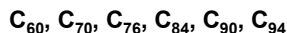


Chemistry and “Magic Numbers”

The Octet Rule: Period 2 nonmetallic elements tend to form compounds resulting in eight electrons around the central atom. You have been told this is because elements desire a pseudo-noble gas configuration.

This is a VAST simplification.

Stable Fullerenes: The allotrope of Carbon known as fullerenes (C_{60} or “Bucky-ball” is the most famous) take on a cage structure and it has been observed that particular numbers of C atoms yield more stable compounds.



Nanoparticles: Metal Nanoparticle are really COOL! It has been observed that “magic numbers” of atoms preferentially come together to form stable structures.

Bonding in TM Complexes: Many TM complexes will form with 18 electrons around the central metal atom. It was first observed by Sedgwick in 1927.

18- Electron Rule.

Recall that for MAIN GROUP elements the **octet rule** is used to predict the formulae of covalent compounds.

Think about Na^+ and Cl^-

This rule assumes that the central atom in a compound will make bonds such that the total number of electrons around the central atom is 8.

THIS IS THE MAXIMUM CAPACITY OF THE s and p orbitals.

**This rule is only valid for
Period 2 nonmetallic elements.**

The **18-electron Rule** is based on a similar concept.

The central TM can accommodate electrons in the s, p, and d orbitals.

s (2) , p (6) , and d (10) = maximum of 18

This means that a TM can add electrons from Lewis Bases (or ligands) in addition to its valence electrons to a total of 18.

This is also known Effective Atomic Number (EAN) Rule

Simple Examples of the 18 Electron Rule

Example 1.



Oxidation state of Co?
Electron configuration of Co?
Electrons from Ligands?
Electrons from Co?
Total electrons?

Example 2.



Oxidation state of Fe?
Electron configuration of Fe?
Electrons from Ligands?
Electrons from Fe?
Total electrons?

What can the EAN rule tell us about $[\text{Fe}(\text{CO})_5]$?

It can't occur..... 20-electron complex.

Approach 1 to counting

Oxidation State Electron Count. Ligands are viewed as "close-shelled" entities. (No radicals). **This is what we did in the earlier examples.**

We dissect the structure

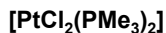
When neutral Lewis base ligands (like NH_3) are considered they are viewed as neutral molecules with 2 electrons for donation to the metal.

Ligands like methyl (CH_3 and Cl) are viewed as anions....**NOT AS NEUTRAL RADICALS. (By definition H is viewed as H^-)**

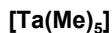
After removal of the ligands the metal is assigned a formal charge.



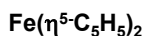
Ni^0 10 e⁻, CO 2 e⁻ each (8) = 18



Pt^{2+} 8 e⁻, Cl⁻ 2 e⁻ each (4), PMe_3 2 e⁻ each (4) = 16



Ta^{5+} 0 e⁻, Me⁻ 2 e⁻ each (10) = 10



Fe^{2+} 6 e⁻, $\eta^5\text{-C}_5\text{H}_5$ 6e⁻ each (12) = 18 Ferrocene

Approach 2 to counting

Neutral Atom Counting.

The general premise to this approach is:

REMOVE ALL THE LIGANDS FROM THE METAL AS NEUTRAL SPECIES.

This approach results in no difference for neutral ligands like NH_3 or CO .

BUT

For ligands such as methyl we remove the ligand as a radical. It is therefore a single electron donor in this model.

Furthermore, in this model both the ligand and the metal must donate an electron to the bond.

This method provides NO information about the metal oxidation state.

Electron Counting Examples

Covalent Counting Rules		Ionic Counting Rules		d Group	Formula	Valence electrons	Structure
	5e 8e 5e 18e		6e (Cp [⊖]) 6e (Fe ²⁺) 6e (Cp [⊖]) 18e	6	$\text{Cr}(\text{CO})_6$	Cr 6 CO <u>12</u> 18	
	6e 6e 6e 18e		6e 6e 6e 18e	7	Mn		
	5e 4e Me 1e 5e 16e		6e 0e Me 2e 6e 2e 16e	8	$\text{Fe}(\text{CO})_5$	Fe 5 CO <u>10</u> 18	
	-1e 5e 9e 5e 18e		6e (Cp [⊖]) 6e (Co ³⁺) 6e (Cp [⊖]) 18e	9	Co		
	Mo 6e 4 H 4e 4 PR3 8e 18		Mo 4+ 2e 4 H- 8e 4 PR3 8e 18	10	$\text{Ni}(\text{CO})_4$	Ni 4 CO <u>10</u> 18	