Chemical Bonding 2

Covalent Bonding

A vast number of compounds (including those of carbon) form covalent bond

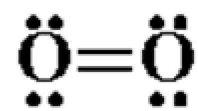
A covalent bond consists of a pair of electrons shared between two atoms

It is formed between non metals

Covalent Bonding

Octet rule: In covalent bonding, atoms go as far as possible towards completing their octets by sharing electron pairs

Covalent Bonding

- *Multiple bonds*
- It is possible for more than one pairs of electrons to be shared between two atoms
  - Sharing of 2 electrons forms a single covalent bond. Example: $\mathrm{H{-}H}$
  - 4 electrons: a double bond; 
  - 6 electrons: a triple bond; $:\mathrm{N}\equiv\mathrm{N}:$

The bond distances decreases from single bond to double bonds to triple bonds

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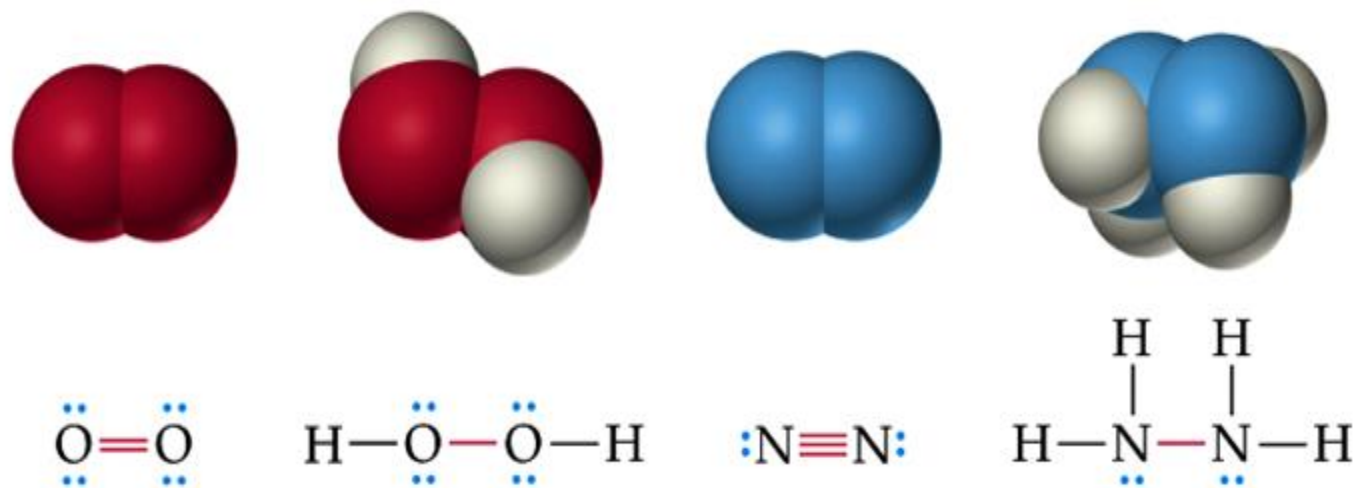
The bond strength however increase from single to double to triple

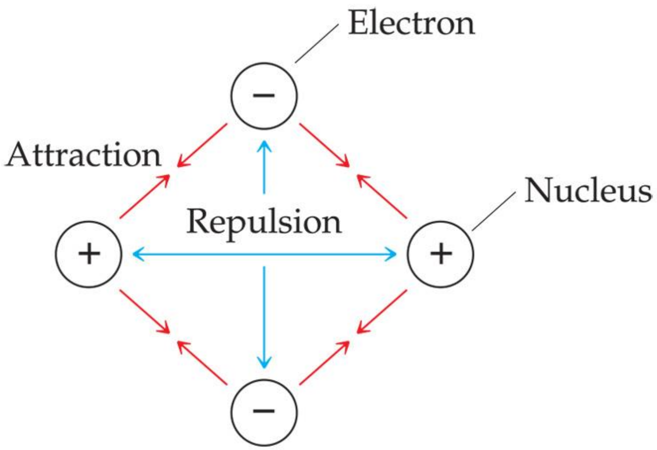


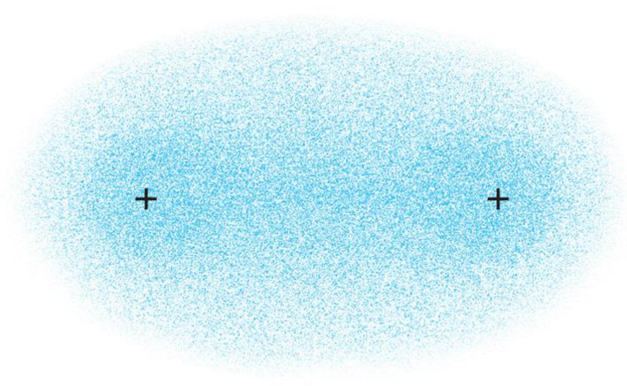
Bond length:	121 pm	148 pm	110 pm	145 pm
Bond strength:	498 kJ/mol	213 kJ/mol	945 kJ/mol	275 kJ/mol

Covalent Bonding

- The attraction between the electrons is electrostatic in nature
  - The atoms have a lower potential energy when bound

Covalent Bonding

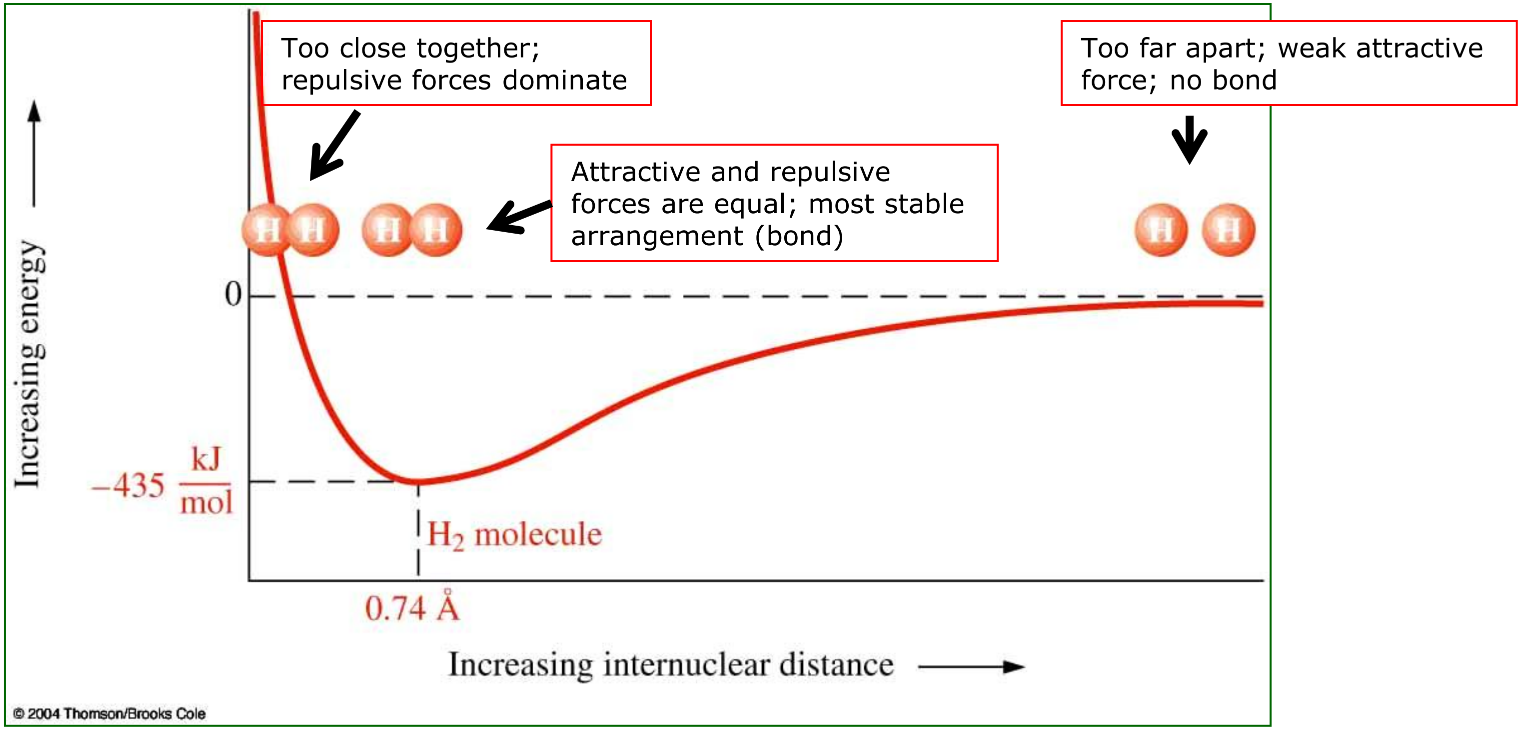




- The electrostatic interactions in these bonds include:
  - Attractions between electrons and nuclei
  - Repulsions between electrons
  - Repulsions between nuclei

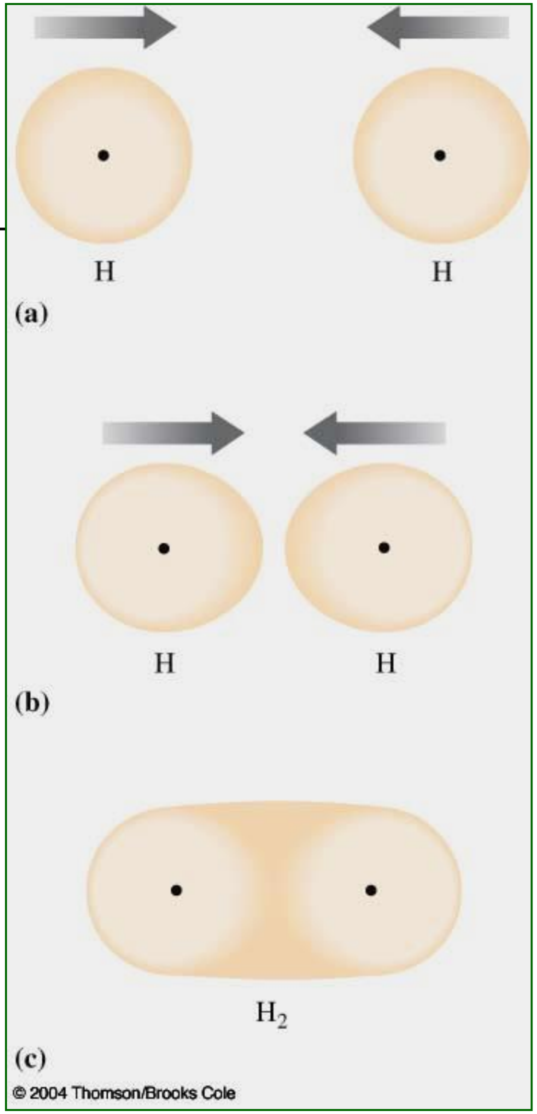
Formation of Covalent Bonds

- This figure shows the potential energy of an H_2 molecule as a function of the distance between the two H atoms.

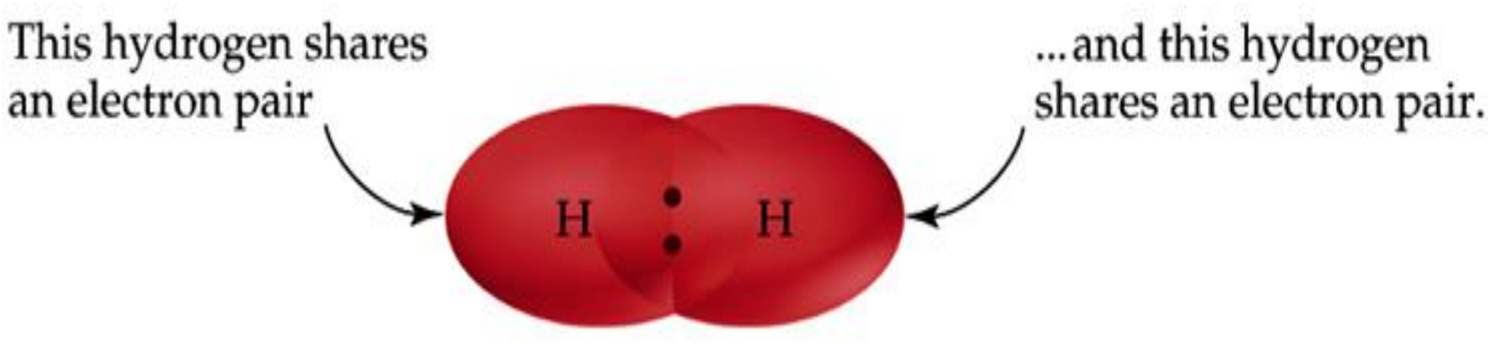


Formation of Covalent Bonds

- Representation of the formation of an H_2 molecule from H atoms.



Bonding in H_2: Covalent Bond



A line between 2 atoms represent a shared electron pair or a covalent bond

$$H—H$$

Formation of Covalent Bonds

- We can use Lewis dot formulas to show covalent bond formation.

1. H molecule formation representation.

$$H\cdot \; + \; H\cdot \longrightarrow H:H \quad \text{or } H_2$$

2. HCl molecule formation

$$H\cdot \; + \; \cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}: \longrightarrow H:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}: \quad \text{or} \quad HCl$$

Lewis Formulas for Molecules and Polyatomic Ions

- Lewis dot formulas of homonuclear diatomic molecules.
  - Two atoms of the same element.

1. Hydrogen molecule, H_2. $H:H$ or $H\text{-}H$
2. Flourine, F_2 $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}:$ or $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}:$
3. Nitrogen, N_2 $:N:::N:$ or $:N\equiv N:$

Lewis Formulas for Molecules and Polyatomic Ions

- Heteronuclear diatomic molecules.
  - Two atoms of different elements.
    - Hydrogen halides are good examples.

1. hydrogen fluoride, HF

$$\mathrm{H} : \underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{F}}} : \quad \text{or} \quad \mathrm{H}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{F}}} :$$

2. hydrogen chloride, HCl

$$\mathrm{H} : \underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}} : \quad \text{or} \quad \mathrm{H}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}} :$$

3. hydrogen bromide, HBr

$$\mathrm{H} : \underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Br}}} : \quad \text{or} \quad \mathrm{H}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Br}}} :$$

Lewis Formulas for Molecules and Polyatomic Ions

- Slightly more complicated heteronuclear molecules.
- Water, H_2O

$$
\begin{array}{ccccc}
 & & \cdot\cdot & & \\
H & : & O & : & \\
 & & \cdot\cdot & & \\
 & & H & &
\end{array}
$$

Lewis Formulas for Molecules and Polyatomic Ions

- Lewis formulas can also be drawn for molecular ions.
- One example is the ammonium ion , NH_4^+.

$$\begin{array}{ccccc} & & H & & + \\ & & \ddot{} & & \\ H & : & N & : & H \\ & & \ddot{} & & \\ & & H & & \end{array}$$

•Notice that the atoms other than H in these molecules have eight electrons around them.

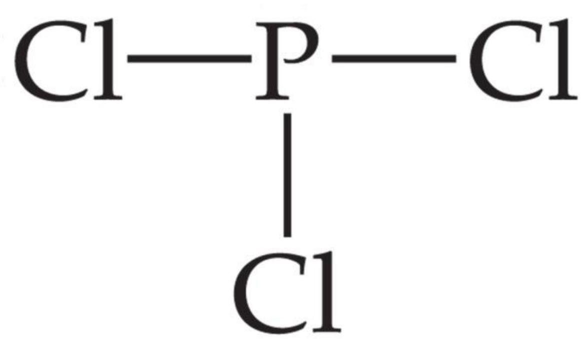
Writing Lewis Formulas

PCl_3

$5 + 3(7) = 26$

1. Find the sum of valence electrons of all atoms in the polyatomic ion or molecule.
    - If it is an anion, add one electron for each negative charge.
    - If it is a cation, subtract one electron for each positive charge.

Writing Lewis Formulas



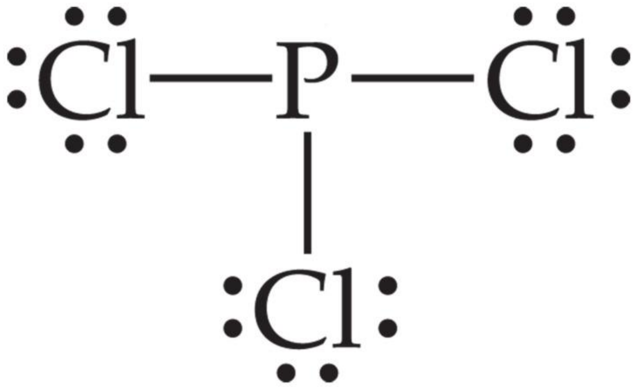
2. The central atom is the *least* electronegative element that isn't hydrogen.

   Connect the outer atoms to it by single bonds.

Keep track of the electrons:

26 - 6 = 20

Writing Lewis Formulas

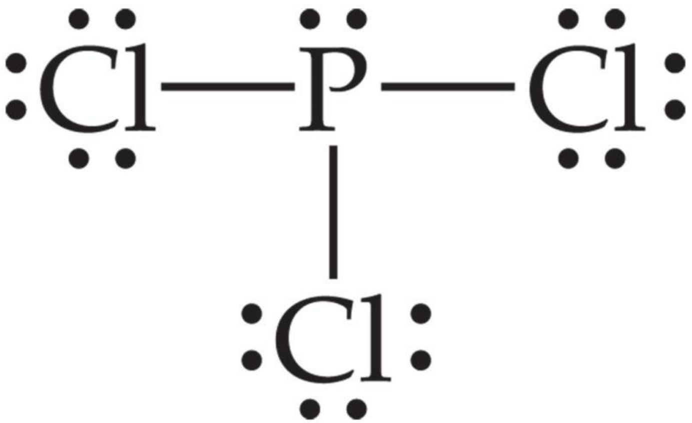


3. Fill the octets of the outer atoms.

Keep track of the electrons:

26 - 6 = 20; 20 - 18 = 2

Writing Lewis Formulas



4. Fill the octet of the central atom.

Keep track of the electrons:

26 - 6 = 20; 20 - 18 = 2; 2 - 2 = 0

Writing Lewis Formulas:

5. If the octet rule is not satisfied for the central atom and lone-pair electrons are nearby, use those electrons to make double or triple bonds to the central atom.

6. Check each atom to see if it has a formal charge. (Singly bonded oxygen will require a negative charge, for example.)

Writing Lewis Formulas: The Octet rule

- Least electronegative element is usually the central element except H- CS_2
- Carbon bonds to 2,3,or 4 (never more than 4!), Nitrogen bonds to 1 (rarely) 2,3 (most commonly) or 4. Oxygen bonds to one, two (most commonly) or three atoms.
- In ternary oxoacid, H atom usually bonds to an O atom, not to the central atom, HNO_2

$$\boxed{S = N - A}$$

S- total no.of electron shared

N- total no. of valence shell electrons needed

A- no of electron available

CO_2 ,H_2O, PF_3, N_2, NO_3^-

EXERCISE

- Draw the Lewis structure for the following molecules/ions:
- 1) HNO_3
- 2) SF_4
- 3) $POCl_3$
- 4) SO_3^{2-}

Writing Lewis Formulas: Formal Charges

- Possible to draw more than one Lewis structure with the octet rules obeyed by all atoms
- Use formal charges to determine the most reasonable structure
- Formal charge is the charge on an atom that it would have if all the atoms have the same electronegativity

Formal Charges

Charges assigned to an atom in a molecule

To calculate formal charge:

Formal charges: (group no.) - (no.of bonds) - (number of unshared electrons)

Practice: Determine the formal charge on C and N.

$$\left[:C\equiv N:\right]^{-}$$

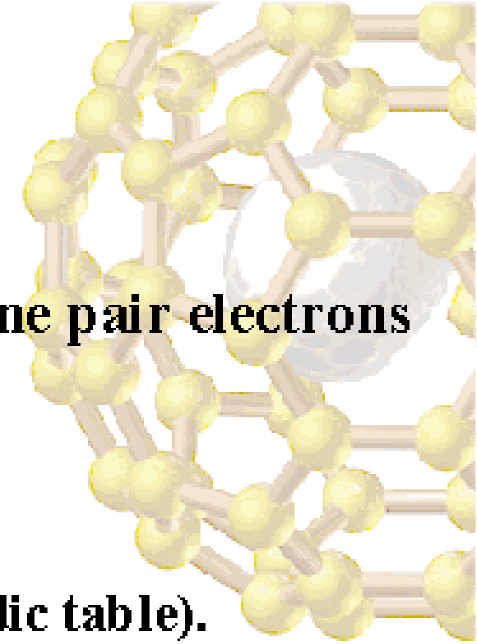
C= 4 – 3 – 2 = -1   N= 5 – 3 – 2 = 0

NOCl, NH_4^+

Formal Charges

- Sum of formal charges on all atoms in neutral molecules is 0
- Sum of formal charges on all atoms in an ion is the charge of the ion

Drawing Lewis Structures



Formal Charge

Formal charge is:

valence electrons - number of bonds - lone pair electrons

Consider: $\left[:C\equiv N:\right]^{-}$

For C:

There are 4 valence electrons (from periodic table).

In the Lewis structure there are 2 nonbonding electrons and 3 from the triple bond. There are 5 electrons from the Lewis structure.

Formal charge: 4 - 5 = -1.

Drawing Lewis Structures

Formal Charge

Consider:

$$\left[:C\equiv N:\right]^-$$

For N:

There are 5 valence electrons.

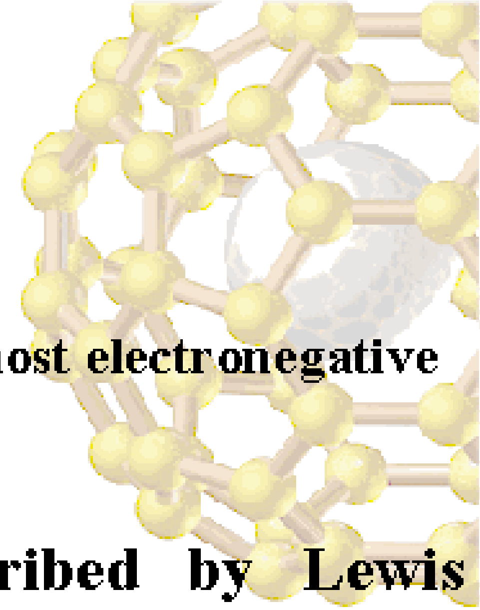
In the Lewis structure there are 2 nonbonding electrons and 3 from the triple bond. There are 5 electrons from the Lewis structure.

Formal charge = 5 - 5 = 0.

We write:

$$\left[:\overset{\ominus}{C}\equiv N:\right]^-$$

Drawing Lewis Structures



Formal Charge

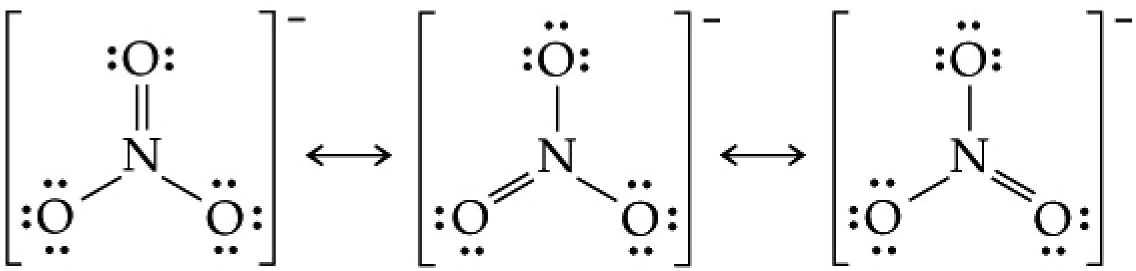
The most stable structure has:

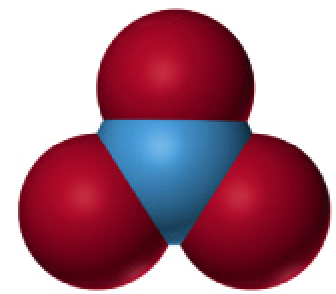
- **the smallest formal charge on each atom,**
- **the most negative formal charge on the most electronegative atoms.**

Resonance Structures

Some molecules are not well described by Lewis Structures.

Typically, structures with multiple bonds can have similar structures with the multiple bonds between different pairs of atoms.



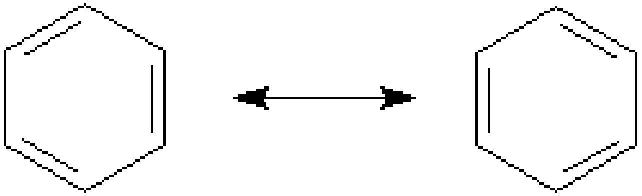


Drawing Lewis Structures

Resonance in Benzene

Benzene consists of 6 carbon atoms in a hexagon. Each C atom is attached to two other C atoms and one hydrogen atom.

There are alternating double and single bonds between the C atoms.



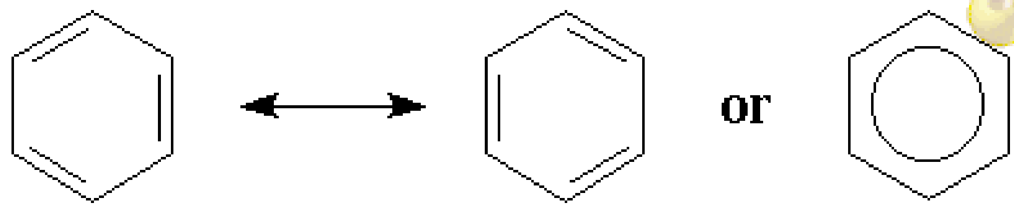
Experimentally, the C-C bonds in benzene are all the same length.

Experimentally, benzene is planar.

Drawing Lewis Structures

Resonance in Benzene

We write resonance structures for benzene in which there are single bonds between each pair of C atoms and the 6 additional electrons are delocalized over the entire ring:



Benzene belongs to a category of organic molecules called aromatic compounds (due to their odor).

Writing Lewis Formulas:
Limitations of the Octet Rule

- There are some molecules that violate the octet rule.

1. The covalent compounds of Be.
2. The covalent compounds of the IIIA Group.
3. Species which contain an odd number of electrons.
4. Species in which the central element must have a share of more than 8 valence electrons to accommodate all of the substituents.
5. Compounds of the d- and f-transition metals.

Writing Lewis Formulas:
Limitations of the Octet Rule

- In those cases where the octet rule does not apply, the substituents attached to the central atom nearly always attain noble gas configurations.
-
- The central atom does not have a noble gas configuration but may have fewer than 8 (exceptions 1, 2, & 3) or more than 8 (exceptions 4 & 5).

Exceptions to the octet rule

- Octet rule
  - 8 electrons fill a shell to give noble gas s^2p^6 configuration
  - predicts the valence of elements and structures of compounds
  - B, C, N, O, F follow rule rigorously
- Exceptions
  - Radicals and biradicals
  - Expanded octets

Exceptions to Octet Rule

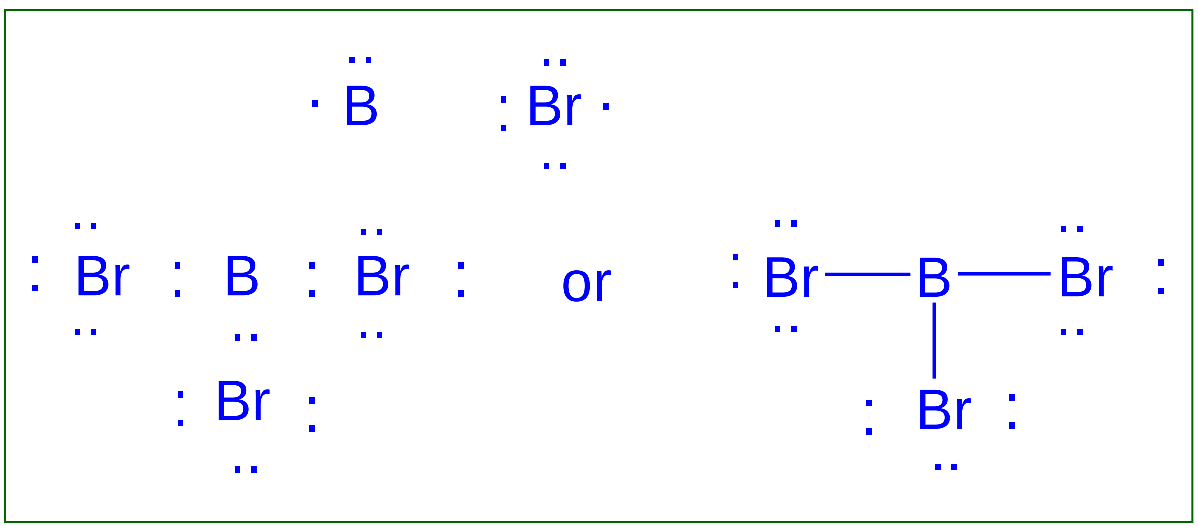
- Radicals
  - odd number of valence electrons (VE)
  - one unpaired electron
  - very reactive
  - CH_3 .(7 VE), · OH (7 VE), NO (11 VE)
  - cause formation and decomposition of ozone in upper atmosphere, rancidity of foods, degradation of plastics in sunlight, human aging
  - anti-oxidants delay action of radicals - vitamin C and E
- Biradicals
  - odd number of valence electrons
  - two unpaired electrons on different atoms of molecule
  - · $CH_2CH_2CH_2CH_2CH_2$ ·

Exceptions to Octet Rule

- Expanded octets
  - more than 8 valence electrons
  - only non-metal atoms in 3rd period - P, S, Cl
    - empty d orbitals in valence shell allow expanded octet
    - size of central atom must be large for accommodation of expanded octet - P more suitable than N
  - exhibit variable covalence
    - PCl_3 (satisfies the octet rule) and PCl_5 (has an expanded octet)
    - SF_4 (satisfies the octet rule) and SF_6 (has an expanded octet)

Writing Lewis Formulas: Limitations of the Octet Rule

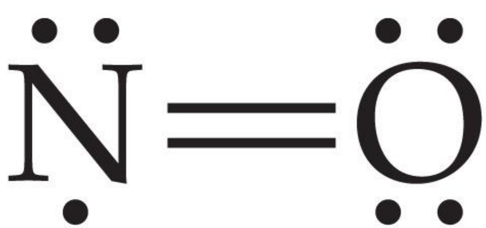
- Write dot and dash formulas for BBr_3.
  - This is an example of exception #2.



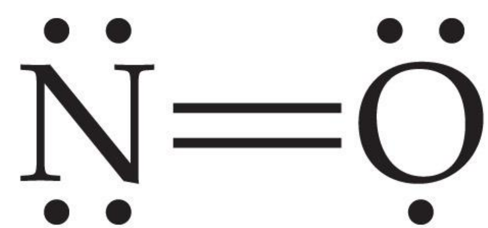
Odd Number of Electrons

Though relatively rare and usually quite unstable and reactive, there are ions and molecules with an odd number of electrons.

This is an example of exception #3.

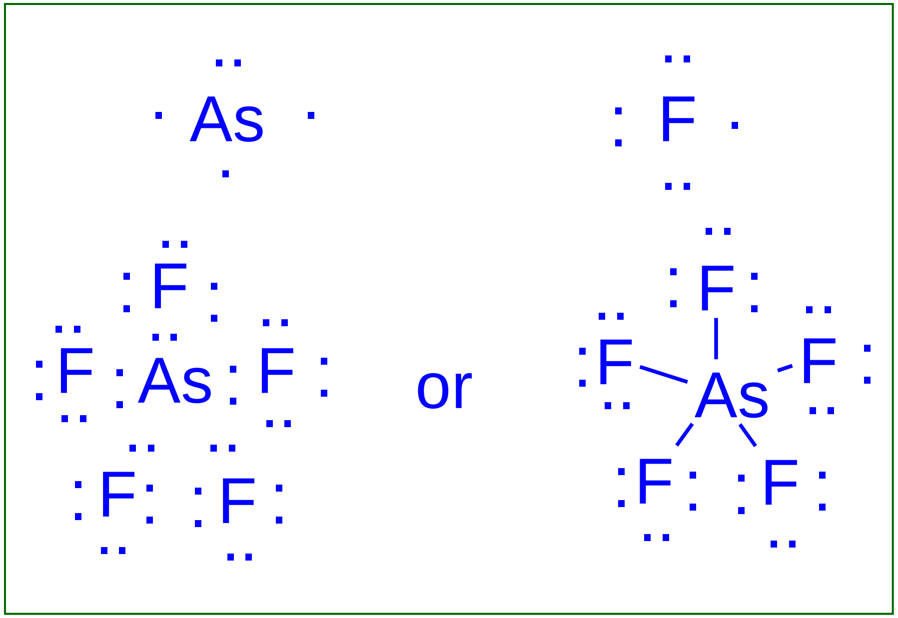


and



Writing Lewis Formulas: Limitations of the Octet Rule

- Write dot and dash formulas for AsF_5.
  Exception # 4, expanded octet



Polar and Nonpolar Covalent Bonds

- Covalent bonds in which the electrons are shared equally are designated as nonpolar covalent bonds.
  - Nonpolar covalent bonds have a symmetrical charge distribution.
- To be nonpolar the two atoms involved in the bond must be the same element to share equally.

Polar and Nonpolar Covalent Bonds

- Some examples of nonpolar covalent bonds.
- H_2

$$H:H \quad \text{or} \quad H-H$$

- N_2

$$:N:::N: \quad \text{or} \quad :N\equiv N:$$

Polar and Nonpolar Covalent Bonds

- Covalent bonds in which the electrons are not shared equally are designated as polar covalent bonds
  - Polar covalent bonds have an asymmetrical charge distribution
- To be a polar covalent bond the two atoms involved in the bond must have different electronegativities.

Polar and Nonpolar Covalent Bonds

- Some examples of polar covalent bonds.
- HF

$$\begin{array}{lcc} & H & F \\ \text{Electronegativities} & \multicolumn{2}{c}{\underbrace{2.1 \quad 4.0}_{1.9}} \end{array}$$

$$\text{Difference} = 1.9 \quad \text{very polar bond}$$

Polar and Nonpolar Covalent Bonds

- Shown below is an electron density map of HF.
  - Blue areas indicate low electron density.
  - Red areas indicate high electron density.
- Polar molecules have a separation of centers of negative and positive charge, an asymmetric charge distribution

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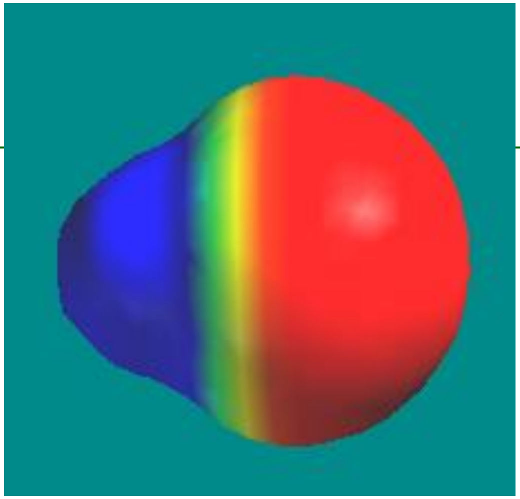


Polar and Nonpolar Covalent Bonds

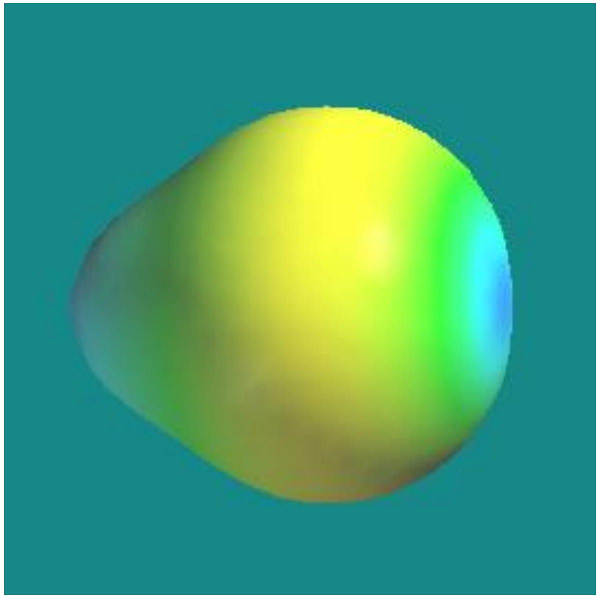
- Compare HF to HI.

$$\begin{array}{lcc} & \text{H} & \text{I} \\ \text{Electronegativities} & \underbrace{2.1 \quad 2.5}_{0.4} & \end{array}$$

$$\text{Difference} = 0.4 \quad \text{slightly polar bond}$$

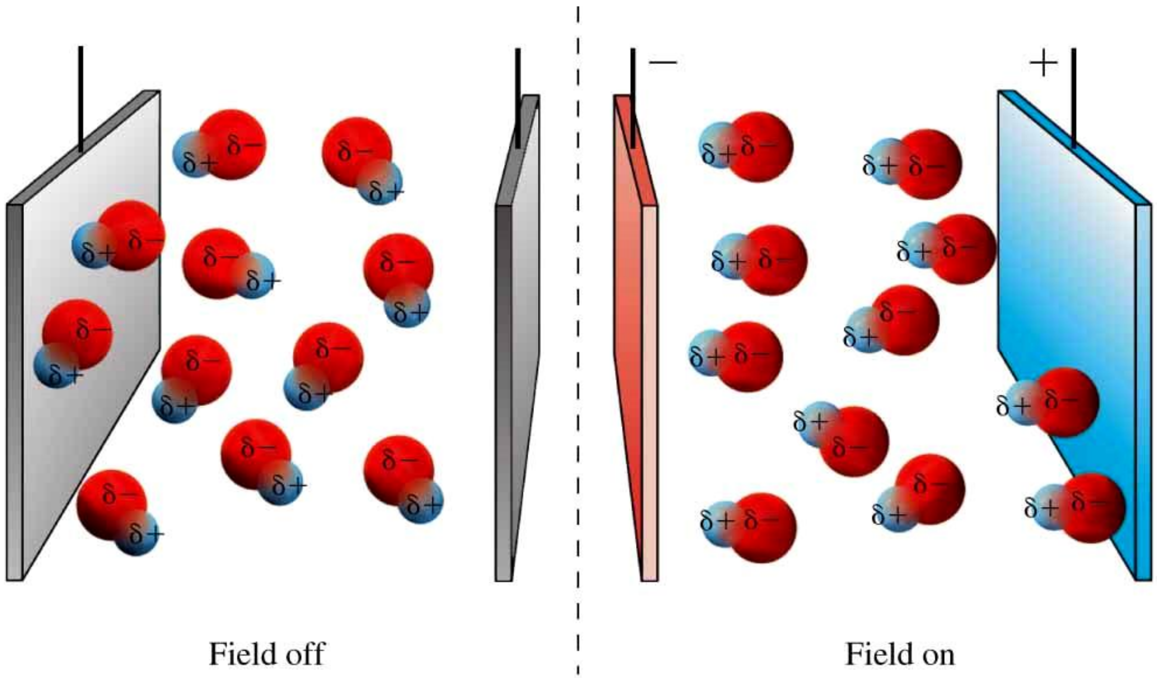
Polar and Nonpolar Covalent Bonds

- Shown below is an electron density map of HI.
  - Notice that the charge separation is not as big as for HF.
    - HI is only slightly polar.



Polar and Nonpolar Covalent Bonds

- Polar molecules can be attracted by magnetic and electric fields.



Dipole Moments

- Molecules whose centers of positive and negative charge do not coincide, have an asymmetric charge distribution, and are polar.
  - These molecules have a dipole moment.
- The dipole moment has the symbol μ.
- μ is the product of the distance, d, separating charges of equal magnitude and opposite sign, and the magnitude of the charge, q.

Dipole Moments

- Molecules that have a small separation of charge have a small μ.
- Molecules that have a large separation of charge have a large μ.
- For example, HF and HI:

$$\overset{\longmapsto}{\delta^{+}\,\mathrm{H}-\mathrm{F}\,\delta^{-}} \qquad \overset{\longmapsto}{\delta^{+}\,\mathrm{H}-\mathrm{I}\,\delta^{-}}$$

$$1.91\ \text{Debye units} \qquad 0.38\ \text{Debye units}$$

Dipole Moments

- There are some nonpolar molecules that have polar bonds.
- There are two conditions that must be true for a molecule to be polar.

1. There must be at least one polar bond present or one lone pair of electrons.
2. The polar bonds, if there are more than one, and lone pairs must be arranged so that their dipole moments do *not* cancel one another.

The Continuous Range of Bonding Types

- Covalent and ionic bonding represent two extremes.

1. In pure covalent bonds electrons are equally shared by the atoms.
2. In pure ionic bonds electrons are completely lost or gained by one of the atoms.

- Most compounds fall somewhere between these two extremes.

Continuous Range of Bonding Types

- All bonds have some ionic and some covalent character.
  - For example, HI is about 17% ionic
- The greater the electronegativity differences the more polar the bond.