Models

- Models are attempts to explain how nature operates on the microscopic level based on experiences in the macroscopic world.

Fundamental Properties of Models

- A model does not equal reality.
- Models are oversimplifications, and are therefore often wrong.
- Models become more complicated as they age.
- We must understand the underlying assumptions in a model so that we don't misuse it.
- When a model is wrong, we often learn much more than when it is right. If a model makes the wrong prediction – it usually means we do not understand some fundamental characteristic of nature. We often learn by making mistakes!

Localized Electron Model

- A molecule is composed of atoms that are bound together by sharing pairs of electrons using the atomic orbitals of the bound atoms. One electron pair represents one bond.
- G.N. Lewis and Linus Pauling developed these concepts about 80 years ago.

Localized Electron Model

- 1. Description of valence electron arrangement (Lewis structure).
- 2. Prediction of geometry (Valence Shell Electron Pair Repulsion model).
- 3. Description of atomic orbital types used to share electrons or hold lone pairs – (Hybridization of atomic orbitals to form localized molecular orbitals).

Lewis Structure

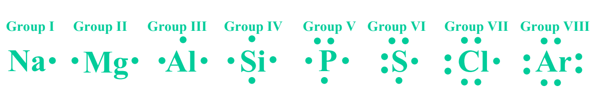
- Shows how valence electrons are arranged among atoms in a molecule.
- Reflects central idea that stability of a compound relates to noble gas electron configuration – $ns^2 np^6$ – or “octet rule”.

Comments About the Octet Rule

- 2nd row elements C, N, O, F observe the octet rule.
- 2nd row elements B and Be often have fewer than 8 electrons around themselves - they are very reactive.
- 3rd row and heavier elements CAN exceed the octet rule using empty valence *d* orbitals.
- When writing Lewis structures, satisfy octets first, then place electrons around elements having available *d* orbitals (n = 3 or higher) .

Lewis Electron-Dot Symbols

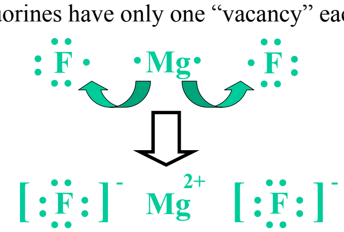
- A **Lewis electron-dot symbol** is a symbol in which the electrons in the valence shell of an atom or ion are represented by dots placed around the letter symbol of the element.



  - Note that the **group number indicates the number of valence electrons (representative elements only)**.

Lewis Electron-Dot Formulas

- The magnesium has two electrons to give, whereas the fluorines have only one “vacancy” each.



- Consequently, magnesium can accommodate two fluorine atoms.

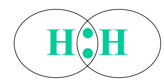
Lewis Structures

- You can represent the formation of the covalent bond in H_2 as follows:

  - This uses the Lewis dot symbols for the hydrogen atom and represents the covalent bond by a pair of dots.

Lewis Structures

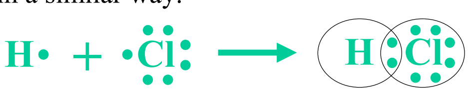
- The shared electrons in H_2 spend part of the time in the region around each atom.



  - In this sense, each atom in H_2 has a helium configuration.

Lewis Structures

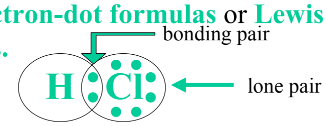
- The formation of a bond between H and Cl to give an HCl molecule can be represented in a similar way.



  - Thus, hydrogen has two valence electrons about it (as in He) and Cl has eight valence electrons about it (as in Ar).

Lewis Structures

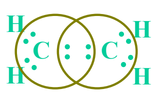
- Formulas such as these are referred to as **Lewis electron-dot formulas** or **Lewis structures.**



  - An electron pair is either a **bonding pair** (shared between two atoms) or a **lone pair** (an electron pair that is not shared).

Multiple Bonds

- In the molecules described so far, each of the bonds has been a **single bond**, that is, a covalent bond in which a single pair of electrons is shared.
  - It is possible to share more than one pair. A **double bond** involves the sharing of two pairs between atoms.



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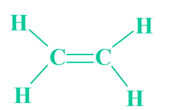
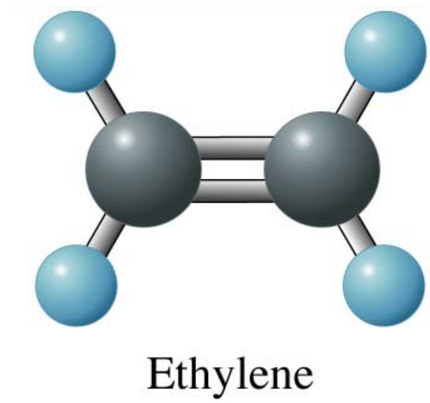
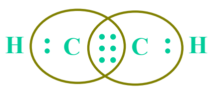




Multiple Bonds

- **Triple bonds** are covalent bonds in which three pairs of electrons are shared between atoms.



or

A model of acetylene.

Writing Lewis Dot Formulas

- The following rules allow you to write electron-dot formulas even when the central atom does not follow the octet rule.
  - To illustrate, we will draw the structure of PCl_3, phosphorus trichloride.

PCl_3

Writing Lewis Dot Formulas

- **Step 1**: Total all valence electrons in the molecular formula. That is, total the group numbers of all the atoms in the formula.

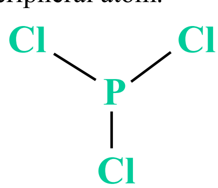
PCl_3 **26 e⁻ total**

5 e⁻ **(7 e⁻) x 3**

  - For a polyatomic anion, add the number of negative charges to this total.
  - For a polyatomic cation, subtract the number of positive charges from this total.

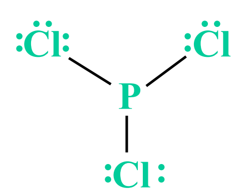
Writing Lewis Dot Formulas

- **Step 2**: Arrange the atoms radially, with the least electronegative atom in the center. Place one pair of electrons between the central atom and each peripheral atom.



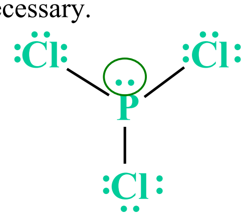
Writing Lewis Dot Formulas

- **Step 3**: Distribute the remaining electrons to the peripheral atoms to satisfy the octet rule.



Writing Lewis Dot Formulas

- **Step 4**: Distribute any remaining electrons to the central atom. If there are fewer than eight electrons on the central atom, a multiple bond may be necessary.



Writing Lewis Dot Formulas

- Try drawing Lewis dot formulas for the following covalent compound.

SCl_2

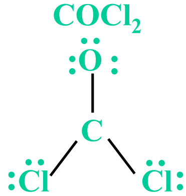
~~20 e$^-$ total~~
~~16 e$^-$ left~~
~~4 e$^-$ left~~

Writing Lewis Dot Formulas

- Try drawing Lewis dot formulas for the following covalent compound.

$COCl_2$

~~24 e$^-$ total~~
~~18 e$^-$ left~~
0 e$^-$ left



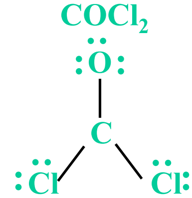
Writing Lewis Dot Formulas

- Note that the carbon has only 6 electrons.

One of the oxygens must share a lone pair.

$COCl_2$

~~24 e$^-$ total~~
~~18 e$^-$ left~~
0 e$^-$ left

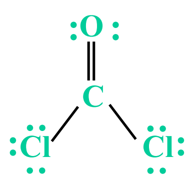


Writing Lewis Dot Formulas

- Note that the carbon has only 6 electrons.

  One of the oxygens must share a lone pair.

$COCl_2$



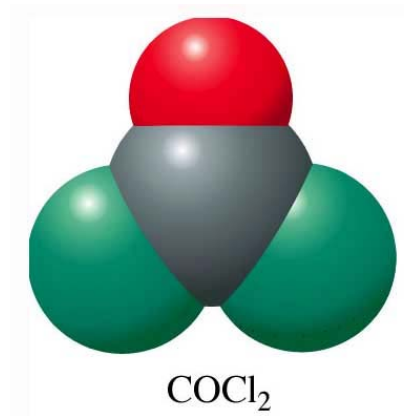
~~24 e⁻ total~~

~~18 e⁻ left~~

0 e⁻ left

Note that the octet rule is now obeyed.

A model of $COCl_2$.



Polyatomic Ions

For ions: anions – add # of extra e

cations – subtract # of missing e

For NH_4^{+}: 5e (from N) + 4e (H) – 1 e = 8 e

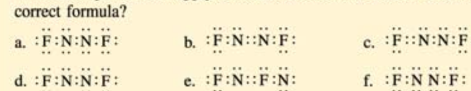
$$\left[\begin{array}{c} H \\ \cdot\cdot \\ H:N:H \\ \cdot\cdot \\ H \end{array}\right]^{+} = NH_4^{+}$$

$$\begin{array}{c} H \\ H:\ddot{N}:H + H^{+} \end{array}$$

Ammonium ion contains a coordinate covalent bond

CONCEPT CHECK 9.2

Each of the following may seem, at first glance, to be plausible electron-dot formulas for the molecule N_2F_2. Most, however, are incorrect for some reason. What concepts or rules apply to each, either to cast it aside or to keep it as the correct formula?



Valence electrons: (2 x 5) + (2 x 7) = 24 valence electrons or 12 pairs

CONCEPT CHECK 9.2

Each of the following may seem, at first glance, to be plausible electron-dot formulas for the molecule N_2F_2. Most, however, are incorrect for some reason. What concepts or rules apply to each, either to cast it aside or to keep it as the correct formula?

a. :F:N:N:F: b. :F:N::N:F: c. :F::N:N:F:

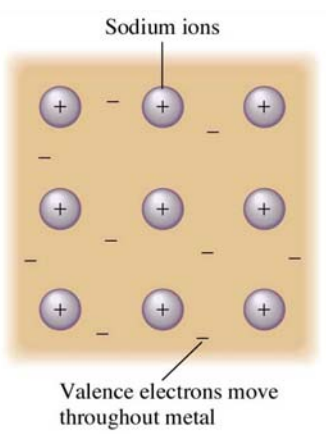
d. :F:N:N:F: e. :F:N::F:N: f. :F:N N:F:

a 26 valence e b correct c left F has 10 e, right N has 6
d left N has 6 e e F cannot form double bonds
f No bond between N's

D **Delocalized Bonding: Resonance** - **delocalized bonding** is a type of bonding in which the bonding pair of electrons is spread over a number of atoms rather than localized between two atoms.

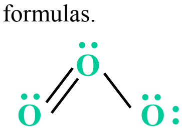
According to the **resonance description**, you describe the electron structure of a molecule having delocalized bonding by writing all possible electron-dot formulas. These structures are called the **resonance formulas** of the molecule. Metals are extreme examples of delocalized bonding

Figure 9.16: Delocalized bonding in sodium metal.

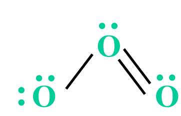


Delocalized Bonding: Resonance

- According to the **resonance description**, you describe the electron structure of molecules with delocalized bonding by drawing all of the possible electron-dot formulas.



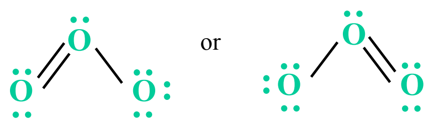
and



- These are called the **resonance formulas** of the molecule.

Delocalized Bonding: Resonance

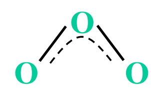
- The structure of ozone, O_3, can be represented by two different Lewis electron-dot formulas.



- Experiments show, however, that both bonds are identical. The structure is the average of the two Lewis structures.

Delocalized Bonding: Resonance

- According to theory, one pair of bonding electrons is spread over the region of all three atoms.



- This is called **delocalized bonding**, in which a bonding pair of electrons is spread over a number of atoms.

F Formal Charge and Lewis Formulas - the formal charge of an atom in a Lewis structure is the hypothetical charge you obtain by assuming that bonding electrons are equally shared between bonded atoms and that the electrons of each lone pair belong completely to one atom. The rules for formal charge to assign the valence electrons to individual atoms:

Formal Charge and Lewis Formulas

1. Half of the electrons of a bond are assigned to each atom in the bond (counting each dash as two electrons)

2. Both electrons of a lone pair are assigned to the atom to which the lone pair belongs

Rule A: Whenever you can write several Lewis structures for a molecule, choose the structure having the formal charges are closest to zero.

Rule B: When two proposed Lewis formulas for a molecule have the same magnitudes of formal charges, choose the one having the negative formal charge(s) on the more electronegative atom(s).

Formal Charge and Lewis Structures

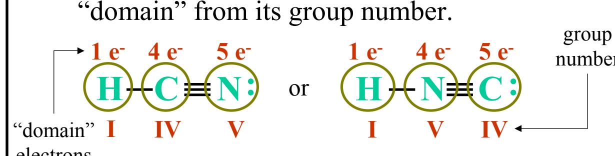
- In certain instances, more than one feasible Lewis structure can be illustrated for a molecule. For example,

H—C≡N: or   H—N≡C:

- The concept of "formal charge" can help discern which structure is the most likely.

Formal Charge and Lewis Structures

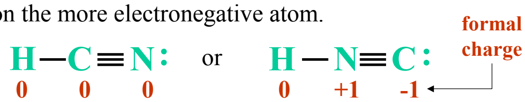
- The formal charge of an atom is determined by subtracting the number of electrons in its "domain" from its group number.



- The number of electrons in an atom's "domain" is determined by counting one electron for each bond and two electrons for each lone pair.

Formal Charge and Lewis Structures

- The most likely structure is the one with the least number of atoms carrying formal charge. If they have the same number of atoms carrying formal charge, choose the structure with the negative formal charge on the more electronegative atom.



- In this case, the structure on the left is most likely correct.

Formal Charge

What is the correct structure for CO_2?

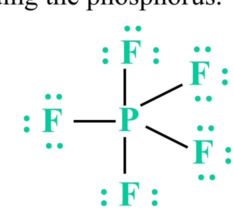
- Not as good Better

Exceptions to the Octet Rule

- Although many molecules obey the octet rule, there are exceptions where the central atom has more than eight electrons.
  - Generally, if a nonmetal is ***in the third period or greater*** it can accommodate as many as twelve electrons, if it is the central atom.
  - These elements have unfilled “d” subshells that can be used for bonding.

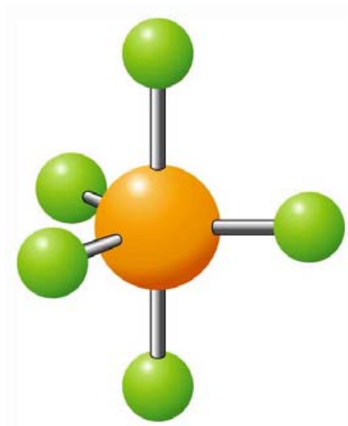
Exceptions to the Octet Rule

- For example, the bonding in phosphorus pentafluoride, PF_5, shows ten electrons surrounding the phosphorus.



5e (P) + 5 x 7e (F) = 40 e

Figure 9.17: Phosphorus pentafluoride, PF_5.



Exceptions to the Octet Rule

- In xenon tetrafluoride, XeF_4, the xenon atom must accommodate two extra lone pairs.

8 e (Xe) + 4 x 7e (F) = 36 e.