

## 2.2.4: Expanded Octets

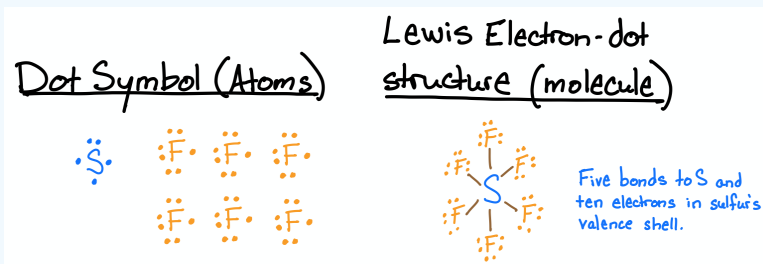
### Hypervalency

The octet rule applies well to atoms in the second row of the periodic table, where a full valence shell includes eight electrons with an electron configuration of  $s^2p^6$ . Even elements in the third and fourth row are known to follow this rule *sometimes*, but not always. In larger atoms, where  $n \geq 3$  the valence shell contains additional subshells: the  $d$ ,  $f$ ,  $g$ ... subshells. Therefore, atoms with  $n \geq 3$  can have higher valence shell counts by "expanding" into these additional subshells. When atoms contain more than eight electrons in their valence shell, they are said to be **hypervalent**. Hypervalency allows atoms with  $n \geq 3$  to break the octet rule by having more than eight electrons. This also means they can have five or more bonds; something that is nearly unheard of for atoms with  $n \leq 2$ . Complete the exercises below to see examples of molecules containing hypervalent atoms.

#### Exercise 2.2.4.1

Draw the Lewis structures for  $\text{SF}_6$ .

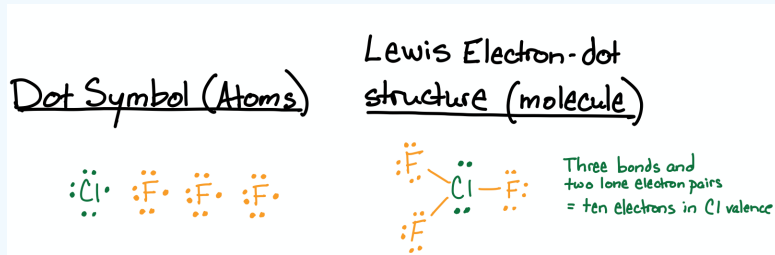
Answer



#### Exercise 2.2.4.2

Draw the Lewis structure for  $\text{ClF}_3$ .

Answer



Is hypervalency real? Not exactly. Hypervalency is a concept associated with hybrid orbital theory and Lewis theory. It's useful for some simple things, like predicting how atoms are connected and predicting molecular shape. But the idea that the  $d$ -orbitals are involved in bonding isn't accurate according to wave mechanics.

For main group molecules, chemists (like Pauling) thought a long time ago that hypervalence is due to expanded  $s^2p^6$  octets. The consensus is now clear that  $d$  orbitals are **NOT** involved in bonding in molecules like  $\text{SF}_6$  any more than they are in  $\text{SF}_4$  and  $\text{SF}_2$ . In all three cases, there is a small and roughly identical participation of  $d$ -orbitals in the wavefunctions. This has been established in both MO and VB theory. However using hybrid orbitals with  $d$ -orbital contributions equips us with a language which can pragmatically describe the geometries of highly coordinated substances.

While hybrid orbitals are a powerful tool to describe the geometries and shape of molecules and metal complexes. However, in "real" molecules, their significance may be debated. Often with a more realistically molecular orbitals approach is needed. However, from an epistemologically simple point of view, bonding theories can only be judged by their predictions. To the extent that hybridization can explain the shapes of  $\text{PF}_5$  and  $\text{SF}_6$ , valence bond theory is a perfectly good theory. To the extent that if you

write out the valence bond wavefunction using hybridized orbitals and calculate energies and other properties à la Pauling (i.e., ionization energy and electron affinities) and find them to be off from experimental results (by tens of kcal/mol), then valence bond theory is not accurate.

*Bonding theories can only be judged by their predictions.*

### An Alternate View of Expanded Octets

Another way to represent main group compounds with more than four bonds is to include ionic bonding character. This allows for compounds with more than 4 bonds to the central atom to not exceed their octets. For example, the Lewis structure of  $\text{SF}_6$  can be redrawn with two ionic S-F bonds and four covalent S-F bonds as shown in Figure 2.2.4.1. In this picture the central S atom has six F atoms coordinated, but only shares four bonding pairs of electrons and has a complete (non-expanded) octet. Considering all the possible resonance structures for  $\text{SF}_6$ , each S-F bond is  $\frac{2}{3}$  covalent and  $\frac{1}{3}$  ionic.

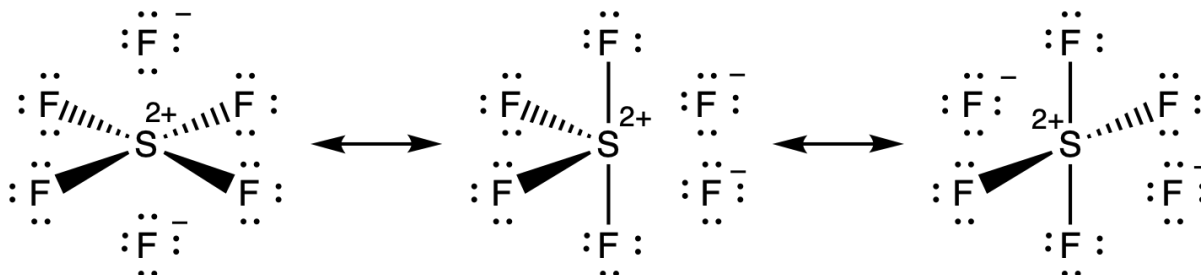


Figure 2.2.4.1: Three of the 15 possible resonance structures for sulfur hexafluorophosphate with four covalent and two ionic S-F bonds. (CC BY-NC-SA; Catherine McCusker)

### Additional Resources

- Gillespie, R. The Octet Rule and Hypervalence: Two Misunderstood Concepts. *Coord. Chem. Rev.* **2002**, 233–234, 53–62. [https://doi.org/10.1016/S0010-8545\(02\)00102-9](https://doi.org/10.1016/S0010-8545(02)00102-9).

### Contributors and Attributions

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