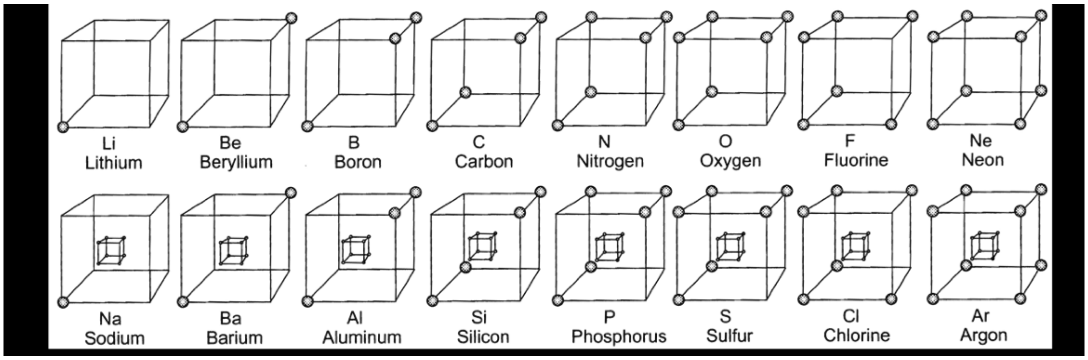
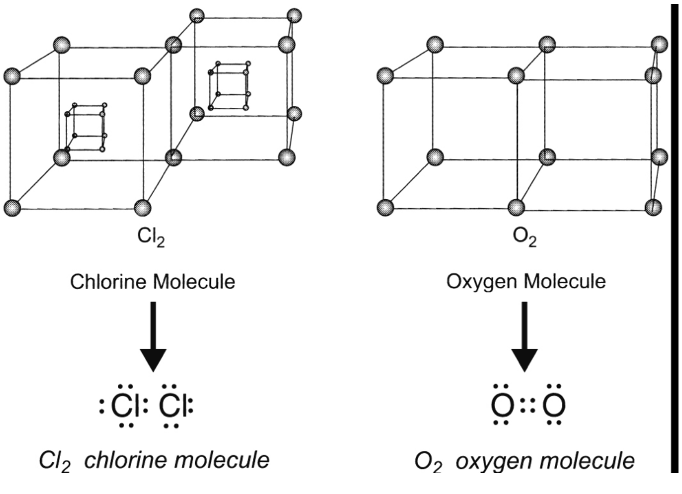
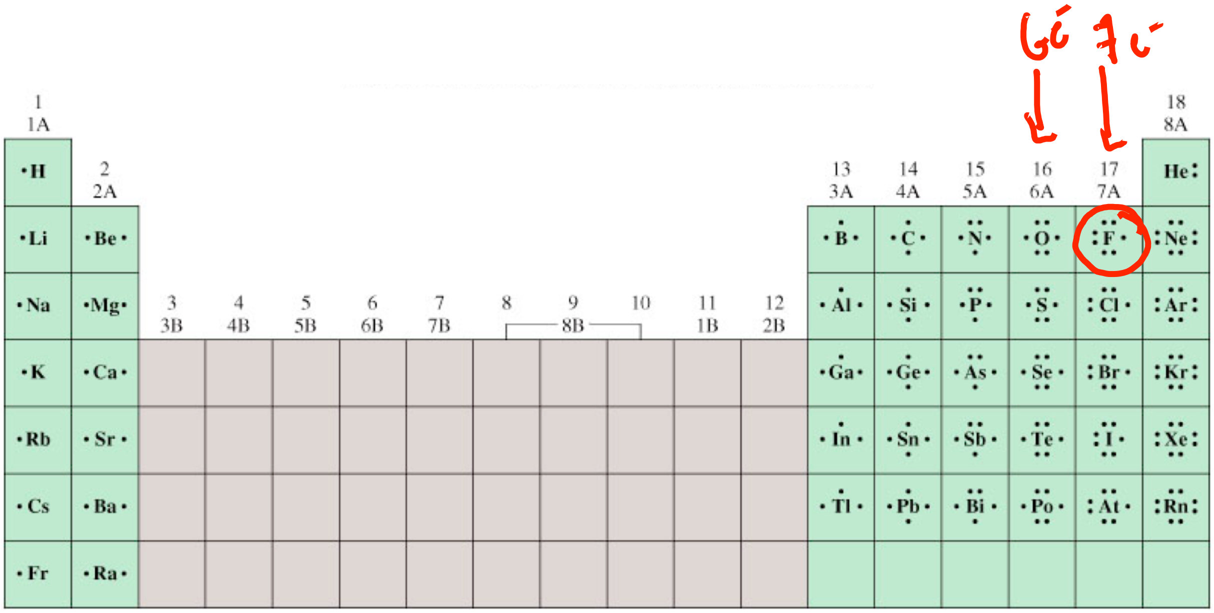
Chemical Bonding
Chapter 9





Lewis Symbols and Valence Electrons

- Around the turn of the century, the American chemist Gilbert N. Lewis came up with the idea of representing valence electron configurations with dots around the atomic symbols. Let's look at some of these Lewis symbols for neutral atoms:



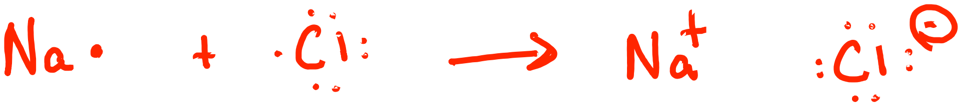
These are usually used only for *main-group elements* (from the *s* and *p* blocks on the periodic table). The electrons are arranged around the atomic symbol in four groups, with electrons paired only if necessary.

$$F : [He]\underbrace{2s^2 2p^5}_{7e^- \text{ valence}}$$

Covalent Bonds and Ionic Bonds: Octet Rule

Explain each of the following observations in terms of the "octet rule":

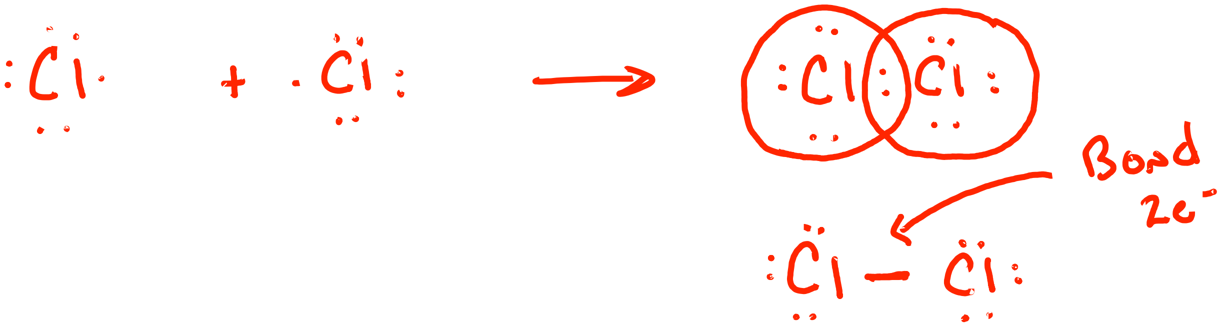
- Na atoms and Cl atoms will combine to form NaCl.



$[Ne]3s^1$ $[Ne]3s^2 3p^5$ $[Ne]$ $[Ne]3s^2 3p^6$ $[Ar]$

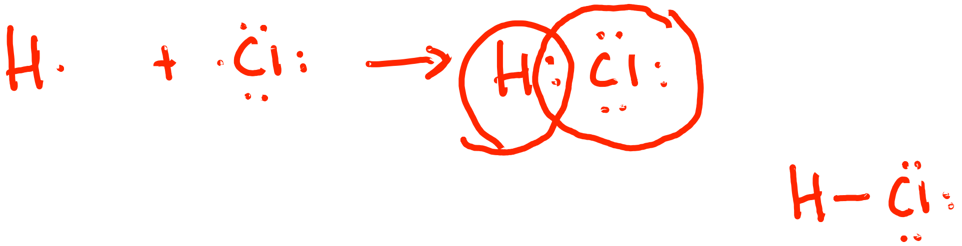
Why does NaCl exist as an ionic solid?

- Cl atoms will react with other Cl atoms to make Cl_2.



Lone pairs e^- (not shared)

- H atoms will react with Cl atoms to make HCl.

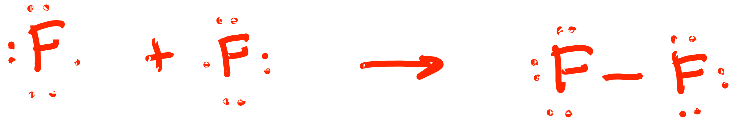


Why do HCl and Cl_2 exist as a diatomic molecules?

Sharing Electrons: Multiple Bonds

Explain the bonding in the following molecules, how does each molecule attain an “octet” of electrons.

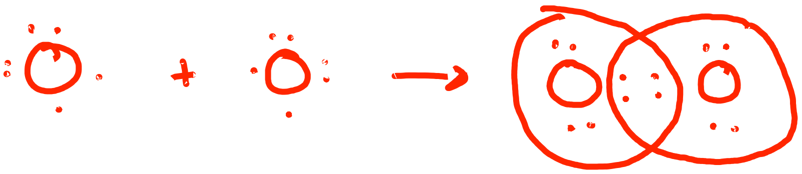
F_2



Single bond

1.4×10^{-10} m

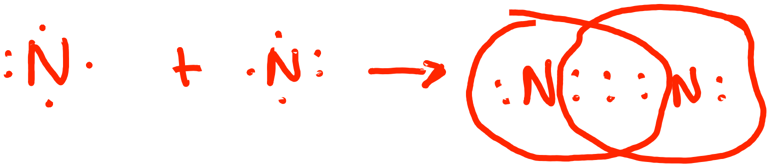
O_2



double bond

1.2×10^{-10} m

N_2



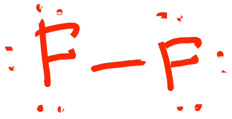
$:N \equiv N:$

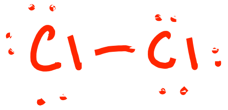
triple Bond

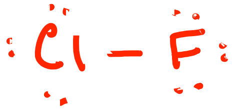
1.09×10^{-10} m

Electronegativity and Polar Bonds

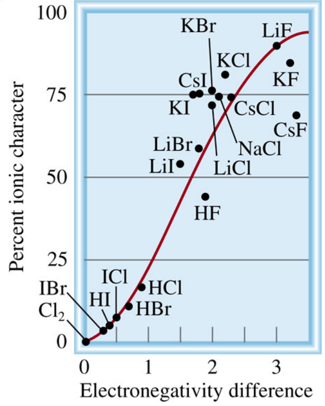
Consider the compounds F_2, Cl_2, and ClF. Draw Lewis structures for these compounds.





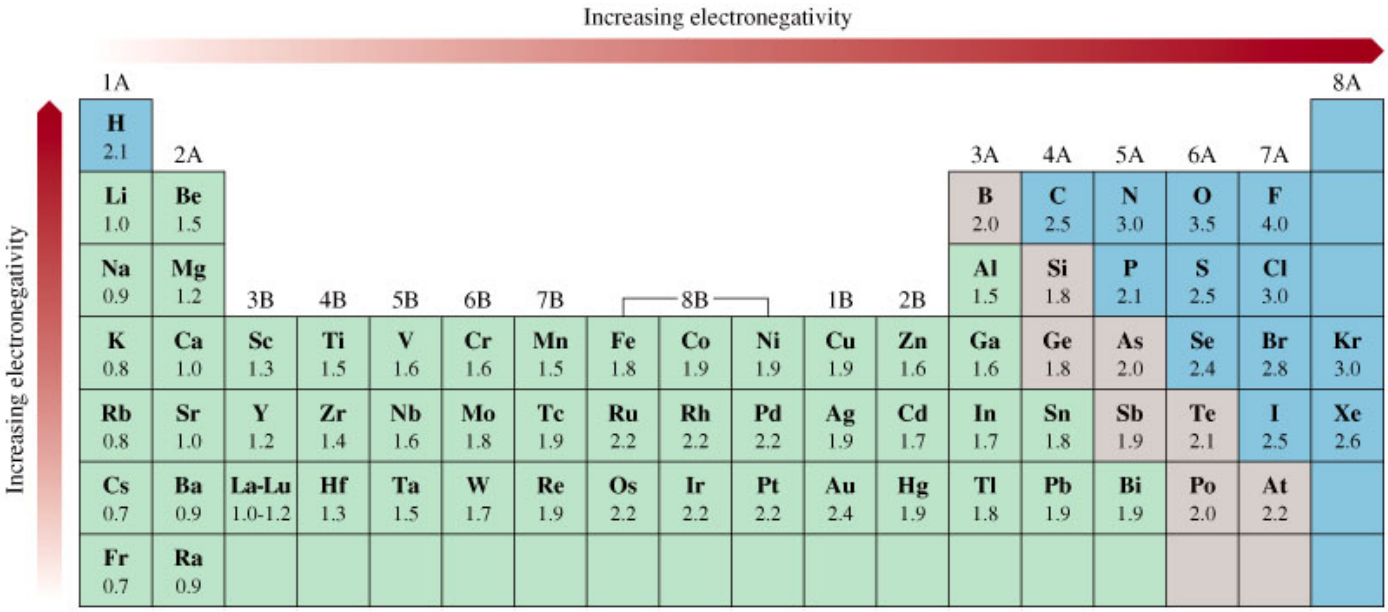


- The bonding in ClF is similar to the bonding in the other two compounds, but there is one important difference. What is this difference?



We say that the bonding in ClF is *polar*.

- We can define *electronegativity* as the attraction that an atom exerts on a *shared* pair of electrons.



1A	2A	3B	4B	5B	6B	7B	8B			1B	2B	3A	4A	5A	6A	7A	8A
H 2.1																	
Li 1.0	**Be** 1.5											**B** 2.0	**C** 2.5	**N** 3.0	**O** 3.5	**F** 4.0	
Na 0.9	**Mg** 1.2											**Al** 1.5	**Si** 1.8	**P** 2.1	**S** 2.5	**Cl** 3.0	
K 0.8	**Ca** 1.0	**Sc** 1.3	**Ti** 1.5	**V** 1.6	**Cr** 1.6	**Mn** 1.5	**Fe** 1.8	**Co** 1.9	**Ni** 1.9	**Cu** 1.9	**Zn** 1.6	**Ga** 1.6	**Ge** 1.8	**As** 2.0	**Se** 2.4	**Br** 2.8	**Kr** 3.0
Rb 0.8	**Sr** 1.0	**Y** 1.2	**Zr** 1.4	**Nb** 1.6	**Mo** 1.8	**Tc** 1.9	**Ru** 2.2	**Rh** 2.2	**Pd** 2.2	**Ag** 1.9	**Cd** 1.7	**In** 1.7	**Sn** 1.8	**Sb** 1.9	**Te** 2.1	**I** 2.5	**Xe** 2.6
Cs 0.7	**Ba** 0.9	**La-Lu** 1.0-1.2	**Hf** 1.3	**Ta** 1.5	**W** 1.7	**Re** 1.9	**Os** 2.2	**Ir** 2.2	**Pt** 2.2	**Au** 2.4	**Hg** 1.9	**Tl** 1.8	**Pb** 1.9	**Bi** 1.9	**Po** 2.0	**At** 2.2	
Fr 0.7	**Ra** 0.9																

Lewis Structures: Rules

These rules are helpful guidelines. Practice using them until they become second-nature.

1. **Count** the total number of valence electrons that must appear in the structure.

    - Be sure to account for the extra or fewer electrons in a polyatomic ion!

2. **Arrange** the atoms in the correct arrangement for the molecule or ion.

    - A few guidelines:
        - Molecules are often written in the order that the atoms are connected.
        - The least electronegative atom is usually the central atom.
        - Hydrogen and fluorine are always terminal atoms.

    - In oxyacids (H_2SO_4, HNO_3, etc.), the oxygen atoms are bonded to the central atom, and the hydrogen atoms are bonded to the oxygens.

3. **Connect** each adjacent atom with a single bond. (Use lines for bonds.)

4. **Complete** the octets of terminal atoms by filling in lone pairs of electrons. (Use dots!)

    - Remember that hydrogen should only have two electrons.

5. **Add leftover electrons** to the central atom (even if that gives it more than an octet).

6. **Try multiple bonds** if the central atom lacks an octet.

    - As a guide for where to place multiple bonds in order to minimize formal charges, the total number of bonds to any **uncharged** atom is usually given by its position on the periodic table. This is a guideline, not a hard-and-fast rule!

Group #:	1A	2A	3A	4A	5A	6A	7A
Example:	H	Be	B	C	N	O	F
# of bonds:	**1**	**2**	**3**	**4**	**3**	**2**	**1**

7. **Check** formal charges on each atom, and write in any non-zero formal charges.

    - Formal charge = (# of valence e^- in free atom) œ(# of dots and lines around atom)
    - The sum of the formal charges on all atoms will equal zero for a neutral molecule, and will equal the charge on the ion for a polyatomic ion.
    - Lewis strucutres should be drawn to minimize formal charges.
    - In general, negative formal charge should go on the most electronegative atoms.

8. **Check** for resonance, and indicate it if necessary.

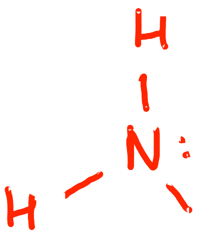
9. **Check** your Lewis structure.

    - Have you drawn the correct number of valence electrons?
    - Do all atoms have octets? (Except for examples of reduced or expanded octets.)
    - Have you minimized formal charges?

Lewis Structures: The Octet Rule

Using the rules for Lewis structures, provide Lewis structures for each of the following:

NH_3 (ammonia)



1N: 1 × $5e^-$ = $5e^-$

3H: 3 × $1e^-$ = $3e^-$

$8e^-$

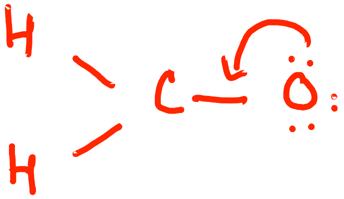
$-6e^-$

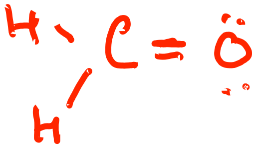
$2e^-$

$-2e^-$

0

H_2CO (formaldehyde)





1C: 1 × $4e^-$ = $4e^-$

1O: 1 × $6e^-$ = $6e^-$

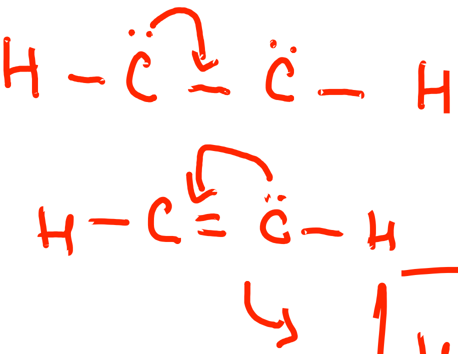
2H: 2 × $1e^-$ = $2e^-$

$12e^-$

$-6e^-$

$6e^-$

C_2H_2 {HCCH} (acetylene)



$\boxed{H-C\equiv C-H}$

2H: 2 × $1e^-$ = $2e^-$

2C: 2 × $4e^-$ = $8e^-$

$10e^-$

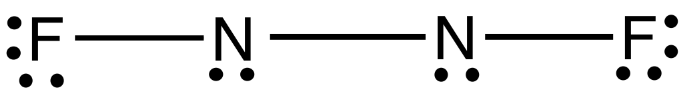
$-6e^-$

$4e^-$

Clicker Questions on Lewis Structures

Below are three possible lewis structures of N_2F_2, we will use these diagrams for several clicker questions.

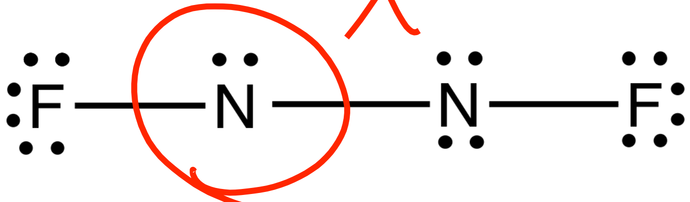
Strucutre ~~#1~~ #3: Is this an acceptable lewis strcture for N_2F_2?



Too MANY $26e^-$

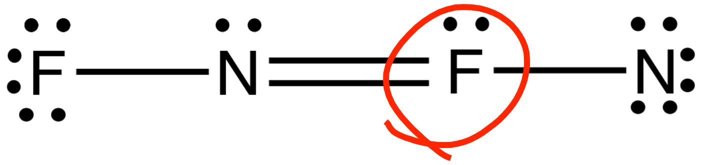
Should Be $24e^-$!

Strucutre #2: Is this an acceptable lewis strcture for N_2F_2?



Needs AN octet

Strucutre #1: Is this an acceptable lewis strcture for N_2F_2?

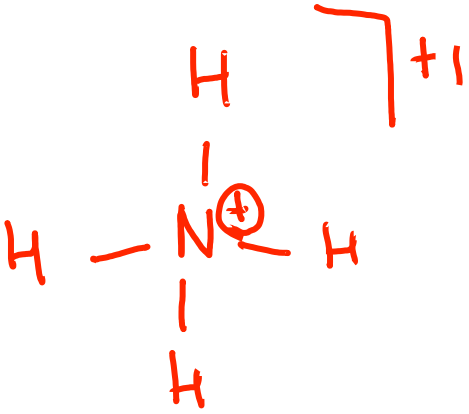


F must be terminal ATOM

Lewis Structures: Ions and Resonance

Using the rules for Lewis structures, provide Lewis structures for each of the following:

NH_4^+ (the ammonium ion)



$1N: 1 \times 5e^- = 5e^-$

$4H: 4 \times 1e^- = 4e^-$

$9e^-$

$+1 = -1e^-$

$8e^-$

$-8e^-$

0

$$\text{Formal Charge} = \left(\text{Total \# of Valence } e^- \text{ Atom}\right) - \left(\text{\# of Dots} + \text{\# Lines}\right)$$

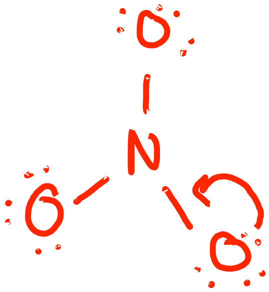
$$\text{Formal Charge of N} = (5) - (0 + 4) = +1$$

$$\text{Formal Charge of H} = (1) - (0 + 1) = 0$$

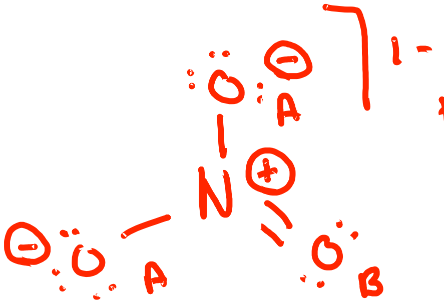
Lewis Structures: Ions and Resonance

Using the rules for Lewis structures, provide Lewis structures for each of the following:

$NO_3^{œ}$ (the nitrate ion)



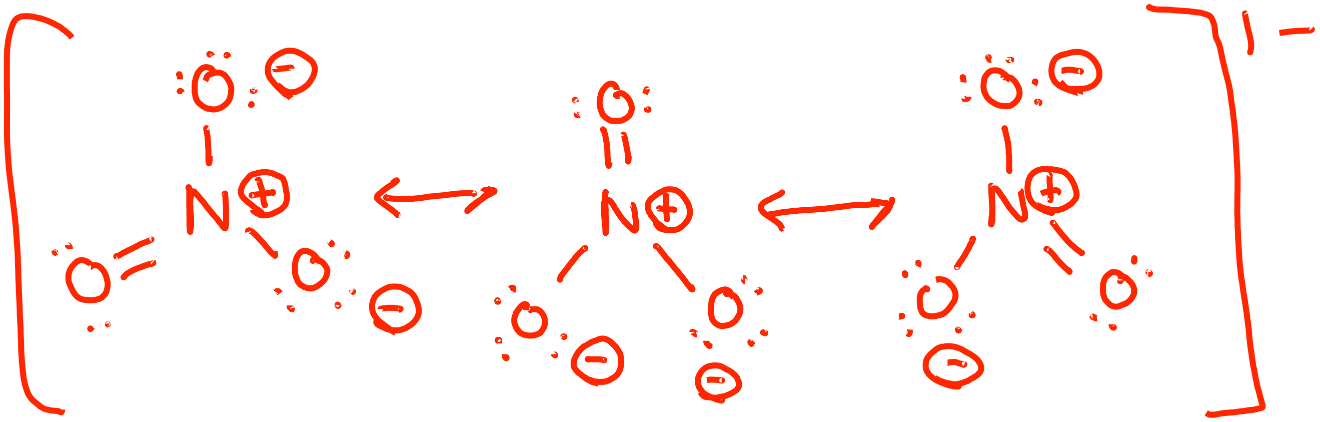
$$\begin{array}{r} 24e^- \\ -\ 6e^- \\ \hline 18e^- \end{array}$$



$F.C._N = 5 - (0+4) = \oplus$

$F.C._{O_A} = 6 - (6+1) - 1$ $\quad$ $F.C._{O_B} = 6 - (4+2) = 0$

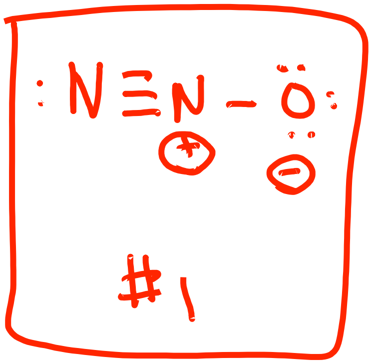
Is there anything *arbitrary* about your structure for $NO_3^{œ}$? What does this signify?

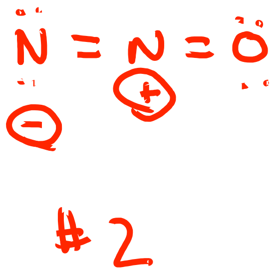


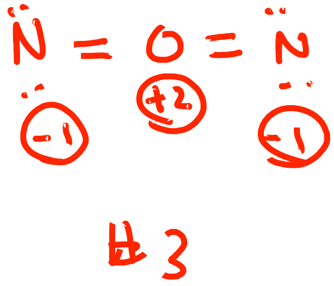
resonance: means that more than 1 equivalent Lewis structure is needed to represent the bonding in a molecule or ion

Lewis Structures: Formal Charge

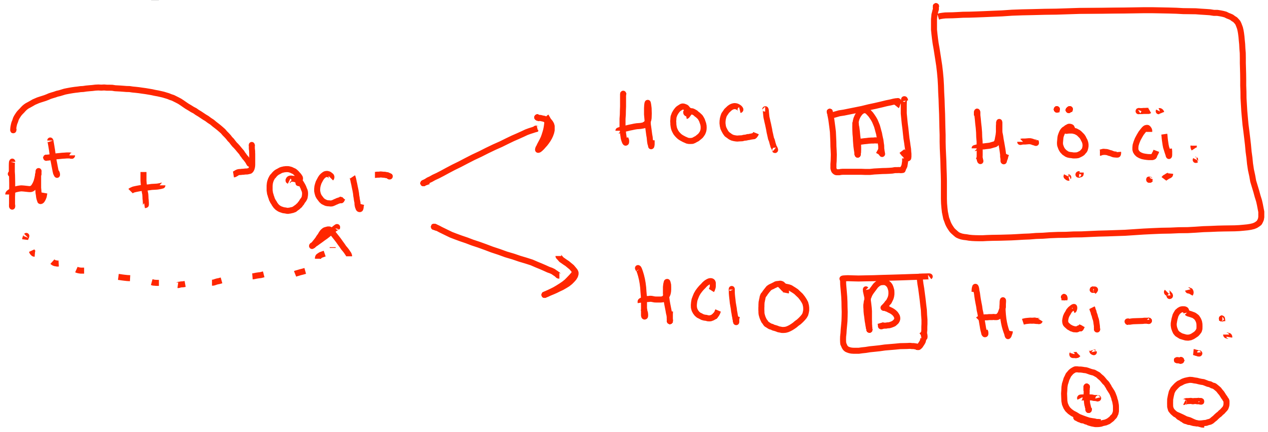
- There are several possible ways of connecting the atoms to form N_2O (nitrous oxide). Should it be NœNœO? or NœOœN? What is the actual structure of N_2O?







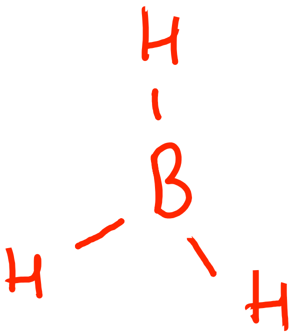
- The OClœ ion will react with H^+ to form hypochlorous acid (HClO). What is its preferred structure: HOCl or HClO?



Lewis Structures: Less than an Octet

Using the rules for Lewis structures, provide Lewis structures for each of the following:

BH_3

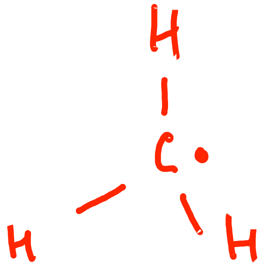


1B: $1 \times 3e^- = 3e^-$
3H: $3 \times 1e^- = 3e$

$6e^-$
$-6e^-$
0

Be, B, Al ← can have less than an octet of e^-

CH_3



1C = $1 \times 4e^- = 4e^-$
3H = $3 \times 1e^- = 3e^-$

$7e^-$
$-6e^-$
$1e^-$

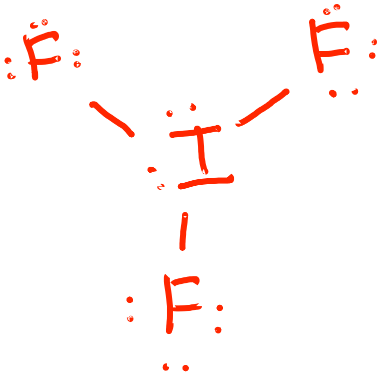
Radical
Lone e^-
on an atom

- What is unusual about these structures? How can we identify these important *exceptions* in drawing Lewis structures?

Lewis Structures: More than an Octet

Using the rules for Lewis structures, provide Lewis structures for each of the following:

IF_3



$I : 1 \times 7e^- = 7e^-$

$3F : 3 \times 7e^- = 21e^-$

$28e^-$

$-6e^-$

$22e^-$

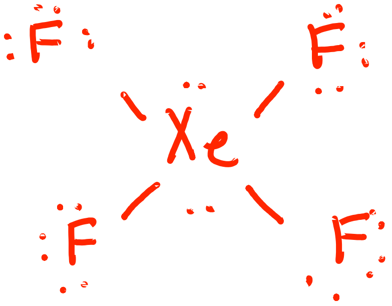
$-18e^-$

$4e^-$

expanded octet

3rd period or Higher can expand

XeF_4 $(36e^-)$



$F.C_{Xe} = 8 - (4+4)$

$F.C_{Xe} = 0$

$36e^-$

$-8e^-$

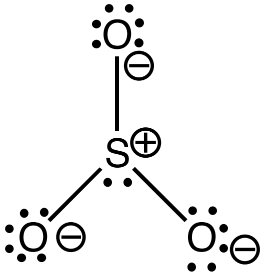
$28e^-$

$-24e^-$

$4e^-$

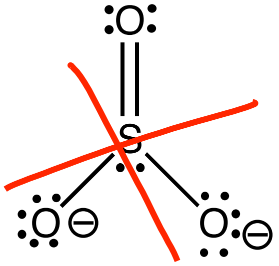
$SO_3^{2œ}$ (Let's think carefully about this one!)

Which is the best Lewis structure for SO_3^{2-}



A

Octet
of
e^- around
sulfur



B

- Minimize
Formal
Charge
- expanded octet

Bond Enthalpies: Concepts

Whenever chemical bonds are formed, energy is ALWAYS released.

Is bond formation endothermic or endothermic?

We can make a simple **approximation** that the energy of a bond depends only on the two atoms participating in the bond. A similar table can be found in table 9.4 of your text:

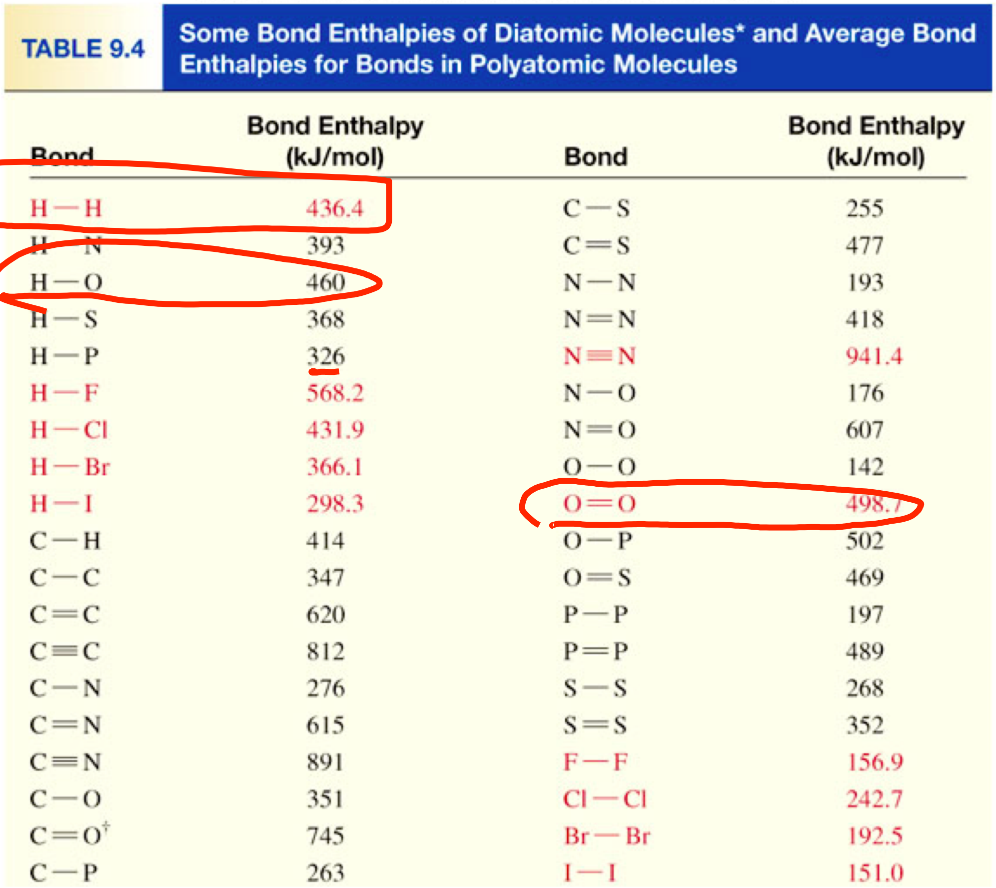


TABLE 9.4 **Some Bond Enthalpies of Diatomic Molecules* and Average Bond Enthalpies for Bonds in Polyatomic Molecules**

Bond	Bond Enthalpy (kJ/mol)	Bond	Bond Enthalpy (kJ/mol)
H—H	436.4	C—S	255
H—N	393	C=S	477
H—O	460	N—N	193
H—S	368	N=N	418
H—P	326	N≡N	941.4
H—F	568.2	N—O	176
H—Cl	431.9	N=O	607
H—Br	366.1	O—O	142
H—I	298.3	O=O	498.7
C—H	414	O—P	502
C—C	347	O=S	469
C=C	620	P—P	197
C≡C	812	P=P	489
C—N	276	S—S	268
C=N	615	S=S	352
C≡N	891	F—F	156.9
C—O	351	Cl—Cl	242.7
C=O†	745	Br—Br	192.5
C—P	263	I—I	151.0

In general, for any reaction in which **all** reactants and products are in the **gas phase**,

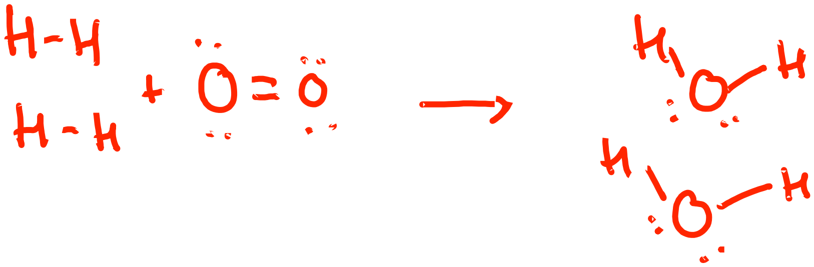
we can **estimate**: $\boxed{\Delta H \approx \sum(\text{bonds broken}) - \sum(\text{bonds formed})}$

$D_{H-H} = 436.4$

Bond Enthalpies: Sample Problem

Using the bond enthalpy table, estimate ΔH for the following reaction:

$$2H_2\,(g) + O_2\,(g) \rightarrow 2\,H_2O\,(g)$$



$$\Delta H_{Rxn} = \sum \text{Bond Broken} - \sum \text{Bond formed}$$

$$= \left(\begin{matrix} H-H & \\ H-H & O=O \end{matrix}\right) - \left(4\ O-H\right)$$

$$= \left(2D_{H-H} + D_{O=O}\right) - \left(4D_{O-H}\right)$$

$$= \left(2 \times \frac{436\ kJ}{mol} + 1 \times \frac{498\ kJ}{mole}\right) - \left(4 \times \frac{460\ kJ}{mole}\right)$$

$$= 1{,}370 - 1{,}840$$

$$\boxed{\Delta H_{Rxn} = -470\ kJ/mole}$$

Reactions: Moving Electrons to Make Bonds

- In many reactions to form a bond we first need to break some bonds. Bonds are made of electrons, to break a bond we need to move electrons, and this requires energy. We have said that energy can take many forms thermal, electrical etc. Last week we did an experiment where we broke a bond by adding light energy.

Here is the reaction:

$H_2\ (g) + Cl_2\ (g) + h\nu \rightarrow 2HCl\ (g)$

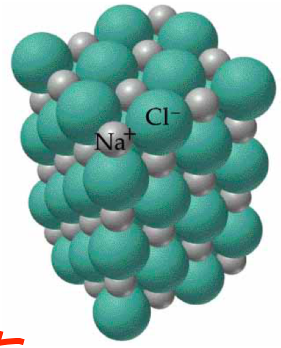
hν means energy in the form of light. Below is the energy of light for each of the following wavelengths:

Color	**Wavelength**	**Energy (E=hc/λ) in Joules**	
Red	700 nm	$2.84 \text{ x}10^{-19}$	Low
Orange	600 nm	$3.31 \text{ x}10^{-19}$	
Yellow	550 nm	$3.61 \text{ X } 10^{-19}$	
Green	500 nm	$3.98 \text{ x}10^{-19}$	
Blue	450 nm	$4.42 \text{ x}10^{-19}$	
Violet	400 nm	$4.97 \text{ x } 10^{-19}$	HiGH

- In order to start the reaction we are going to need to add enough energy to move electrons.

Bonding in Ionic Solids:
The Born-Haber Cycle

- Ionic solids are held together by the attraction of ions of opposite charge. Consider, once again, the crystal lattice for NaCl. How much energy would be required to separate all those ions into individual ions in the gas phase?



$Na^+_{(g)} + Cl^-_{(g)} \rightarrow NaCl_{(s)}$ $\Delta H = -L.E$

$\rightarrow Na^+ (g) + Cl^- (g)$

X*

$\boxed{NaCl_{(s)} \rightarrow Na^+_{(g)} + Cl^-_{(g)} \quad \Delta H = L.E.}$ (Lattice Energy)

The ΔH of such a reaction is called the **lattice energy** of a crystalline solid. It is a measure of the strength of the ionic forces in such a solid.

- Lattice energies cannot be determined using an experiment, but we can use Hess's Law to construct a **Born-Haber Cycle** and determine the lattice energy indirectly. Let's do this for NaCl.

$Na_{(s)} + \frac{1}{2} Cl_{2(g)} \longrightarrow NaCl_{(s)}$ $\Delta H = \Delta H_f = -411\ kJ/mol$

$Na_{(s)} \longrightarrow Na_{(g)}$ $\Delta H = \Delta H_{sub} = 108\ kJ/mol$

$Cl_{2(g)} \longrightarrow 2Cl_{(g)}$ $\Delta H = D_{Cl-Cl} = 242\ kJ/mol$

$Na_{(g)} \longrightarrow Na^+_{(g)} + e^-$ $\Delta H = IE(Na) = 496\ kJ/mol$

• $Cl_{(g)} + e^- \rightarrow Cl^-_{(g)}$ $\Delta H = EA_{(Cl)} = -349\ kJ/mol$

Useful Information:

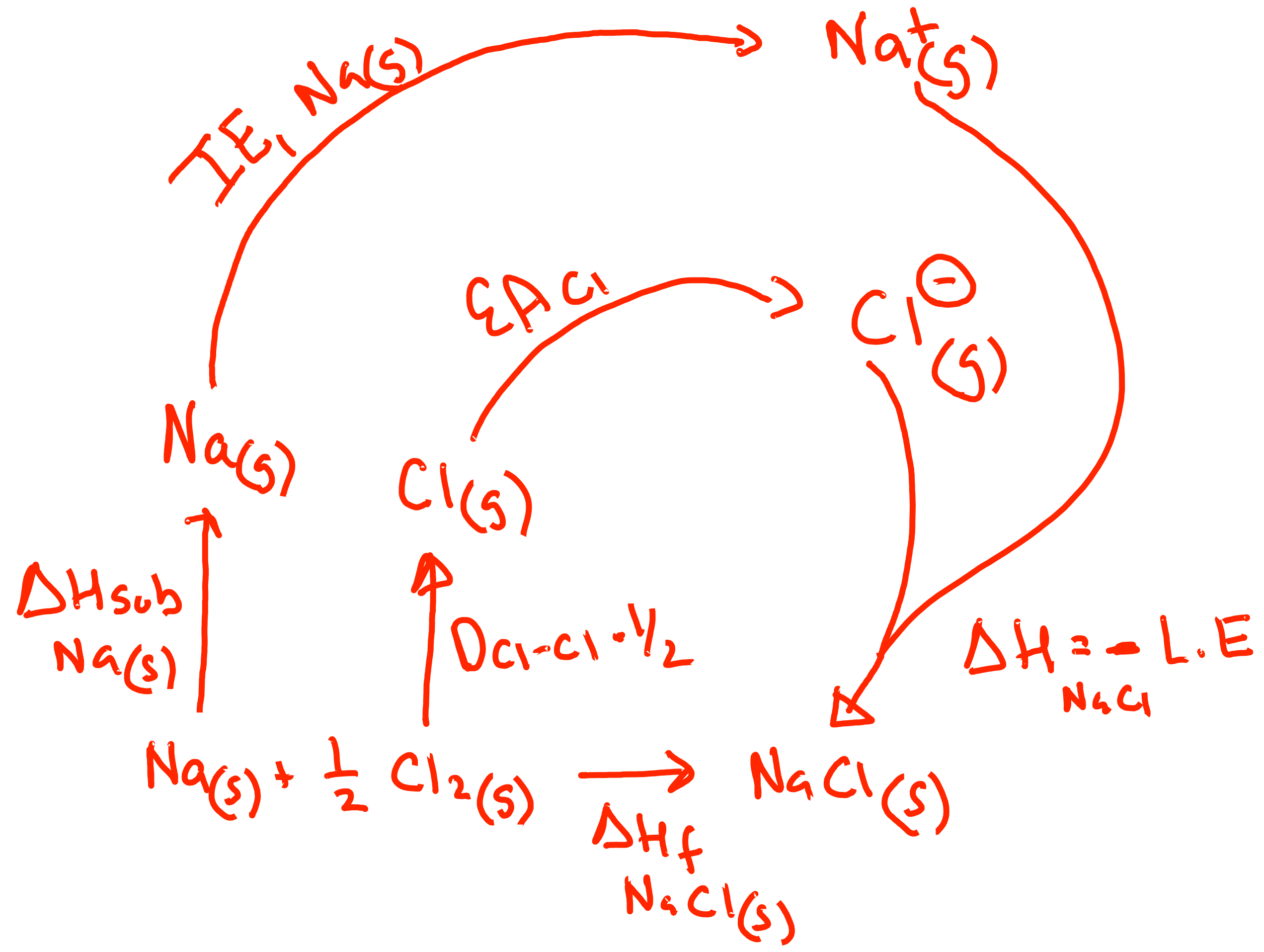
$\Delta H°_f$ (NaCl (*s*)) = –411 kJ/mol

ΔH_{sub} (Na) = 108 kJ/mol

$D_{Cl–Cl}$ = 242 kJ/mol

IE_1 (Na) = 496 kJ/mol

EA (Cl) = –349 kJ/mol



$$\Delta H f_{NaCl} = \Delta H_{sub} + IE_{1\,Na} + \tfrac{1}{2} \cdot D_{Cl\text{-}Cl} + EA_{Cl} - L.E_{NaCl}$$

$$-411\,\frac{kJ}{mol} = 108\,\frac{kJ}{mol} + 498\,\frac{kJ}{mol} + \frac{1}{2} \cdot 242\,\frac{kJ}{mol} + -349\,\frac{kJ}{mol} - L.E_{NaCl}$$

$$\boxed{787\,\frac{kJ}{mol} = L.E._{NaCl}}$$

$$NaCl_{(s)} \rightarrow Na^{+}_{(a)} + Cl^{-}_{(a)}$$

$$\Delta H = 787\ kJ/mol$$