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## How can one represent the structure of a polyatomic covalent species?

## The Model: Expanded Octets

There are two phosphorous fluorides: $\mathrm{PF}_{3}$ and $\mathrm{PF}_{5}$. In each compound, it is the Phosphorous that is the central atom. Phosphorous is in the same family as Nitrogen, so we may write the dot symbol of Phosphorous as:


Therefore we see that Phosphorous, like Nitrogen, may form three single bonds. Since Fluorine wants to form only one single bond, it works out perfectly for $\mathrm{PF}_{3}$ to have the Lewis structure:

```
    Total # valence e}\mp@subsup{e}{}{-
1P}+3\mathbf{F}=1(5)+3(7
    = 5+21
    = 26
```



Total \# valence $\mathrm{e}^{-}$in structure:

$$
\begin{aligned}
3 \mathrm{~B}+10 \mathrm{Lp} & =3(2)+10(2) \\
& =6+20 \\
& =\mathbf{2 6}
\end{aligned}
$$

Another way to draw the dot symbol for "ready-to-bond" Phosphorous is:


Thus we see how Phosphorous can also form 5 single bonds, and the Lewis structure of $\mathrm{PF}_{5}$ is:

| Total $\#$ valence $\mathbf{e}^{-}:$ |  |
| ---: | :--- |
| $1 \mathbf{P}+5 \mathbf{F}$ | $=1(5)+5(7)$ |
|  | $=5+35$ |
|  | $=\mathbf{4 0}$ |


Total \# valence $\mathrm{e}^{-}$in structure
Total \# valence $\mathrm{e}^{-}$in structure
$5 \mathrm{~B}+15 \mathrm{Lp}=5(2)+15(2)$
$5 \mathrm{~B}+15 \mathrm{Lp}=5(2)+15(2)$
$=10+30$
$=10+30$
$=40$
$=40$

## Key Questions

1a. What is the principal quantum number of the highest-energy electron of Phosphorous?
b. With this value of $n$, what orbitals are allowed, and how many total orbitals are there forming bonds?
c. Why is it okay for there to be more than 8 electrons drawn around P (a $3^{\text {rd }}$ period element) in a Lewis structure? (Keep in mind that a single bond is the sharing of two electrons between two adjacent atoms. An orbital is a region of space in which an electron is likely to be found, and an orbital may accommodate up to two electrons. So a single bond is an orbital - a region of space between two adjacent atoms where it is likely to find an electron.)
d. In general, what is required for an atom to "expand" its valence shell and violate the octet rule?
e. Circle each of the following atoms that can expand its valence shell: F, S, H, Al, Se, Cl

## The Model: Double and Triple Bonds

We will see that in order for two (or more) atoms to both have an octet, it may be necessary for the atoms to share more than just a single pair of electrons. Thus we have multiple bonding between two atoms in many compounds.

## Example 1. Nitrosyl Bromide, NOBr

In general, the first element is often the central atom. So we'll proceed under the assumption that Nitrogen is the central atom. We start off by writing:

$$
\begin{array}{lll}
\mathrm{O} & \mathrm{~N} & \mathrm{Br}
\end{array}
$$

$\underline{\text { Total } \# \text { valence } e^{-}}=1 \mathrm{~N}+1 \mathrm{O}+1 \mathrm{Br}=1(5)+1(6)+1(7)=\mathbf{1 8}$
We put line segments (each representing a pair of bonding electrons) where we know there is at least a single bond:

$$
\mathrm{O}-\mathrm{N}-\mathrm{Br}
$$

We ask: "What are the preferred numbers of bonds?" Oxygen wants two bonds, Nitrogen wants three bonds, and Bromine (being in the same family as Fluorine) wants one bond (at least when it is not the central atom). We can manage that by putting a second line segment between the Nitrogen and Oxygen atoms:


Now we place pairs of dots (lone pairs) until every atom has an octet:


## Example 2. Hydrogen Cyanide, HCN

This time, we know that Hydrogen cannot be a central atom-do you know why? So we'll assume that the carbon atom is since it is central in the formula. We put line segments between atoms where we know there is going to be at least one bond:

$$
\mathrm{H}-\mathrm{C}-\mathrm{N}
$$

Carbon wants four bonds and Nitrogen wants three bonds, so:

$$
\mathrm{H}-\mathrm{C} \equiv \mathrm{~N}
$$

Finally, to give Nitrogen an octet, we put a lone pair on the N:


The total number of valence electrons should be 1 from the Hydrogen atom plus 4 from the Carbon atom, plus 5 from the Nitrogen atom for a total of 10 . The above Lewis structure shows 8 electrons in the bonds and 2 electrons in the lone pair for a total of 10.

## Exercises

Draw Lewis Structures for the following compounds.
2. $\mathrm{H}_{2} \mathrm{CO}_{3}$ (Each oxygen is bound to the carbon, and each hydrogen is bound to a different oxygen atom.)
3. $\mathrm{POCl}_{3}$ (The phosphorous is the only central atom.)
4. $\mathrm{HCCCH}_{3}$ (One carbon is bound to 1 hydrogen, another carbon is bound to 3 hydrogen atoms.)
5. $\mathrm{N}_{2} \mathrm{~F}_{2}$

## The Model: Polyatomic Ions

We need to look at an example of a polyatomic ion, within which the atoms are held together by covalent bonds.

Example 3. Iodate, $\mathrm{IO}_{3}{ }^{-}$
We proceed under the assumption that the Iodine atom is the central atom. We put a line segment between the central I and each of the O's.


The total number of valence electrons is:


We now distribute pairs of electrons so that the atoms each have an octet:


Because the species is charged, it is appropriate to enclose the entire structure in brackets and write the overall charge as a superscript.

## Exercises

Draw Lewis Structures for the following ions.
6. $\mathrm{H}_{3} \mathrm{O}^{+}$
7. $\mathrm{NO}_{2}^{-}$
8. $\mathrm{SO}_{3}{ }^{2-}$ (Hint: two of the oxygen atoms with the negative charge have single bonds)

