The 18 Electron Guideline: A Primmer
## *This can be given to students to read*

The 18 electron "rule" is a very useful tool for predicting which complexes will behave as "closed shell" or "saturated" species. Generally speaking, transition metal compounds with more or fewer than 18 valence electrons will be less stable than close analogs that *do* have 18 electrons. The 18 electron "rule" (*s* orbital, 3 *p*-orbitals, 5 *d*-orbitals, 2 e^- in each) (is a close analog to the "octet rule" (1 *s* orbital, 3 *p*-orbitals, 2 e^- in each) in general and organic chemistry, but the much larger number of exceptions in transition metal chemistry is such that it's really more of a "guideline" than a "rule".

But how do we learn to count to 18? There are two primary methods (somewhat analogous to the "oxidation state/ionic model" and the "formal charge/covalent model" in general chemistry. In these more traditional models, we can count the electrons around carbon in CO_2 in one of two ways:

Oxidation State method:

1. Remove "ligands" (oxygen) as *closed shell* (full octet) species, and assign oxidation states to the resultant cations and anions:
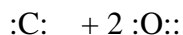
$$C^{4+} + 2\ O^{2-}$$
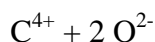
2. Now bring the "ligands" back in. Each bond is worth two electrons (4 for double bonds, 6 for triple)

    2 double bonds = 8 electrons, carbon is an "8 electron species"

Formal Charge method:

1. Remove "ligands" (oxygen) as *neutral species* and leave the central atom *also* neutral. Deal with formal charges at the end as an "add on".

$$:C: \quad + 2 :O::$$

2. Now bring the "ligands" back in. Count all the electrons on your central atom, and count all the electrons donated by the "ligand" to make the bonds.

    4 e^- on C, each oxygen is donating 2 electrons, so carbon is an "8 electron species"

OK, so this is sorta contrived. But this is basically analogous to how we count to 18 with transition metals. In one method (the "Closed Shell Method", we'll do it exactly like we did the oxidation state method above, and in the "Neutral Ligand Method", we'll do it exactly like how we did the formal charge method above.

I'll illustrate these two methods with an example, $Mn(CO)_5Br$, shown at right, an "18 e^- species".

$Mn(CO)_5Br$ by the Closed Shell Method:

$$Br^-, 5\ CO, Mn^+$$
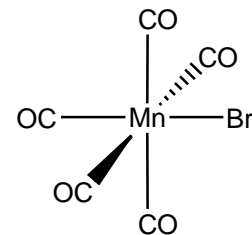
How did I know Mn was +1? Well, I know that Br with all 8 electrons is *-1*, and the CO molecules are *neutral*, and the whole thing overall is neutral. So Mn must be +1 to make the charge balance. I now need to know the amount of electrons on Mn. Neutral Mn in solution phase is s^0d^7 (go back and review why we "dump to the ds" when it comes to electron configuration for transition metals in real complexes if you don't remember why). Hence, Mn^+ is d^6, for 6 e^-. Each of six ligands brings in a pair of electrons for 12 e^-, for 18 total.

Mn^+	6 e^-
5 x CO	5x 2 =10 e^-
Br^-	2 e^-
Total:	18 e^-

Malcolm Green has codified ligands (Green, M. L. H. *J. Organomet. Chem.* **1995**, *500*, 127-148.) by whether they are "anionic" or "X-type" ligands (like Br^-) or "neutral" or "L type" ligands (like CO). In the closed-shell method, both X and L ligands donate 2 electrons each, but the oxidation state can be determined by the number of X ligands.

$Mn(CO)_5Br$ by the Neutral Ligand Method:

$$•Br + {:}CO + Mn\ (d^7)$$
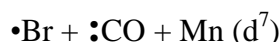
In this case, Mn is neutral, and so d^7, Br is neutral, and so, as a radical, it's a 1 e^- donor. This will be true for all X ligands in this method. CO is still a 2 e^- donor (as are all L ligands in this system). Whether something is an X or L ligand doesn't change between the systems, just how you *count* the electrons.

Ligand Type	Closed Shell	Neutral Ligand
X	2	1
L	2	2

OK. On the next few pages, we'll go through a whole bunch of examples in which the electron counting scheme becomes more interesting. You can assume that all of these are 18 e^- unless specified otherwise, and this will act as a sort of "grand tour" of the different sorts of ligands and bonding modes, and issues that come up with electron counting in them.

A few words about counting: which to use, and why do we care?

You may be wondering, "Why do we have two systems? This seems crazy and needlessly hard!". You are correct. The problem is that there is no "correct" way of accounting for electrons. To a first approximation, the "closed shell" method assumes metal-ligand bonds are ionic, and the neutral method assumes bonds are covalent. Which is better? Of course, it depends. We're used to this. Which is better for water? Is it 2 H^+ + O^{2-} or are all the atoms neutral? If you say the former, you ignore the enormous amount of covalent bonding, and you can't explain why water is a molecular substance rather than an infinite lattice. If you say the latter, you can't explain why water is so polar and hydrogen bonds. The truth is "somewhere in between". The electronegativity differences between metals and ligands are such that the answer here is also "somewhere in between".

So which do you use? What are the pros and cons?

Closed Shell

Pros: All ligands are 2 electrons, you get the metal oxidation state for free as part of the process, and you get the d-electron count. This is particularly useful if you are involved in chemistry in which oxidation states are important, or where the d-electron count is important. Many students find this easier because both L and X ligands are counted the same. This method is generally closest to reality for early metals. Ti-CH_3 is very strongly polarized, such that Ti^+ $^-CH_3$ is not a wholly crazy way to think about the Ti-C bond (though there *is* a large amount of covalent character).

Cons: Some ligands are confusing or downright ambiguous to assign oxidation states to. In particular, carbenes and NO ligands (not covered in this exercise) are notorious for this. This method is also quite far from reality for many late transition metals. Pt-CH_3 bonds are *not* close to Pt^+ $^-CH_3$.

Neutral Ligand

Pros: You don't have to worry about or define oxidation states or d-electron counts. This is particularly useful if you use ligands for which oxidation state is ambiguous or where oxidation state does not change in the reactions being studied. Once you recognize what X and L ligands are, counting becomes very straightforward. Many students find this easier because you don't have to fuss with oxidation state (which is, under the best of circumstances, a fiction).

Cons: In many cases, oxidation state and d-electron count are very important for reactivity, coordination number, structure, and so on, and if you have to determine these anyway, many of the neutral ligand method are lost.

Take home message: These are *formalisms*. They are ways of *keeping track of electrons*. Do not ever think of these accounting systems as ways of telling where the electrons *actually are*. Use more advanced techniques (such as MO theory) for that!