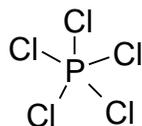


“Expanded Octet” in Lewis Structures

“Expanded octet” refers to the Lewis structures where the central atom ends up with more than an octet, such as in PCl_5 or XeF_4 . In drawing the Lewis structure for PCl_5 , there is a total of 40 valence electrons to put in ($5 + 5 \times 7 = 40$). One can easily see that if the central atom, P, is to be joined to five Cl atoms, P would have 10 electrons instead of the octet. (Remember that one does **NOT** string out the elements to look thus: P-Cl-Cl-Cl-Cl-Cl. ← **No !!**)



Clearly there is a violation of the “Octet Rule”.

How do we know to allow this violation? It’s simply this: PCl_5 exists. Our rules have to be revised to accommodate observations. If PCl_5 exists, then this violation must be permitted, since there is no other way to explain it.

A word of caution: Does this mean that we can violate the Octet Rule any time we wish? No! We can violate the Octet Rule only when there is no other way to explain it.

Limitations to the “expanded octet”:

The expanded octet is limited to elements with atomic numbers greater than 10 (beyond Ne).

In the discussion of hybridization, we see that when there are 5 or 6 “groups” on the central atom, d-orbitals are involved. This cannot occur with elements that do not contain d-orbitals!

Which elements would that be?

First of all, elements smaller than neon (atomic number 10) have electrons only in the first two main energy levels ($n = 1$ and $n = 2$), and those energy levels do not contain d-orbitals.

Second of all, expanded octets generally occur when there are *too many* electrons to fit in. Since double bonds and triple bonds occur usually when there are *insufficient* number of electrons, you would not normally apply the “expanded octet” to central atoms with multiple bonds! In other words, the extra electrons should be added first as *lone pairs and NOT as double or triple bonds!* After having done that if and only if the central atom has a *positive formal charge*, you may move a lone pair from the outside atoms to share by forming a double bond. Remember you can do that *only* in order to neutralize the positive formal charge. You should not be forming the double bond indiscriminately.

Summary of limitations of applying the “expanded octet”:

- 1) The central atom with an expanded octet MUST have an atomic number larger than 10 (beyond neon).**
- 2) Extra electrons should be first placed on the outside atoms. After the outside atoms have fulfilled the Octet Rule, and there are still extra electrons, start with placing them as lone pairs on the central atom. If the central atom does not have a positive formal charge, do not go any further. You have the correct Lewis structure. Only if the central atom has a positive charge should you move a lone pair from the outside atoms to share.**

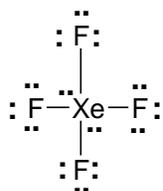
Let's take the example of XeF₄.

Step One: Count the total number of valence electrons. Answer: 8 + 4x7 = 36 = 18 pairs.

Step Two: The first element is usually the central atom, and then you cluster the other atoms around it.

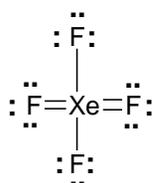


Step Three: The 4 covalent bonds shown above account for 4 pairs. As you put lone pairs onto the surrounding F, you would account for 12 more pairs, giving you a total of 16 pairs. Where are you going to put two more pairs? The only place would be on the central atom (on Xe) as lone pairs. Xe would therefore have 4 atoms and 2 lone pairs (AX₄E₂). It has six groups attached to it and so the hybridization is sp³d² (Check: sp³d² = 1s + 3p + 2d = 6 orbitals)



Xenon now has twelve electrons instead of the octet! This is called an “expanded octet”, expanding beyond the octet.

Notice we do NOT put a double bond between the Xe and one of the F(!), a mistake that students often make. In the structure shown above, Xe has a formal charge of zero, so there is no reason to do any more to the structure.



This structure is incorrect because Xe now has a formal charge of 2+ (6 electrons instead of 8) and the two F with double bonds each has a formal charge of -1 (8 electrons instead of 7). Compared to the structure above which has no formal charges, this is certainly not preferred.

In addition, in terms of the Octet Rule, F has exceeded the Octet and it is not an element than can exceed the Octet Rule (atomic number less than 10).

I strongly urge that you practice by doing the Lewis structures of the following:

BrF₃ SF₄ XeF₅⁺ ICl₃ XeOF₄ XeF₄ SbF₅

If your instructor requires you to learn the molecular geometries of expanded octet, you should conclude that the hybridization and geometries for the above are (in the order of the formulas given above): sp³d (T-shaped), sp³d (see-saw shaped), sp³d²(square pyramidal), sp³d (T-shaped), sp³d²(square pyramidal), sp³d² (square planar), sp³d (trigonal bipyramidal)

I welcome comments on this tutorial, and appreciate it if you tell me of typos or if you have questions about this tutorial. You may contact me at cvau@cubcmd.edu

If you need help with figuring out “formal charges” you can return to my website and study the tutorial on formal charges.