The 18 Electron Rule

References: Gray: chapter 5
            OGN: chapter 18
Element Groups

Alkali metals

H Li Na K Rb Cs Fr

Alkali earths

Be Mg Ca Sr Ba Ra Sc Y La Ac Ti Zr Hf V Nb Ta Cr Mo W Mn Tc Re Fe Ru Os Co Rh Ir Ni Pd Pt Cu Ag Au Zn Cd Hg

Lanthanides

Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr

Transition metals

B C N O F Ne Al Si P S Cl Ar Ga Ge As Se Br Kr Ga Ge As Se Br Kr In Sn Sb Te I Xe Tl Pb Bi Po At Rn

Halogens

Inert or Noble gases

He Ne Ar

Actinides

Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr
The Chemists

Geoffrey Wilkinson  E. O. Fischer

Nobel Prize, chemistry, 1973

“For their pioneering work, performed independently, on the chemistry of the organometallic, so called sandwich compounds”
18 e\textsuperscript{-} Rule for Transition Elements

• Remember the dot structure for CO?
  \[
  \cdot\text{C} \cdots \cdot\text{O} \quad \Rightarrow \quad \cdot\text{C} \equiv \cdot\text{O} \quad \Rightarrow \quad \cdot\text{C} \equiv \cdot\text{O} \quad \text{(-1, +1)}
  \]

• Consider Cr, a transition element:
  Chromium: \([\text{Ar}] (4s)^2 (3d)^4 \rightarrow 6\) valence e\textsuperscript{-}

• Like most transition elements, Cr needs 18 e\textsuperscript{-} in its shell.

\[
\cdot\text{O} \equiv \cdot\text{C} \quad \cdot\text{Cr} \quad \cdot\text{O} \equiv \cdot\text{C} \quad \cdot\text{C} \equiv \cdot\text{O} \\
12\text{ e}^{-}\text{ from CO’s} + 6\text{ e}^{-}\text{ from Cr} = 18\text{ total e}^{-} \quad \text{; formula is Cr(CO)\textsubscript{6}}
\]

Dot structures can predict molecules; if we are given an exception, we can explain its existence, and figure out some of its chemical properties.
Using the 18 e− rule

• Given that $\text{H}_2\text{Fe(CO)}_x$ exists, what does $x$ equal?
  
  Iron: $[\text{Ar}] (4s)^2 (3d)^6 \rightarrow 8$ valence e−
  Hydrogen: $(1s)^1 \rightarrow 1$ valence e−

• Fe wants to have 18 e−, because it’s a transition element, but it only has 8. The H’s give 2 e−, but we still need 8 electrons. Since each CO supplies 2 e−, there must be 4 CO’s:

$$\text{H}_2\text{Fe(CO)}_4$$
Dimer-Forming Transition Elements

• Given that Mn(CO)₅ exists, find its chemical properties:
  Manganese: \([\text{Ar}] (4s)^2 (3d)^5 \rightarrow 7 \text{ valence e}^-\)

• 5 CO’s provide 10 electrons to Mn, leaving Mn with 17 total e⁻; but Mn wants 18 electrons. So, Mn forms a dimer:

• Halides, like fluorine, also act this way, because they also need only one electron to fill their shell. There are other similarities between transition elements with 7 valence e⁻ and halides...
Transition Metals That Are Like Halides

• As we have seen, transition elements with 7 valence e⁻ (like Mn and Re) which are bonded to 2 e⁻ donors (like CO) form dimers, because they need only one extra e⁻.
• Another similarity is reactivity with light:

\[ \text{Br}_2 \xrightarrow{h\nu} 2 \text{Br} \quad \text{Mn}_2(\text{CO})_{10} \xrightarrow{h\nu} 2 \text{Mn(.CO)}_5 \]

• Another similarity is a phenomenon called “coupling”:

\[ \text{Br} + \text{I} \rightarrow \text{Br—I} \]

\[ \text{Mn(CO)}_5 + \text{Re(CO)}_5 \]
Another Transition Element Structure

• Given that Os₃(CO)₁₂ exists, what is its structure?
  Osmium:  [Xe] (6s)² (5d)⁶  →  8 valence e⁻

• By symmetry, there must be 4 CO’s attached to every Os. That would give us $8 + 4(2) = 16$ e⁻ for each Os. But each Os needs 2 more e⁻ to make 18. So the Os’s can form a triangle, with each Os contributing 2 valence e⁻’s to the single bonds:
What’s the Best Way to Count Things?

• 1 e⁻ donor: Anything that has one e⁻ that is not in a bond. Examples:
  \[
  \begin{align*}
  &\text{H} \cdot \\
  &\text{:F} \cdot \\
  &\text{:Cl} \cdot \\
  &\text{·CH}_3
  \end{align*}
  \]

• 2 e⁻ donor: Anything that has two e⁻’s that are not in a bond (called a “lone pair”). Examples:
  \[
  \begin{align*}
  &\text{:CO} \quad \text{(the one we have been using)} \\
  &\text{H} − \text{N} − \text{H} \\
  &\text{H}
  \end{align*}
  \]

• 3 e⁻ donor: Anything having three e⁻’s to spare. Example:
  
  The allyl radical: 
  \[
  \begin{align*}
  &\text{H} \\
  &\text{H} \quad \text{H} \\
  &\text{H} \quad \text{C} \quad \text{C} \quad \text{H}
  \end{align*}
  \]
  This bond \underline{can donate two e⁻ to a metal}; So this radical is \underline{either a 1 or a 3 e⁻ donor}

Radical: atom or molecule with an incomplete valence shell, making it very reactive
How Many e\textsuperscript{-} Do We Want Donated?

• It depends on the specific case. For example, allyl—Mn(CO\textsubscript{5}) \rightarrow Mn(CO\textsubscript{5}) has 17 e\textsuperscript{-}, so we want 1 e\textsuperscript{-} donated

\[
\text{H}_2\text{C} = \text{C} - \text{C} - \text{CH}_3 + \text{Mn} \rightarrow \text{H}_2\text{C} = \text{C} - \text{C} - \text{CH}_3 - \text{Mn}\text{CO}
\]

• On the other hand, if we have... allyl—Mn(CO\textsubscript{4}) we now need 3 e\textsuperscript{-} from the allyl radical

\[
\text{H}_2\text{C} = \text{C} - \text{C} - \text{CH}_3 + \text{Mn} - \text{CO} \rightarrow \text{H}-\text{C} = \text{C} - \text{C} - \text{CH}_3 - \text{Mn}\text{CO}
\]
What is $\eta$?

- The **hapticity** $\eta$ of a molecule is the number of its atoms within bonding distance of the metal atom (from the Greek *haptein*, “to fasten”).

- The value of $\eta$ gives us an idea of how many electrons are being donated from the molecule to the metal atom.

$$\text{Ti}(\eta^1\text{-C}_5\text{H}_5)_2(\eta^5\text{-C}_5\text{H}_5)_2$$

$$\text{W}(\eta^3\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2$$
More Electron Donors

- 4 electron donor:

\[
\begin{align*}
\text{Butadiene: can be used as a 2 or 4 electron donor.}
\end{align*}
\]

**Carbon Structure Shorthand:**
In order to make drawing hydrocarbon structures simpler and more compact, repetitive information is left out.

- C is implied at any corner
- H are added to each C as necessary to satisfy the 8 e\textsuperscript{-} rule.
More Electron Donors

- 5 e⁻: Cyclo-pentadienyl (Cp)
  —can be a 1, 3, or 5 e⁻ donor

- 6 e⁻ donor: benzene
  —can be a 2, 4, or 6 e⁻ donor
Another Transition Element Structure

- Given \((C_4H_4)Fe(CO)_x\) exists, what is the value of \(x\)?

- Fe has eight e-

- Butadiene \((C_4H_4)\) donates 4 e-

- We need 6 more e-, so we use three CO’s.

\[4 + 8 = 12\text{ e- so far}\]

3 CO’s donate 6 e-, making 18 e- for Fe
Yet Another Structure

• Can we draw Fe₄(Cp)₄(CO)₄?

— By symmetry, each Fe gets a Cyclo-pentadienyl (Cp) and a CO

— Cp donates 5 e⁻, so now we have 15 e⁻ for each Fe

— If we put the Fe’s at the corners of a tetrahedron, then each Fe can share a single bond with three other Fe’s; we end up with 18 e⁻ per Fe.
<table>
<thead>
<tr>
<th>Reactions/Products</th>
<th>Production/yr $10^3$ Metric tons (1990)</th>
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<tr>
<td>Olefin additions</td>
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<tr>
<td>Olefin polymerizations</td>
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<td>Alkane and arene oxidations</td>
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</tr>
</tbody>
</table>
\[
\text{CH}_3\text{OH} + \text{CO} \rightarrow \text{CH}_3\text{COOH}
\]
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