

Eighteen Electron Rule

The main group element such as lead uses its four valence electrons for the formation of four σ bonds and as a result a stable compound such as PbEt_4 is obtained. In such compounds, the total number of valence electrons becomes equal to 8, i.e., these compounds obey octet rule. On the other hand PbEt_3 contains only six valence electrons and therefore does not obey octet rule and is unstable. However there are some complexes which do not obey the octet rule and are unstable.

In general organometallic compounds of transition metals are formed with metals that are in low oxidation states (-1, 0 and +1). According to Sidwick's effective atomic number (EAN) rule, the EAN of a metal is equal to the sum of electrons on metal plus the electrons donated by the ligands and EAN is equal to the atomic number of next noble gas, [i.e., equal to 36 (Kr), 54 (Xe) or 86 (Rn)].

An alternate and more general rule is the 18-electron rule. According to this rule, in an organometallic compounds and other complexes the sum of valence shell electrons of transition metal or metal ion and electrons donated by the ligands is equal to 18. It provides a closed and stable valence shell configuration $(n-1)d^{10}ns^2np^6$. In transition metals, the electrons of $(n-1)d$ and ns electrons are considered to be valence electrons. The complexes which obey the EAN or 18-electron rule are considered to be stable. The EAN and 18-electron rules are similar. The 18-electron rule is a

rule of thumb and is more advantageous than EAN because there is no need to remember the atomic number of the noble gases. However, there are some exceptions which obey neither EAN nor 18-electron rule. The mononuclear compounds in which the number of total valence electrons is odd never obey either EAN or 18-electron rule.

The first row transition metal carbonyls mostly obey the 18-electron rule. Each metal contributes the same number of electrons as its group number and each CO ligand contributes two electrons, π -back bonding makes no difference to the electron count for the metal. In cases of transition metals with odd electrons, even number of electron 18 is never obtained by adding two electron ligands such as CO. In each case the system resolves this problem in a different way. The complex $V(CO)_6$ has 17 valence electron and easily reduced to the 18-electron $[V(CO)_6]^-$ anion. In $V(CO)_6$, the vanadium is too small to permit a seventh coordination site because there would be strong steric hindrance. Therefore, no metal-metal bonded dimer is formed which would give an 18-electron configuration. Unlike $V(CO)_6$, the $Mn(CO)_5$ species which is also a 17-electron species, does dimerize with the formation of M—M bond. This is due to the reason that the coordination of the 5-coordinate species has more space available to make the M—M bond. Each metal atom in the dimer obeys 18-electron rule because the unpaired electron in each 5-coordinate species is shared with the other in forming the M—M bond much as the 7-electron methyl radical dimerizes to give the 8-electron compound, C_2H_6 . Similarly, the 17-electron $Co(CO)_4$ species dimerizes with the formation of M—M bond but a pair of CO ligands also form bridges with metals. This makes no difference in the electron count because the bridging CO shares one electron with each metal, thus an M—M bond is still required to attain 18-electron. The even electron transition metal complexes achieve 18-electrons without M—M bond formation and they achieve 18-electrons by binding the appropriate number of CO ligands. For example, Cr Fe and Ni metals bond with 6, 5 and 4 CO ligands respectively to attain 18-electrons. The odd electron transition metals need to form M—M bonds. The complexes with coordination number 6, 5 and 4 adopt octahedral, trigonal or square pyramidal and tetrahedral or square planar geometries respectively.

In most of the transition metal complexes electrons are filled in the bonding molecular orbitals leaving the antibonding molecular orbitals vacant. Since there are nine bonding molecular orbitals in transition metal complexes, maximum 18-electrons will filled in them as predicted by the 18 electron rule. Thus according to 18-electron rule, these complexes are considered to be stable.

Electron Count in Complexes

By counting number of valence electrons surrounding each metal atom or metal ion, in a complex it is possible not only to predict the complex would be stable but also in some cases, whether there will be M—M bonds, or not or the ligands will be terminal or bridging etc.

There are two methods for counting electrons :

- (1) Oxidation state or ionic method
- (2) Neutral ligand or covalent method

Both the methods have roughly the equal number of supporters and lead to exactly the same net results. They differ only in the way that the electrons are considered as coming from the metal or from the ligands. Either of the methods can be used quite successfully but care must be taken not to





mix the two. The neutral atom method will be more useful because it does not require the correct assignment of oxidation states, which may be some times difficult for organometallic compounds. The oxidation state method is widely used for the reactions in which oxidation state of the central metal atom is changed. For both the electron counting methods, it is necessary to know how many electrons each ligands in a complex donates to the metal. The contribution of electrons for a variety of ligands for both the neutral atom and the oxidation state methods is shown in Table 1.2. It is to be noted that the electron count for neutral ligands is the same for either of the two methods. Therefore, CO and phosphine ligands behave as two electron donors for both neutral atom and oxidation state methods. The neutral atom method is probably more appropriate for low valent transition metal complexes, especially with the unsaturated ligands. On the other hand, the oxidation state method is more appropriate for high-valent complexes with N, O or X^- ($X = \text{Cl}, \text{Br}, \text{I}$) ligands, such as are found in coordination as well as organometallic compounds.

In the neutral atom method, each metal atom and ligand is treated as neutral. If the complex is charged the appropriate number of electrons are added (if the complex has negative charge) or subtracted (if the complex has positive charge) to the total. In this method, the ligands are considered to donate the number of electrons equal to their negative charge as free ions.

In oxidation state method, to determine the total valence electron count, it must be taken into account the charge on each ligand and determine the formal oxidation of metal.

Table 1.2 : Electron Count for Common Ligands

Ligand	Neutral Atom Method	Oxidation State Method
Carbonyl (M—CO)	2	2
Thiocarbonyl (M—CS)	2	2
Phosphine (M—PR ₃)	2	2
Amine (M—NR ₃)	2	2
Amide (M—NR ₂)	1	2 (NR ₂ ⁻)
Nitrosyl, bent (M— $\overset{\cdot\cdot}{\text{N}}=\text{O}$)	1	2
Nitrosyl, linear (M—N≡O)	3	2
Halogen (M—X)	1	2 (X ⁻)
Hydrogen (M—H)	1	2 (H ⁻)
Alkyl (M—R)	1	2 (R ⁻)
Aryl (M—Ph)	1	2 (Ph ⁻)

Acyl $\left(\begin{array}{c} \text{O} \\ \\ \text{M}-\text{C}-\text{R} \end{array} \right)$	1	2 $\left(\begin{array}{c} \text{O} \\ \\ \text{C}-\text{R}^- \end{array} \right)$
Alkoxide (M—OR)	1	2 (OR ⁻)
Phosphide (M—PR ₂)	1	2 (PR ₂ ⁻)
Thiolate (M—SR)	1	2 (SR ⁻)
Isocyanide (M—CNR)	2	2
Dihydrogen $\left(\begin{array}{c} \text{H} \\ \\ \text{M}- \\ \\ \text{H} \end{array} \right)$	2	2
Dinitrogen (M—N ≡ N)	2	2
Alkene $\left(\begin{array}{c} \diagup \\ \text{C} \\ \\ \text{M}- \\ \\ \text{C} \\ \diagdown \end{array} \right)$	2	2
Alkyne $\left(\begin{array}{c} \\ \text{C} \\ \\ \text{M}- \\ \\ \text{C} \\ \end{array} \right)$	2	2
Carbene or Alkylidene (M = CR ₂)	2	4 (CR ₂ ²⁻)
Carbyne or alkylidyne (M ≡ CR)	3	6 (CR ³⁻)
η ¹ -allyl (M—CH ₂ )	1	2 (⁻ CH ₂ )
η ³ -allyl (M— )	3	4 () or 2 (C ₃ H ₅ ⁺)
η ¹ -cyclopentadienyl $\left(\text{M}-\text{C}_5\text{H}_5 \right)$	1	2 (C ₅ H ₅ ⁻)