

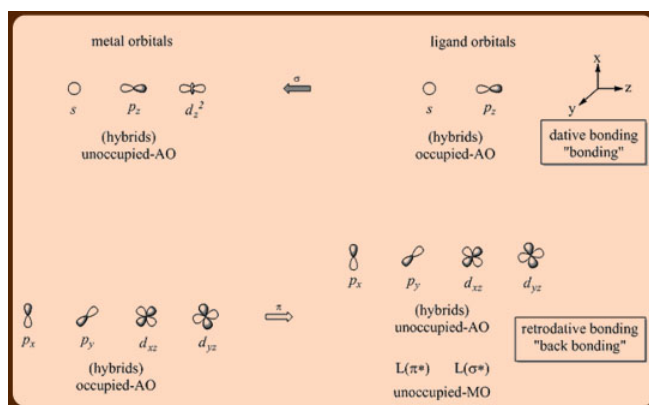
24.3: The 18-electron Rule

Learning Objectives

In this lecture you will learn the following

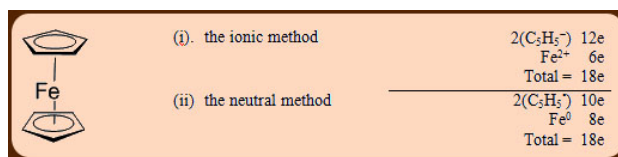
- Have an insight about the stability of the transition metal complexes with respect to their total valence electron count.
- Be aware of the transition metal complexes that obey or do not obey the 18 Valence Electron Rule.
- Have an appreciation of the valence electron count in the transition metal organometallic complexes that arise out of the metal-ligand orbital interactions.

The transition metal organometallic compounds exhibit diverse structural variations that manifest in different chemical properties. Many of these transition metal organometallic compounds are primarily of interest from the perspectives of chemical catalysis. Unlike the main group organometallic compounds, which use mainly ns and np orbitals in chemical bonding, the transition metal compounds regularly use the $(n-1)d$, ns and np orbitals for chemical bonding (Figure 1). Partial filling of these orbitals thus render these metal centers both electron donor and electron acceptor abilities, thus allowing them to participate in σ -donor/ π -acceptor synergic interactions with donor-acceptor ligands like carbonyls, carbenes, arenes, isonitriles and etc.,

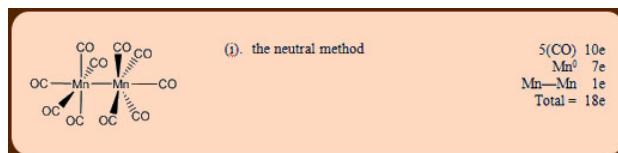


The 18 Valence Electron (18 VE) Rule or The Inert Gas Rule or The Effective Atomic Number (EAN) Rule: The 18-valence electron (VE) rule states that thermodynamically stable transition metal compounds contain 18 valence electrons comprising of the metal d electrons plus the electrons supplied by the metal bound ligands. The counting of the 18 valence electrons in transition metal complexes may be obtained by following either of the two methods of electron counting, (i). the ionic method and (ii). the neutral method. Please note that a metal-metal bond contributes one electron to the total electron count of the metal atom. A bridging ligand donates one electron towards bridging metal atom.

Example 1: Ferrocene $Fe(C_5H_5)_2$



Example 2. $Mn_2(CO)_{10}$



Transition metal organometallic compounds mainly belong to any of the three categories.

1. **Class I** complexes for which the number of valence electrons do not obey the 18 VE rule.
2. **Class II** complexes for which the number of valence electrons do not exceed 18.
3. **Class III** complexes for which the valence electrons exactly obey the 18 VE rule.

The guiding principle which governs the classification of transition metal organometallic compounds is based on the premise that the antibonding orbitals should not be occupied; the nonbonding orbitals may be occupied while the bonding orbitals should be occupied.

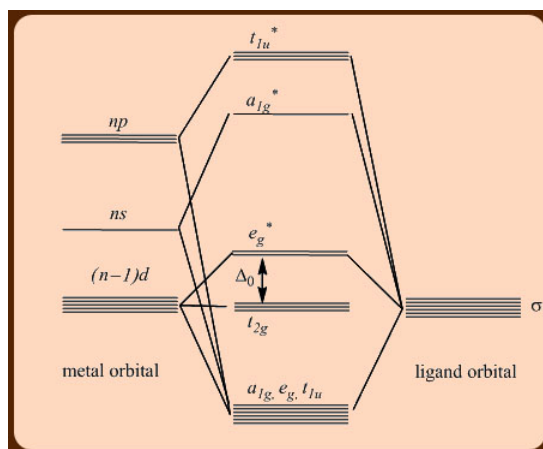


Figure 2. A simplified molecular orbital diagram for an octahedral transition metal complex showing σ -interactions only.

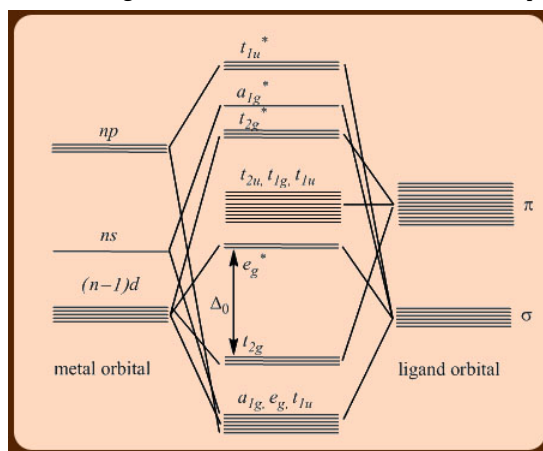


Figure 3. A simplified molecular orbital diagram for an octahedral transition metal complex showing σ - and π -interactions only.

Class I:

In **class I** complexes, the Δ_o splitting is small and often applies to $3d$ metals and σ ligands at lower end of the spectrochemical series. In this case the t_{2g} orbital is nonbonding in nature and may be occupied by 0–6 electrons (Figure 2). The e_g^* orbital is weakly antibonding and may be occupied by 0–4 electrons. As a consequence, 12–22 valence electron count may be obtained for this class of compounds. Owing to small Δ_{tet} splitting energy, the tetrahedral transition metal complexes also belongs to this class.

Class II:

In **class II** complexes, the Δ_o splitting is relatively large and is applicable to $4d$ and $5d$ transition metals having high oxidation state and for σ ligands in the intermediate and upper range of the spectrochemical series. In this case, the t_{2g} orbital is essentially nonbonding in nature and can be filled by 0–6 electrons (Figure 3). The e_g^* orbital is strongly antibonding and is not occupied at all. Consequently, the valence shell electron count of these type of complexes would thus be 18 electrons or less.

Class III:

In **class III** complexes, the Δ_o splitting is the largest and is applicable to good σ donor and π acceptor ligands like CO, PF_3 , olefins and arenes located at the upper end of the spectrochemical series. The t_{2g} orbital becomes bonding owing to interactions with ligand orbitals and should be occupied by 6 electrons. The e_g^* orbital is strongly antibonding and therefore remains unoccupied.

Problems

State the oxidation state of the metal and the total valence electron count of the following species.

1. $V(C_2O_4)_3^{3-}$

Ans: +3 and 14 2. $\text{Mn}(\text{acac})_3$ Ans: +3 and 16 3. $\text{W}(\text{CN})_8^{3-}$ Ans: +5 and 17 4. $\text{CpMn}(\text{CO})_3$ Ans: 0 and 18 5. $\text{Fe}_2(\text{CO})_9$ Ans: 0 and 18 Self Assessment test

State the oxidation state of the metal and the total valence electron count of the following species.

1. TiF_6^{2-}

Ans: +4 and 12 2. $\text{Ni}(\text{en})_3^{2+}$ Ans: +2 and 20 3. $\text{Cu}(\text{NH}_3)_6^{2+}$ Ans: +2 and 21 4. $\text{W}(\text{CN})_8^{4-}$ Ans: +4 and 18 5. $\text{CH}_3\text{Co}(\text{CO})_4$ Ans: 0 and 18

Summary

The transition metal complexes may be classified into the following three types. (i). The ones that do not obey the 18 valence electron rule are of class I type (ii). the ones that do not exceed the 18 valence electron rule are of class II and (iii). the ones that strictly follow the 18 valence electron rule. Depending upon the interaction of the metal orbitals with the ligand orbitals and also upon the nature of the ligand position in spectrochemical series, the transition metal organometallic compounds can form into any of the three categories.

The 18-electron rule is used primarily for predicting and rationalizing formulae for stable metal complexes, especially organometallic compounds. The rule is based on the fact that the valence shells of transition metals consist of nine valence orbitals (one s orbital, three p orbitals and five d orbitals), which collectively can accommodate 18 electrons as either bonding or nonbonding electron pairs. This means that, the combination of these nine atomic orbitals with ligand orbitals creates nine molecular orbitals that are either metal-ligand bonding or non-bonding. When a metal complex has 18 valence electrons, it has achieved the same electron configuration as the noble gas in the period. The rule and its exceptions are similar to the application of the octet rule to main group elements.

This rule applies primarily to organometallic compounds, and the 18 electrons come from the 9 available orbitals in d orbital elements (1 s orbital, 3 p orbitals, and 5 d orbitals). The rule is not helpful for complexes of metals that are not transition metals, and interesting or useful transition metal complexes will violate the rule because of the consequences deviating from the rule bears on reactivity. If the molecular transition metal complex has an 18 electron count, it is called **saturated**. This means that additional ligands cannot bind to the transition metal because there are no empty low-energy orbitals for incoming ligands to coordinate. If the molecule has less than 18 electrons, then it is called **unsaturated** and can bind additional ligands.

Electron counting

Two methods are commonly employed for electron counting:

1. Neutral atom method: Metal is taken as in zero oxidation state for counting purpose
2. Oxidation state method: We first arrive at the oxidation state of the metal by considering the number of anionic ligands present and overall charge of the complex

To count electrons in a transition metal compound:

1. Determine the oxidation state of the transition metal and the resulting d-electron count.
 - Identify if there are any overall charges on the molecular complex.
 - Identify the charge of each ligand.
2. Determine the number of electrons from each ligand that are donated to the metal center.
3. Add up the electron counts for the metal and for each ligand.

Typically for most compounds, the electron count should add up to 18 electrons. However, there are many exceptions to the 18 electron rule, just like there are exceptions to the octet rule.

Reactivity

The 18 electron rule allows one to predict the reactivity of a certain compound. The associative mechanism means that there is an addition of a ligand while a dissociative mechanism means that there is a loss of a ligand. When the electron count is less than 18, a molecule will most likely undergo an associative reaction. For example: $(\text{C}_2\text{H}_4)\text{PdCl}_2$

- 16 electron count
- Would it more likely lose a C_2H_4 or gain a CO? Losing a C_2H_4 results in a 14 electron complex while gaining a CO gives an 18 electron complex. From the 18 electron rule, we will expect that the compound will more likely undergo an associative addition

of CO.

Example 24.3.1:

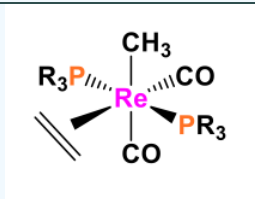


Figure 24.3.1: Saturated Re metal complex with 18 electron count. (CC SA-BY 4.0; Derrekli)

1. There is no overall charge on the molecule and there is one anionic ligand (CH_3^-)
 - The Re metal must have a positive charge that balances out the anionic ligand charge to equal the 0 overall molecular charge. Since there is a -1 charge contribution from the methyl ligand, the Re metal has a +1 charge.
 - Because the Re metal is in the +1 oxidation state, it is a d^6 electron count. It would have been its regular d^7 electron count if it had a neutral (0) oxidation state.
2. The CH_3^- ligand contributes 2 electrons. Each CO ligand contributes 2 electrons. Each PR_3 ligand contributes 2 electrons. The $\text{H}_2\text{C}=\text{CH}_2$ ligand contributes 2 electrons.
3. Adding up the electrons:
 - Re(1): 6 electrons
 - CH_3^- : 2 electrons
 - 2 x CO: 2 x 2 electrons = 4 electrons
 - 2 x PR_3 : 2 x 2 electrons = 4 electrons
 - $\text{H}_2\text{C}=\text{CH}_2$: 2 electrons
 - Total: 18 electrons

In this example, the molecular compound has an 18 electron count, which means that all of its orbitals are filled and the compound is stable.

Example 24.3.2: $[\text{M}(\text{CO})_7]^+$

The 18 electron rule can also be used to help identify an unknown transition metal in a compound. Take for example $[\text{M}(\text{CO})_7]^+$. To find what the unknown transition metal M is, simply work backwards:

1. 18 electrons
2. Each (CO) ligand contributes 2 electrons
 - 7 x 2 electrons = 14 electrons
3. 18 - 14 = 4 electrons
4. d^4
5. M(I) oxidation state
6. The unknown metal M must be V, Vanadium

Example 24.3.3: $[\text{Co}(\text{CO})_5]^z$

Similarly to Example 2, the 18 electron rule can also be applied to determine the overall expected charge of an molecule. Take for example $[\text{Co}(\text{CO})_5]^z$. To find the unknown charge z:

1. 18 electrons
2. Each CO ligand contributes 2 electrons
 1. 5 x 2 electrons = 10 electrons
3. Co is typically d^9
4. 9 + 10 = 19 electrons
5. To satisfy the 18 electron rule, the $[\text{Co}(\text{CO})_5]^z$ compound must have a charge of $z = +1$.

Ligand Contributions

Below is a list of common organometallic ligands and their respective electron contributions.

Neutral 2e donors	Anionic 2e donors	Anionic 4e donors	Anionic 6e donors
PR ₃ (phosphines)	X ⁻ (halide)	C ₃ H ₅ ⁻ (allyl)	Cp ⁻ (cyclopentadienyl)
CO (carbonyl)	CH ₃ ⁻ (methyl)	O ²⁻ (oxide)	O ²⁻ (oxide)
alkenes	CR ₃ ⁻ (alkyl)	S ²⁻ (sulfide)	
alkynes	Ph ⁻ (phenyl)	NR ²⁻ (imide)	
nitriles	H ⁻ (hydride)	CR ₂ ²⁻ (alkylidene)	
	R _n E ⁻ (silyl, germyl, alkoxo, amido etc.)	OR ⁻ (alkoxide, bridging ligand)	
		SR ⁻ (thiolate, bridging ligand)	
		NR ₂ ⁻ (inorganic amide, bridging ligand)	
		PR ₂ ⁻ (phosphide, bridging ligand)	

Exceptions

Generally, the early transition metals (group 3 to 5) could have an electron count of 16 or less. Middle transition metals (group 6 to group 8) commonly have 18 electron count while late transition metals (group 9 to group 11) generally have 16 or lower electron count. When a structure has less than an 18 electron count, it is considered electron-deficient or coordinately unsaturated. This means that the compound has empty valence orbitals, making it electrophilic and extremely reactive. If a structure has "too many electrons," that means that not all of the bonds are covalent bonds, and thus some has to be ionic bonds. These bonds are weaker compared to covalent bonds. However, these organometallic compounds that have an electron count greater than 18 are fairly rare.

Summary

The 18-electron rule is similar to the octet rule for main group elements, something you might be more familiar with, and thus it may be useful to bear that in mind. So in a sense, there's not much more to it than "electron bookkeeping".

References

1. Pfenning, Brian (2015). *Principles of Inorganic Chemistry*. Hoboken, New Jersey: John Wiley & Sons, Inc. pp. 629–631. [ISBN 9781118973868](#).

Contributors and Attributions

- Wikipedia (CC-BY-SA-3.0)
- Openstack

– dekiscript –