, Ca, Sr, Ba)} > \text{alkali metals (Li, Na, …)}
\]
4. Common oxidation states for many elements that follow from electronegativities:

**F**: Always –1, except F₂

**O**: Almost always –2 (exceptions: cmpds. w/ O-O or O-F bonds)

**Alkali metals**: Always +1 (except pure metal (0))

**Alkaline earths**: Always +2 (except pure metal (0))

**H**: +1 when bonded to main group (C, O, N, halide groups)
-1 when bonded to metals

5. Ranges of oxidation states for an element. There are some useful clues to notice with respect to the correspondence between maximum oxidation state (either + or -) and the Lewis Octet to some families of compounds.

Nitrogen, for example, can either gain 3 e⁻ (oxidation state –3 as in ammonia) or lose 5 electrons (ox. state +5 as in nitrate) to attain closed shell electron configuration around it. Oxygen has such a high electronegativity that in most of its compounds its oxidation state corresponds to its maximum: –2.

The two extreme oxidation states for carbon are –4 and +4 as indicated by the stared carbon in series of compounds below. Some examples in which the central carbons carry “0” formal charges but have widely varying formal oxidation numbers:
6. Metal centered complexes can be quite challenging with respect to electron bookkeeping. Classic inorganic complexes with neutral and/or anionic 2e$^-$ donor ligands are the easiest to consider. It is important to note that in a metal complex the formal charge on the metal is identical to its oxidation state. Generally it is best to determine the metal oxidation state/charge last, after summing the charges on all the ligands and comparing with the overall charge on the complex.

Before determining the charge/oxidation state on the metal, though, one must first distinguish between inner and outer sphere ligands in the molecular formula.

An inner sphere ligand may be neutral or charged. It occupies a distinct position in the coordination sphere of the metal. It interacts directly with the metal ion.

An outer sphere ligand is not really a ligand at all. It must be charged since its only purpose is to act as a counter ion to balance the overall charge on the metal complex ion (= metal ion with all inner sphere ligands). An outer sphere ligand does not interact with the metal ion in any specific way and frequently dissociates from the complex ion when dissolved in an ion solvating solvent. The conductivity of a solution of a complex with outer sphere ions is proportional to the concentration of the dissolved complex ion.

Aquo and amine complexes are good examples to illustrate the difference between inner and outer sphere ligands.

- **Cr(NH$_3$)$_6$Cl$_3**  Octahedral complex with 6 inner sphere amine ligands; the chlorides are all outer sphere counter ions; the oxidation state of the chromium is +3

- **Co(NH$_3$)$_4$Cl$_3**  An octahedral complex

- **Fe(H$_2$O)$_5$Cl$_3**  An octahedral complex

In the first example above, all the chloride ions are outer sphere while two of the chloride ions are inner sphere ligands and one is an outer sphere ligand in the second example. What about the third example?

When determining metal oxidation states in complexes, determine the charges on all ligands first, then set metal oxidation state so that sum of oxidation states equals overall charge on complex.

Examples:  

- **ReCl$_5$** – a neutral complex  
  \[ ? + 5 \times (-1) = 0 \rightarrow Re^{5+} \text{ (Re(V))} \]

- **KMnO$_4$** (or MnO$_4^-$)  
  \[ (+1) + ? + (4 \times -2) = 0 \quad \text{Mn oxidation state +7} \]

- **K$_2$Cr$_2$O$_7$** (or Cr$_2$O$_7^{2-}$)  
  \[ (2 \times +1) + 2 \times ? + -14 = 0 \quad \text{Cr oxidation state 6+} \]

- **HNO$_3$** (or NO$_3^-$)  
  \[ (+1) + ? + (3 \times -2) = 0 \quad \text{N oxidation state +5} \]
NH₃ \quad ? + (3 \times + 1) = 0 \quad \text{N oxidation state } -3

Recognizing oxidation state extremes can be quite helpful when considering metal ions such as KMnO₄, K₂Cr₂O₇ on the previous page.

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**Formal Charges on Atoms in Lewis Structures**

The Octet Rule and Sum of atomic formal charges is the more traditional approach to writing Lewis structures for organic molecules. To review,

1. **Octet Rule**: Each atom must have an octet of electrons around it for the Lewis structure to be correct.

   Bond and lone pairs around an atom both count 2 toward the octet count.

2. The **formal charge** on an atom in a Lewis structure is determined by subtracting the valence electron count around an atom from its group number. The valence count is calculated in the following manner:

   \[
   \text{Valence Count} = \text{bonds} + (2 \times \text{lone pairs on the atom})
   \]
   
   (bonds count 1; lone pairs count 2 to valence count)

   \[
   \text{Formal Charge on an atom} = \text{Group} \# - \text{Valence Count}
   \]

In most cases atomic oxidation states/numbers do **not** agree with the formal charge on an atom in a compound or ion. The only point in common between the two systems have is that the sum of either must add up to the overall charge on the molecule or ion.