Chapter 11: Oxidation Numbers (also known as Oxidation States)

- These are charges assigned to every atom in a species-- whether ionic or covalent (!)
- The underlying idea is to assign every electron in a species to only one of its constituent atoms. (This is fundamentally different from the Lewis structure paradigm.)
- If possible, the oxidation number equals the charge an atom would have if it were isoelectronic with a noble gas—*again, the atom's quest for an octet (or duet)*
- Unless the compound is actually ionic, oxidation numbers do not correspond to the actual "charge" on an atom—these numbers are only for "bookkeeping purposes". What is physically meaningful is the **change** in oxidation number effected by a redox reaction.
- In a covalent species, an atom's oxidation number will not usually match its formal charge in the Lewis structure (not surprisingly).
- However (like formal charges), the sum of the oxidation numbers in any species must equal the real overall charge of that species.

Rules for Assigning Oxidation Numbers

(1) In substances consisting of one element, the oxidation number is **zero** for all atoms.

In compounds…

(2) Group 1 (alkali metals): **Always +1**
Group 2 (alkaline earth elements): **Always +2**
Other metals (elements to the left of the periodic table diagonal): **Usually positive**

(3) H is **usually +1**…
…but **–1 with metals** (*e.g.* LiH lithium hydride)

(4) F is **always –1** (*e.g.* NaF, HF)

(5) O is **usually –2** (*e.g.* Li_2O)
but has a higher (*i.e.* less negative) oxidation state in species with O-O single bonds
e.g. Na_2O_2 sodium peroxide
KO_2 potassium superoxide

(6) Other Group 17 elements besides F are **often –1**
(a) However, the above rules take precedence (*e.g.* HOCl and other compounds in Table 11.1 of your text—note the relationship between nomenclature and oxidation state).
(b) In "interhalogen compounds" (*e.g.* ICl), give the more electronegative atom the –1 state.

(7) The transition metals and elements in Groups 13, 14, 15 will have a variety of oxidation states. The above rules will usually let us assign their oxidation numbers.

(8) Remember (*i.e.* memorize) the overall charges of polyatomic cations and anions. These provide essential clues when trying to assign oxidation numbers.