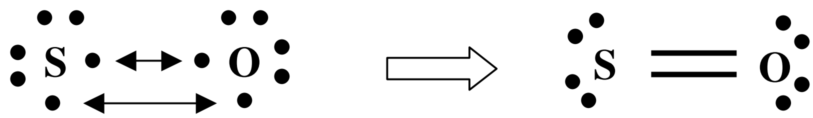
Unit 1, Lesson 08: Variations on Covalent Bonding by the Octet Rule

There are numerous covalent molecules that exist, but can not be drawn using the "rules" that we have discussed so far.

For example, looking at the electron dot diagrams for sulfur and oxygen, we would predict that the only possible compound that could form between these atoms is sulfur monoxide, SO.



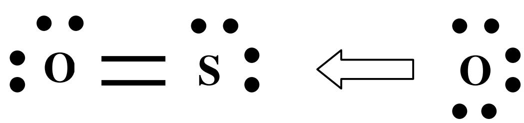
However, we know that SO_2 and SO_3 also exist. We must adapt our model of covalent bonding to account for these molecules.

There are three extensions of covalent bonding. The first two obey the octet rule, while the third does not.

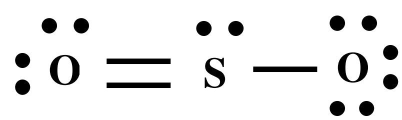
1. **<u>Co-ordinate Covalent Bonds</u>**: covalent bonds in which both of the bonding electrons are contributed by the same atom.

   If we draw sulfur monoxide with a double bond (as shown above), and if we draw oxygen with its valence electrons paired up, you can see that the free oxygen atom can share one of sulfur's lone pairs.

eg. SO_2

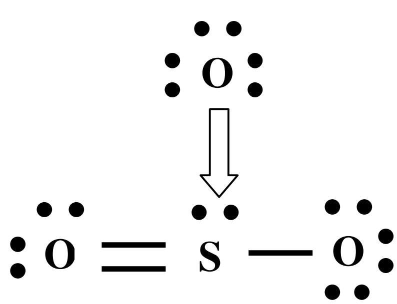


and we get:

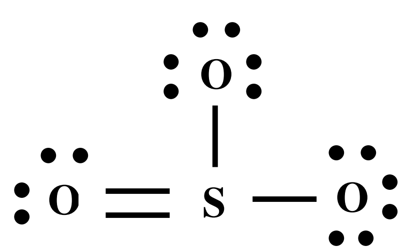


Sulfur does not gain or lose anything by this transaction, because it already had a stable octet electron arrangement, but the second oxygen atom now also has a completed stable octet, so it will be more stable. The energy of the total system will be lower, which is why this bond can form. Because the sulfur atom provided both of the electrons for the bond, it is a called a "**<u>co-ordinate covalent bond</u>**".

Similarly, sulfur trioxide can be formed if another oxygen forms a co-ordinate covalent bond with sulfur. Oxygen atoms generally do not bond to other oxygen atoms except in O_2, O_3 and H_2O_2.



and we get:



There is no real way of knowing whether bonds are "regular" or "co-ordinate" bonds. The end result is the same: a shared pair of valence electrons. So, how do we know how to draw these structures? Let's use the technique described in McGraw-Hill on pages 173-174 to see how the perbromate ion (BrO_4^{1-}) is put together, because we know that this covalent ion exists.

eg. BrO_4^{1-}

1. Determine which atom is the central atom:
- the atom with the lowest electronegativity (except hydrogen) is the central atom
- in this example, bromine has the lowest EN so it is the central atom

2. Calculate the total number of valence electrons that we *have*
- add up the number of valence electrons for all of the atoms in the molecule
- for negative ions, there are additional electrons available, so ***add*** the number of negative charges to the number of valence electrons
- for positive ions, there are fewer electrons available, so ***subtract*** the number of positive charges from the number of valence electrons
- in this example, there are:

4 x 6 valence electrons for oxygen = 24
1 x 7 valence electrons for bromine = 7
charge of 1- on the ion = 1

we ***have*** (24 + 7 + 1) = 32 valence electrons

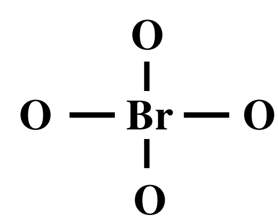
3. Calculate the number of valence electrons that we *need* to complete a stable octet for each atom
- there are 4 oxygen atoms; each needs 8 electrons, for a total of 32
- there is one bromine atom which needs 8 electrons, for a total of 8
- we ***need*** (32 + 8) = 40 valence e-

4. Calculate the number of electrons that are in bonds
- subtract the number of valence electrons that we ***have*** (step 2) from the number of valence electrons that we ***need*** (step 3)
- we ***need*** 40 valence electrons
- we ***have*** 32 valence electrons

(40 – 32) = 8 electrons must be shared in bonds

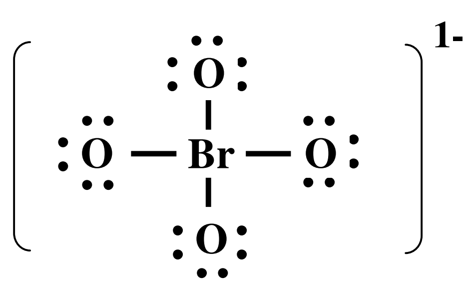
5. Calculate how many bonds must form (each bond is made up of two shared electrons)
- divide the number of shared electrons (step 4) by 2 to find the number of bonds that will form
- 8) 2 = 4 bonds must form

6. Draw a skeleton structure by distributing these bonds around the central atom to attach all atoms



7. Find the number of unshared electrons (lone pairs)
- take the number of valence electrons we ***have*** (step 2) and subtract the number of these electrons that are in bonds (step 4)
- we ***have*** 32 valence electrons but 8 of these are bonded, so there are 24 electrons to be added as lone pairs (=12 LP)

8. Complete the Lewis structure:
- add the electrons in lone pairs (step 7) around the atoms to complete stable octets for all atoms (except H)
- for ions, draw brackets around the finished structure and include the charge on the ion



eg. $CO_3{}^{2-}$

1. **The central atom is carbon**

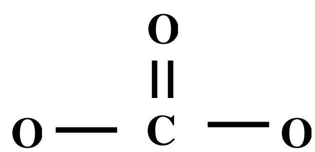
2. **We *have*:** 1 x 4 valence electrons for carbon = 4
3 x 6 valence electrons for oxygen = 18
charge of 2- on the ion = 2
we ***have*** 24 valence electrons

3. **We *need*:** 1 x 8 valence electrons for carbon = 8
3 x 8 valence electrons for oxygen = 24
we ***need*** 32 valence electrons

4. **The number of electrons in bonds:** we ***need*** 32 valence electrons
we ***have*** 24 valence electrons
(32 – 24) = 8 electrons must be shared in bonds

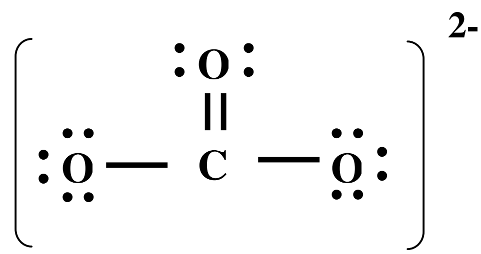
5. **The number of bonds is:** 8 electrons in bonds)2 electrons per bond = 4 bonds

6. **Skeleton structure:**
(four bonds)



7. **Draw in the lone pairs**
- we ***have*** 24 valence electrons but 8 of these are bonded
- there are (24 – 8) = 16 electrons to be added as lone pairs

8. **Complete the Lewis structure:**
- add the lone pairs to complete stable octets for all atoms (except H)
- for ions, draw brackets and include the charge on the ion

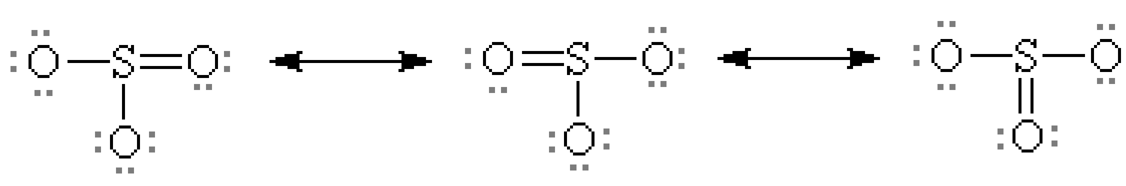


Now- in step 6 of the example above, how do we know where to put the double bond? It could go between the carbon and any of the three oxygen atoms. In fact, according to experimental evidence, it seems to go in between all of the oxygen atoms in a structure which is called a resonance structure, which is our next special case in covalent bonding.

2. <u>**Resonance Structures**</u>:

Double bonds are shorter than single bonds. When scientists measure the length of the bonds in sulfur trioxide (SO_3) they would expect to find one short double bond and two longer single bonds. However, it turns out that the bond length of all three bonds is exactly the same, somewhere in between the length of a single and a double bond. Somehow, the extra pair of electrons from the double bond gets shared between all three bonds in a resonance structure. That is, the bond resonates or moves rapidly between the three oxygen atoms. We show this by drawing all three possible forms of the molecule, and drawing double-headed arrows in between them.

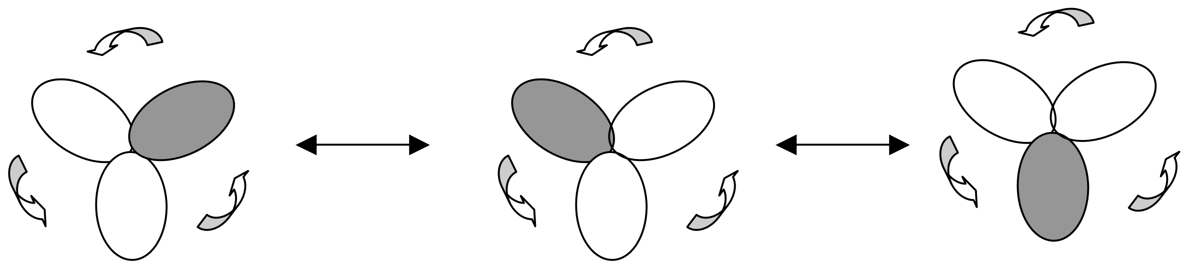
eg. for SO_3:



To be correct, it should be noted that the three resonance forms of SO_3 that we have drawn do not actually exist. SO_3 molecules do not change back and forth between these forms. Instead, all molecules of SO_3 are identical, with three bonds of equal length and strength, part-way between a double and single bond. The electrons in the double bond are distributed over the three bonding positions and "delocalized", which stabilizes the molecule.

A way to help visualize this is to think of the blades on a fan turning. The electrons in the double bond are spinning around between the oxygen atoms so quickly, that you can't really determine where the double bond is at any one time.

eg.



Resonance structures are a possibility any time that a central atom in a molecule has both double and single bonds between two or more of the same type of atom in that molecule.