Let's look at NITROGEN ...



We know that nitrogen exists in air as the diatomic molecule $N_{\rm 2}$

The nitrogen atoms share THREE pairs of electrons. This is called a TRIPLE BOND



OR

Nitrogen gas is fairly inert ... it's hard to break the triple bond in nitrogen gas apart!

A few notes on the triple bond:



- For atoms to share three pairs of electrons, they have to move closer to one another than they would if they were sharing one or two pairs of electrons. Triple bonds have the shortest BOND DISTANCE of all covalent bonds.

2

- It takes more energy to break a triple bond between two atoms than it would to break either a single or double bond between the same two atoms. The triple bond has the largest BOND ENERGY of all three kinds of covalent bonds. Atoms may share one, two, or three pairs of electrons with each other.

2 Atoms will usually share enough electrons so that each atom ends up with a share in EIGHT electrons - the "octet rule"

- HYDROGEN will only end up with two electrons!

- Some other atoms may end up with more or less than eight electrons. Exceptions to the octet rule are covered in Chapter 9.

NOW, how could we come up with dot structures for some more complicated (and therefore, more interesting) molecules?



²⁰⁹ DRAWING DOT STRUCTURES FOR SIMPLE MOLECULES

) Count valence electrons

Pick central atom and draw skeletal structure

- central atom is usually the one that needs to gain the most electrons!

- skeletal structure has all atoms connected to center with single bonds

Distribute remaining valence electrons around structure, outer atoms first. Follow octet rule until you run out of electrons.

Check octet rule - each atom should have a share in 8 electrons (H gets 2). if not, make double or triple bonds.

 $C: 1 \times 4$ () (_\. ₂_ 0:146 (1.2x)24e Choose CARBON as the central atom, since it needs to gain more electrons than either O or Cl. This meeans it will form more bonds! Distribute remaining electrons ... stop when we run out. ... but the carbon atom has a share in only SIX electrons... To get more electrons for carbon, we'll need to make a DOUBLE BOND. We will need electrons from We'll pick

OXYGEN, since it needs to gain

more elecrons than chlorine.

This structure has all atoms with a share in eight electrons!

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-N-C|

We pick NITROGEN as the central atom since it needs more electrons than O or Cl.

D-N-C

We ran out of space on outer atoms, so the last two electrons go to the central nitrogen atom

... but even with the two electrons, nitrogen only has a share in SIX electrons. We'll need a double bond. Just like the last example, we'll use OXYGEN for the double bond...

$$O = N - C$$

Now each atom has a share in eight electrons...

211

Pick central atom and draw skeletal structure

central atom is
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most electrons!
skeletal structure

has all atoms connected to center with single bonds

Distribute remaining valence electrons around structure, outer atoms first. Follow octet rule until you run out of electrons.

Check octet rule - each atom should have a share in 8 electrons (H gets 2). if not, make double or triple bonds.

(:) ኑዓ 16e Carbon is the central atom. ... but the carbon atom only has a share in four electrons. **: - (-**:0=(-O: ... now it has six ... adding a second double bond gives carbon a share in eight electrons. The two oxygen atoms are in the same : 0 = 0environment, and SHOULD be bonded the same way ... so this structure looks wrong. Also, the structure in green says something about the carbon dioxide molecule ... that it has TWO DIFFERENT kinds of bond (and two different bond lengths) between oxygen and carbon. This is testable! Experimental bond length data supports the structure with double bonds - there's only one C=O bond distance in carbon dioxide.

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3 Distribute remaining valence electrons around structure, outer atoms first. Follow octet rule until you run out of electrons.

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Check octet rule - each atom should have a share in 8 electrons (H gets 2). if not, make double or triple bonds.

HNO2 "nitrous acid" In oxyacids, the acidic hydrogen atoms are attached to OXYGEN atoms in the structure! $H: | \times |$ N: YS 0:2×6 18e OXYACID requires H attached to O... ... but NITROGEN has a share in only six electrons!

Unlike the previous example, these two oxygen atoms are in DIFFERENT environments, so we don't expect them to bond in exactly the same way. 1) Count valence electrons

Pick central atom and draw skeletal structure

central atom is usually the one that needs to gain the most electrons!
skeletal structure has all atoms connected

to center with single bonds

Distribute remaining valence electrons around structure, outer atoms first. Follow octet rule until you run out of electrons.

Check octet rule - each atom should have a share in 8 electrons (H gets 2). if not, make double or triple bonds.

(K2 OH

H

CHR

H - (

Η

The remaining four electrons go on oxygen, since there's no other place for them.

[3]

20

 $C: 4 \times 2 = 8$

A DOT STRUCTURE FOR A MOLECULE WITH DELOCALIZED BONDS

0:3x6218 See text, 9,7

) Count valence electrons

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Check octet rule - each atom should have a share in 8 electrons (H gets 2). if not, make double or triple bonds.

Jz (OZONE)

- P 356 357
 - Central oxygen has only six electrons
- O = O O; All atoms have a share in eight electrons!

The structure we drew implies that one of the outer oxygen atoms is closer to the central oxygen atom than the other one.

Experimentally, though, we find the two oxygen atoms to be the SAME distance from the center.

In the ozone molecule, electrons are actually being shared between ALL THREE oxygen atoms at the same time. This is called a DELOCALIZED BOND.



The structures in the green box are called RESONANCE STRUCTURES. The "real" structure of ozone is an "average" of the two resonance structures. The "double bond" electrons in these structures are actually shared between all three oxygen atoms A DOT STRUCTURE FOR A POLYATOMIC ION

Count valence electrons

Pick central atom and draw skeletal structure

- central atom is usually the one that needs to gain the most electrons!

- skeletal structure has all atoms connected to center with single bonds

3 Distribute remaining valence electrons around structure, outer atoms first. Follow octet rule until you run out of electrons.

Check octet rule - each atom should have a share in 8 electrons (H gets 2). if not, make double or triple bonds. NHL N: 1x5 H:4x1 e. 8e +4

An ODD number of electrons? All the structures we've seen so far have even numbers.

But ammonium is charged. We need to subtract an electron to give the molecule a +1 charge. (To make an anion, we'd add electrons)

> Draw brackets around the structure of the ion and indicate charge in the upper right-hand corner ... similar to how we indicate charge for other ions...

Ma, CI, etc.

- Some atoms do not always obey the octet rule. A few, like BORON, will bond in such a way that they end up with less than eight electrons.



... but many more bond in such a way that they end up with a share in MORE THAN EIGHT electrons!

- Any atom in period three or greater can do this. SULFUR and PHOSPHORUS compounds commonly do this!

... these atoms have unfilled "d" orbitals that may participate in bonding!

- All noble gas compounds (example: XENON compounds with oxygen and fluorine) exhibit this behavior!

EXAMPLES:





- The central SULFUR atom has a share in TWELVE total electrons, not eight!

- The SHAPE of the sulfur hexafluoride molecule in three dimensions agrees with the picture of six fluorine atoms each sharing a pair of electrons with a sulfur center.



This molecule does NOT obey the octet rule. Phosphorus ends up with ten electrons instead of eight.

²¹⁸ FORMAL CHARGE

- You can often draw more than one structure for a molecule that appears correct. How can you determine which one is more likely?

- USE FORMAL CHARGE!

- Formal charge is a hypothetical charge on each atom in a structure. It assumes:

All bonding electrons are shared EQUALLY between atoms

(1) Lone pairs are NOT shared.

FORMAL = ORIGINAL # OF CHARGE = VALENCE ELECTRONS	NUMBER OF BONDS	- NUMBER OF UNSHARED ELECTRONS
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* The sum of the formal charges of all atoms in a structure should equal to the charge of the molecule (0 for neutral molecules)

The "better" Lewis structure will have:

- Lower magnitudes of formal charge (00 is better than +2 -2)

- Negative formal charges on ELECTRONEGATIVE atoms, or positive formal charges on atoms that are less electronegative.

EXAMPLE: LOLL



... calculate formal charges to tell which structure is more likely!

BASED ON FORMAL CHARGE, the structure on the left is preferred. It has lower formal charges than the one on the right.

... we can determine which of these structures is more likely by calculating formal charges!

$$H: | -1 - 0 = 0$$

$$C: 4 - 3 - 2 = -1$$

$$N: 5 - 4 - 0 = +1$$

$$H: |-| - 0 = 0$$

$$C: 4 - 4 - 0 = 0$$

$$N: S - 3 - 2 = 0$$

Which structure is more likely?

- The HCN structure is more likely, based on its lower formal charges.