Electron Counting, Formal Oxidation States
and the 18 Electron Rule in Transition Metal Chemistry

The 18 Electron Rule

In 1927 Sidgwick proposed that the coordinate bond arises from donation of an electron pair from the ligand to the metal ion. Since noble gases are inert (relatively !!) and have filled s, p, and d shells for a total of 18 electrons in the 9 valence orbitals, he reasoned that metal complexes with 18 electrons might also exhibit particularly high stability. This "18 electron rule" (also called the effective atomic number rule) is analogous to the octet rule discussed in earlier courses and is essentially kinetic in origin. This is because a compound which makes full use of its valence orbitals has no low lying vacant orbitals into which electrons can be promoted to initiate thermal decomposition or into which donation can occur in the case of nucleophilic attack.

We can understand the effectiveness of the 18 electron rule by considering the simple molecular orbital diagram of an octahedral complex ML₆. The 18 electron rule is of limited use in ionic systems because the HOMO-LUMO gap is small (another way of stating this is to say that $\Delta_o$, from crystal field theory, is small) (Fig. 1a below). As the covalent character of the metal ligand bonding increases, the size of the HOMO-LUMO gap also increases (because $e_g^*$ is higher in energy when the orbital overlap is better) (Fig. 1b, 1c and Fig. 2) and therefore the 18 electron rule becomes more important. Finally, in cases where the ligands can function as $\pi$-acceptors as well as $\sigma$-donors, the interaction of the $t_{2g}$ set of orbitals (remember these are $\sigma$-nonbonding) with the ligand $\pi$-symmetry orbitals results in an effective increase in the HOMO-LUMO gap ($\Delta_o$ in Fig. 3a) and we would expect the 18 electron rule to hold best for these types of complexes. This is indeed the case and, as we shall see in carbonyl complexes, the rule is seldom violated in stable covalent complexes with $\pi$-acceptor ligands (Table 1).
Figure 1 Interaction diagram for metal and ligand orbitals

(a) essentially ionic  
(b) polar  
(c) covalent

Figure 2 Qualitative M.O. diagram for an octahedral ML₆ complex where only σ-bonding is considered
Table 1 Scope of the 18e⁻ rule

<table>
<thead>
<tr>
<th>Ligands</th>
<th>18 e⁻ rule useful</th>
<th>Intermediate</th>
<th>18 e⁻ rule not useful</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO, NO, N₂, CS, RNC</td>
<td>H, CH₃, Ph, CN</td>
<td>NH₃, H₂O, halide, OR</td>
<td></td>
</tr>
<tr>
<td>ethene, alkenes, alkynes, PR₃</td>
<td>bipy, R₂S, RS⁻</td>
<td></td>
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<td>(especially PF₃)</td>
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Electron Counting

Given the usefulness of the 18 electron rule, especially in organometallic chemistry where the bonding is predominantly polar covalent and often involves \( \pi \)-acceptor ligands, it is very important to be able to determine quickly how many electrons reside in the valence orbitals of the metal. Electron counting can be done by either a neutral or charged (with ligands negative where necessary in accord with general polarity considerations) formalism. The neutral scheme is more common in the literature and in texts but many will find the charged counting scheme somewhat easier to use. I will present both schemes below. It makes no difference which you adopt but you MUST BE CONSISTENT or you will make errors.

(a) neutral counting

By this method, the metal and its bonded ligands are all counted as neutral fragments. Thus a methyl group is considered to be a 1 electron ligand because \( \cdot \text{CH}_3 \) is the corresponding neutral fragment. Similarly, ligands which are already neutral in their free state (eg. CO, pyridine, PMe\(_3\)) are viewed as donating a pair of electrons to the metal. A few examples will help clarify this:

\[
\begin{align*}
\text{Ni(CO)}_4 & \quad \text{Ni 10 e}^- \text{ (group 10), CO 2 e}^- \text{ each } = 18 \text{ e}^- \text{ total} \\
\text{PtCl}_2(\text{PMe}_3)_2 & \quad \text{Pt 10 e}^-, \text{Cl 1 e}^- \times 2, \text{PMe}_3 2 \text{ e}^- \times 2 = 16 \text{ e}^- \\
\text{TaMe}_5 & \quad \text{Ta 5 e}^- \text{ (group 5), Me 1 e}^- \times 5 = 10 \text{ e}^- \\
\text{Fe(}\eta^5\text{-C}_5\text{H}_5)_2 & \quad \text{Fe 8 e}^- \text{ (group 8), } \eta^5\text{-C}_5\text{H}_5 5 \text{ e}^- \times 2 = 18 \text{ e}^- \\
\text{Co(}\eta^4\text{-C}_4\text{H}_6)(\eta^3\text{-C}_3\text{H}_5) & \quad \text{Co 9 e}^- \text{ (group 9), } \eta^4\text{-C}_4\text{H}_6 4 \text{ e}^-, \eta^3\text{-C}_3\text{H}_5 3 \text{ e}^- = 16 \text{ e}^- \\
\end{align*}
\]

NB: \( \eta^4\text{-C}_4\text{H}_6 \) is butadiene \( H_2C=CH-CH=CH_2 \) bonding through both C=C bonds (2 e\(^-\) each)

NB: for hydrocarbon ligands the hapto number equals the number of electrons donated in this counting scheme.
(b) charged counting (counting ligands as closed shell entities)

By this method, ligands are removed from the metal as closed shell species (no radicals). In the case of neutral Lewis bases such as pyridine this is the same as in (a) above (ie. it is still a 2 e⁻ ligand). However, species such as methyl groups and halides (X) are no longer removed as their neutral (radical) units (ie. •CH₃ or X•) but rather as closed shell species CH₃⁻ and X⁻. In some ways this makes good chemical sense since CH₃ in metal complexes is generally nucleophilic (ie. has a partial negative charge) and X⁻ is the normal form of this ligand in all salts. By convention, H is removed as H⁻ (hydride) rather than H⁺ (proton). After removal of the ligands, the metal is assigned a formal charge that will balance the overall charge on the complex. The number of electrons contributed by the metal to the bonding will then be the group number less the formal charge. Some examples:

- Ni(CO)₄ (same as above)  
  Ni⁰ 10 e⁻ (group 10), CO 2 e⁻ each = 18 e⁻

- PtCl₂(PMe₃)₂ 
  Pt²⁺ 8 e⁻, Cl⁻ 2e⁻ x 2, PMe₃ 2 e⁻ x 2 = 16 e⁻

- TaMe₅ 
  Ta⁵⁺ 0 e⁻ (group 5), Me⁻ 2 e⁻ x 5 = 10 e⁻

- Fe(η⁵-C₅H₅)₂ 
  Fe²⁺ 6 e⁻ (group 8), η⁵-C₅H₅⁻ 6 e⁻ x 2 = 18 e⁻

- Co(η⁴-C₄H₆)(η³-C₃H₅) 
  Co⁺ 8 e⁻ (group 9), η⁴-C₄H₆ 4 e⁻, η³-C₃H₅⁻ 4 e⁻ =16 e⁻

NB: the electron count must be the same regardless of how you count.
Formal oxidation state

The formal oxidation state of the metal is useful in identifying redox reactions and assessing the d electron count at the metal in the complex under study. In the case of charged counting, the formal oxidation state is obtained directly as the charge on the metal required to balance the total charge on the complex after removal of the ligands as closed shell species. If you adopt a neutral counting procedure you will need to switch to charged counting to assess the oxidation state of the metal. The d electron count of the metal is simply the number of electrons contributed by the metal under the charged counting scheme (e.g. $d^6 \text{Fe}^{2+}$ in $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$).

Oxidative-Addition and Reductive-Elimination Reactions

Oxidative-addition reactions and their reverse, reductive-elimination reactions, are of central importance in transition metal organometallic chemistry and are intimately involved in many catalytic cycles. These reactions involve a change in the formal charge on the metal atom, usually by two units. For reactions of this type to occur the metal must have at least two accessible oxidation states of reasonable stability.

General: $\text{M} + \text{X-Y} \rightarrow \text{X-M-Y}$

oxidation st. 0 2+

Examples:

$\text{Pt(PPh}_3)_2 + \text{ArX} = \text{cis-Pt(PPh}_3)_2(\text{Ar})(\text{X}) + \text{PPh}_3$