Chemistry Lecture #40: Lewis Structures of Polyatomic Ions & Octet Rule Exceptions

The atoms in polyatomic ions are covalently bonded. In essence a polyatomic ion is a molecule with a charge. Since polyatomic ions are molecules, we can draw their Lewis structures.

The steps for drawing the Lewis structure of a polyatomic ion is the same for other molecules. Just remember to account for the extra electrons on the molecule when you count up the total number of valence electrons.

Draw the Lewis structure of PO_4^{3-}.

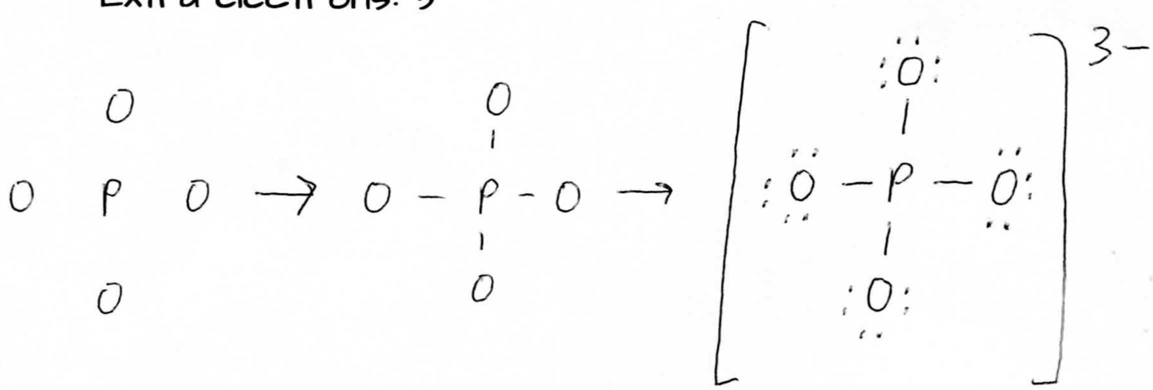
This ion has a charge of -3, so it has 3 extra electrons.

P: 1 x 5 = 5

O: 4 x 6 = 24

Extra electrons: 3

Total # of valence & extra electrons = 5 + 24 + 3 = 32



Notice that all atoms now have 8 valence electrons.

Draw the Lewis structure of NO_3^-

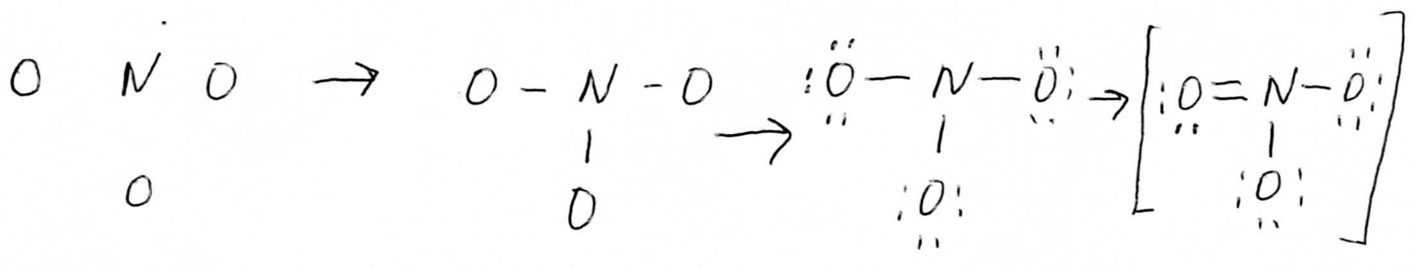
N: 1 x 5 = 5

O: 3 x 6 = 18

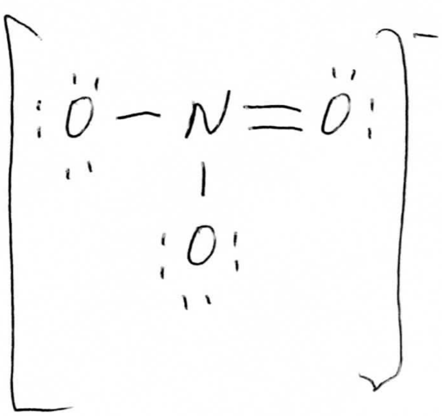
Extra electron = 1

Total number of valence and extra electrons =

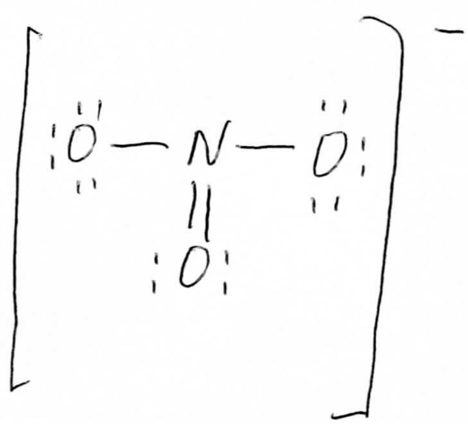
5 + 18 + 1 = 24



Nitrate can also be drawn as



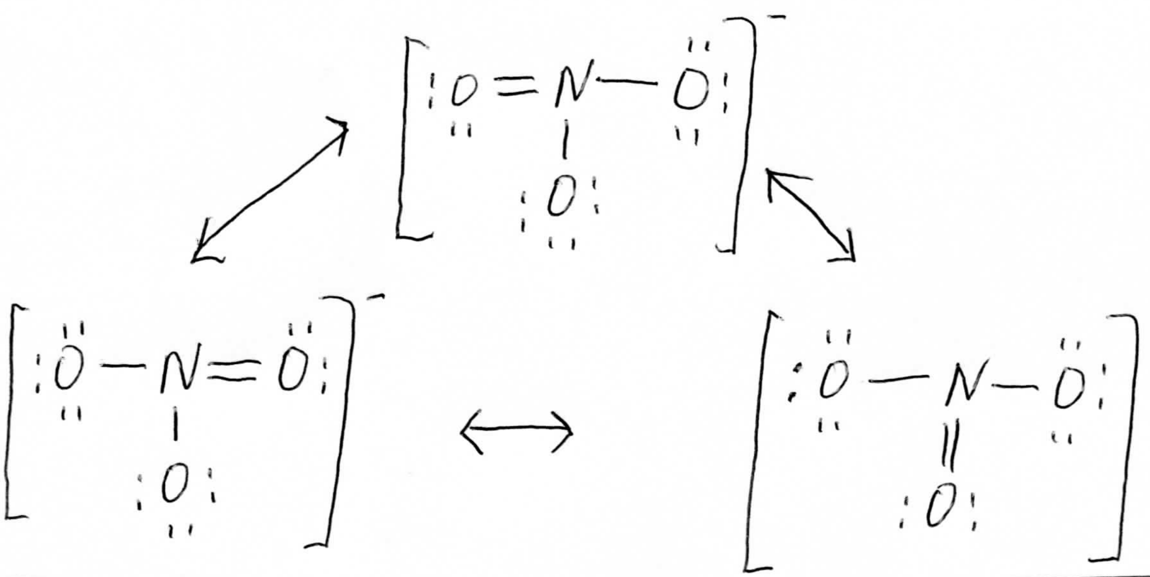
Or



The actual structure that exists is the *average of all three types of structures.* The electron pairs do not jump back and forth. Rather, the electrons are simultaneously spread out equally over all three bonding positions. Pretty weird, eh?

Single bonds are longer than double bonds. Experiments show that NO_3^- has three exactly equal bond lengths that are shorter than single bonds, but longer than double bonds. Thus, nitrate does not have single bonds and double bonds, but a combination of the two.

To show the resonance structure of nitrate, all three Lewis diagrams are drawn, or a single structure with dotted lines is drawn.



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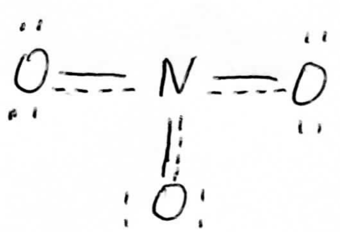


The two or more correct Lewis structures for a molecule are called resonance structures. The actual structure that exists is an average of the possible structures.

Draw the Lewis structure for NH_4^+.

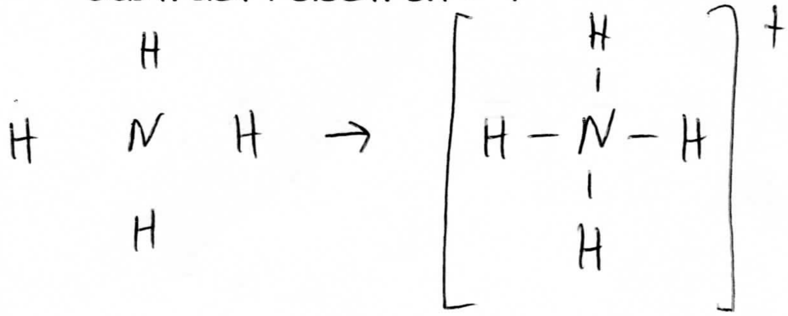
This ion has a positive charge, so it is missing an electron. We subtract an electron when we figure out the total.

N: $1 \times 5 = 5$

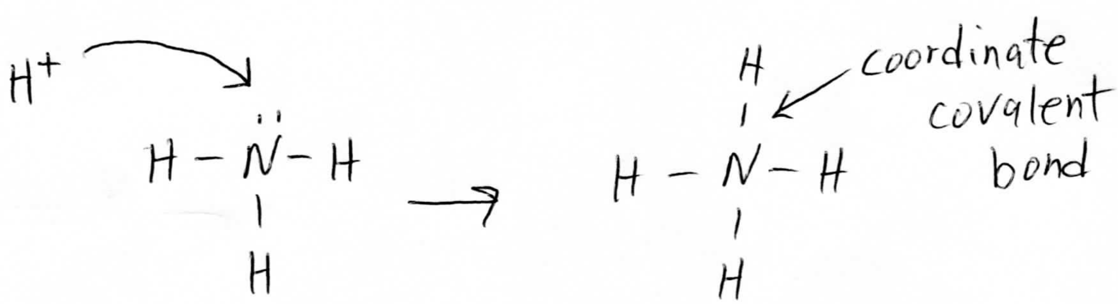
H: $4 \times 1 = 4$

Subtract 1 electron = -1

total number of electrons = $5 + 4 - 1 = 8$



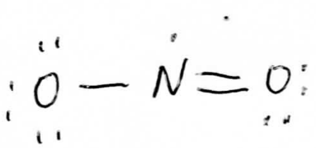
Ammonium is formed when an H^+ ion attaches itself to the unshared electrons that are on NH_3.



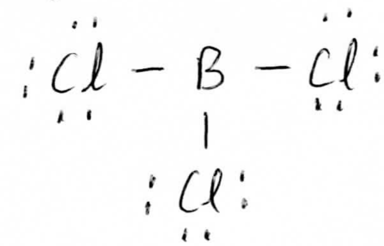
A bond is formed when two atoms share a pair of electrons. If one atom contributes both electrons to the bond, we have a *coordinate covalent bond*. In the above example, nitrogen contributes both electrons to the bond between itself and H^+.

There are some molecules whose atoms do not follow the octet rule. You just learn that they are the exceptions. Here are some molecules that don't follow the rules but still exist.

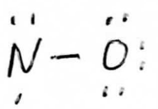
NO_2



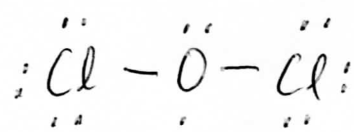
BCl_3



NO



ClO_2



NO_2 , NO, and ClO_2 each have an unpaired electron on the central atom. Not all of the atoms have an octet. Yet these molecules still exist. Darn rule breakers!

In some molecular compounds, the central atoms have more than 8 valence electrons. When an atom has more than 8 valence electrons, it has an expanded octet. For example, PCl_5 has 5 covalent bonds. Thus, phosphorous will have 10 valence electrons.

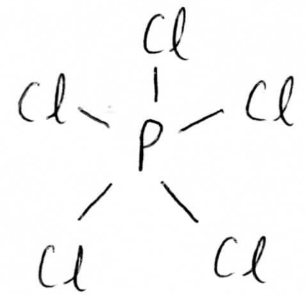
To draw molecules with expanded octets, you follow the same procedure used when drawing polyatomic ions. Add up the valence electrons. Distribute pairs of electrons between the central atom and the terminal atoms. Add electrons to the terminal atoms until each has an octet. Place any remaining electrons on the central atom.

Draw PCl_5.

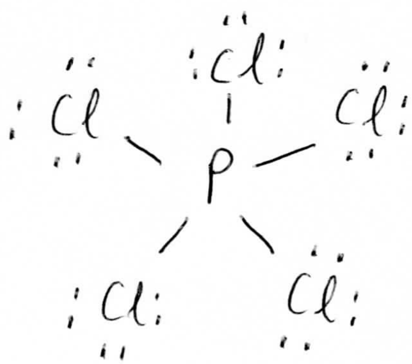
P: 1 x 5 = 5

Cl: 5 x 7 = 35

Total electrons = 40



Distributing electrons between the central atom and the terminal atoms uses 10 electrons.



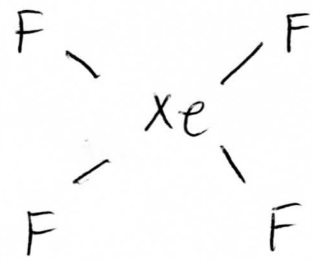
Putting electrons on the terminal atoms uses 30 electrons, and that uses up the remaining electrons.

Draw XeF_4

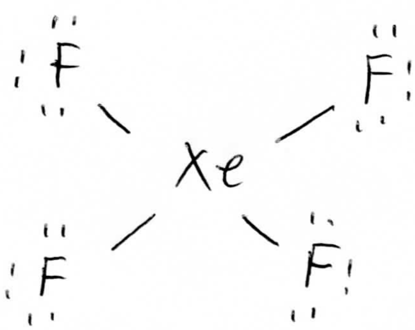
$Xe: 1 \times 8 = 8$

$F: 4 \times 7 = \underline{28}$

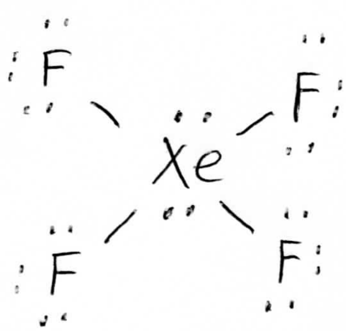
Total electrons $= 36$



Distributing electrons between the central atom and terminal atom uses 8 electrons.



Putting electrons on the terminal atoms uses 24 electrons. We have 4 electrons left over.



Putting the remaining 4 electrons on the central atom uses up all of the electrons. Notice that Xe has 12 electrons.