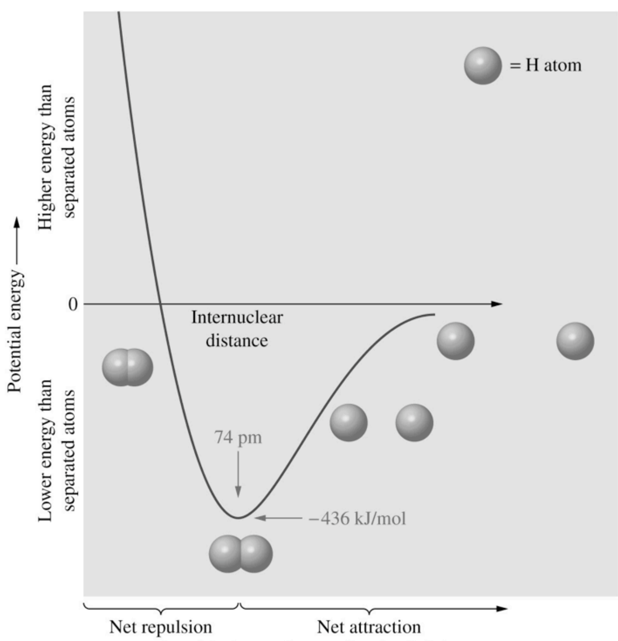
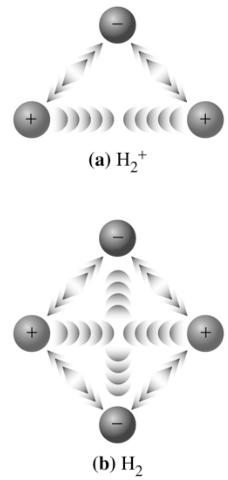
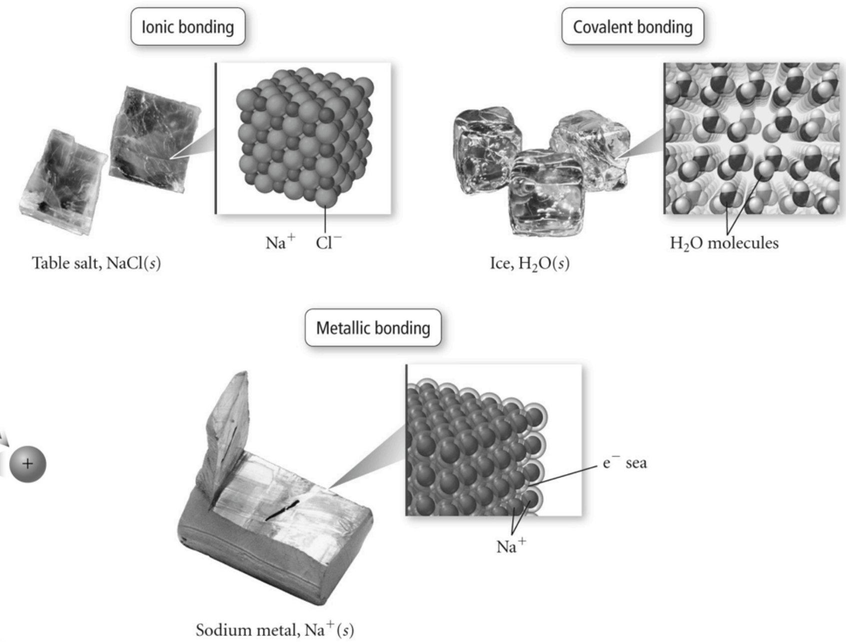
Chemical Bonds: A Preview Chapter 9 Section 1.1

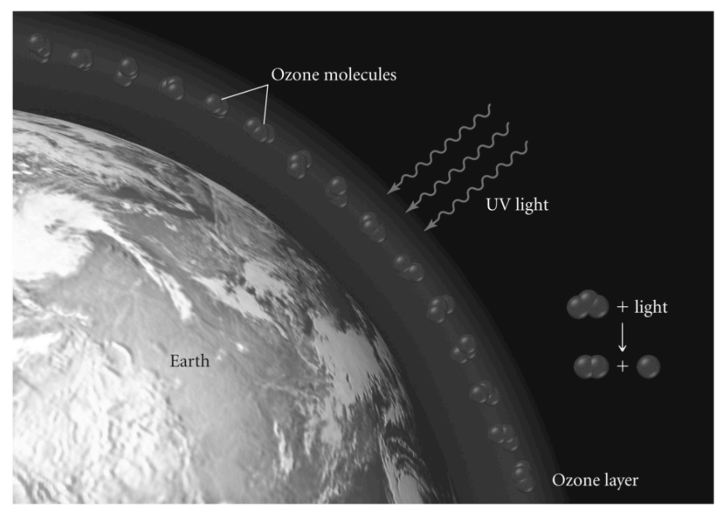
Forces called ***chemical bonds*** hold atoms together in molecules and keep ions in place in solid ionic compounds.

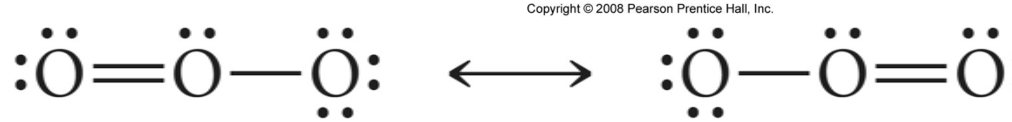
Chemical bonds are ***electrostatic*** forces; they reflect a balance in the forces of attraction and repulsion between electrically charged particles.











The Lewis Theory of Chemical Bonding: An Overview

Valence electrons play a fundamental role in chemical bonding.

When metals and nonmetals combine, valence electrons usually are transferred from the metal to the nonmetal atoms, giving rise to ***ionic bonds***.

In combinations involving only nonmetals, one or more ***pairs*** of valence electrons are ***shared*** between the bonded atoms, producing ***covalent bonds***.

In losing, gaining, or sharing electrons to form chemical bonds, atoms tend to acquire the electron configurations of noble gases.

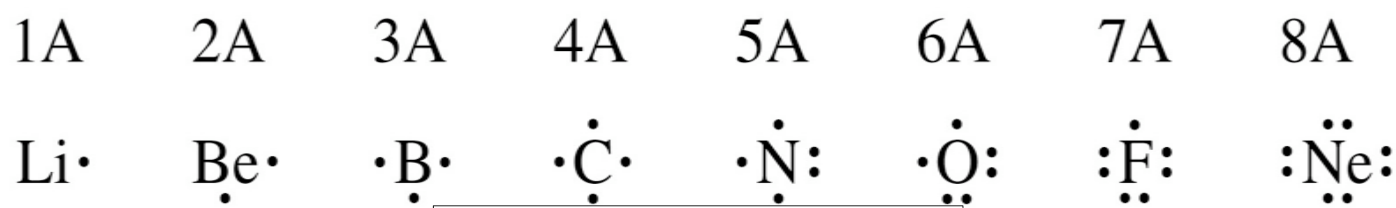
In a ***Lewis symbol***, the chemical symbol for the element represents the nucleus and core electrons of the atom.

Dots around the symbol represent the ***valence*** electrons.

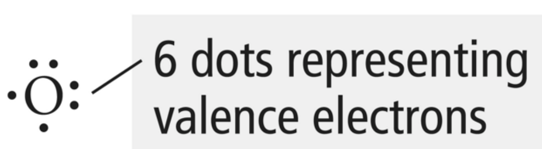
In writing Lewis symbols, the first four dots are placed singly on each of the four sides of the chemical symbol.

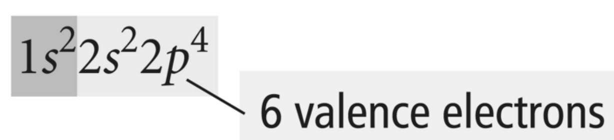
Dots are paired as the next four are added.

Lewis symbols are used primarily for those elements that acquire noble-gas configurations when they form bonds.



Give Lewis symbols for magnesium, silicon, and phosphorus.

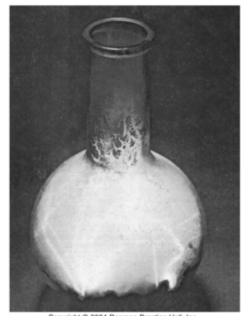


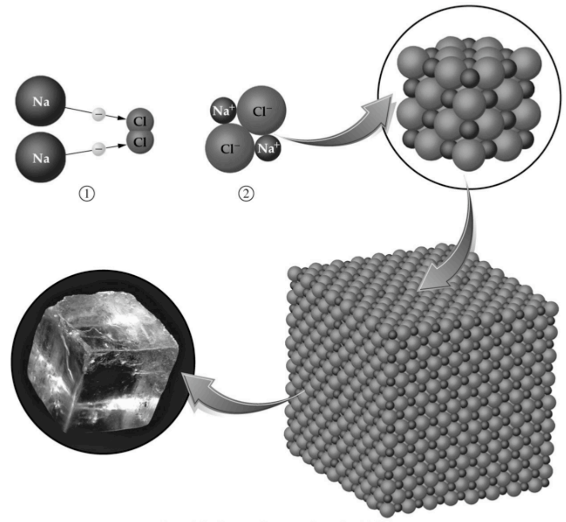


Ionic Bonds and Ionic Crystals

When atoms lose or gain electrons, they may acquire a noble gas configuration, but do not *become* noble gases.
Because the two ions formed in a reaction between a metal and a nonmetal have opposite charges, they are strongly attracted to one another and form an ***ion pair***.
The net attractive electrostatic forces that hold the cations and anions together are ***ionic bonds***.
The highly ordered solid collection of ions is called an ***ionic crystal***.

Lewis symbols can be used to represent ionic bonding between nonmetals and: the *s*-block metals, some *p*-block metals, and a few *d*-block metals.
Instead of using complete electron configurations to represent the loss and gain of electrons, Lewis symbols can be used.





$$[\mathrm{Na}\cdot] + [:\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}:] \longrightarrow [\mathrm{Na}]^{+} + [:\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}:]^{-}$$

Use Lewis symbols to show the formation of ionic bonds between magnesium and nitrogen. What are the name and formula of the compound that results?

Energy Changes in Ionic Compound Formation

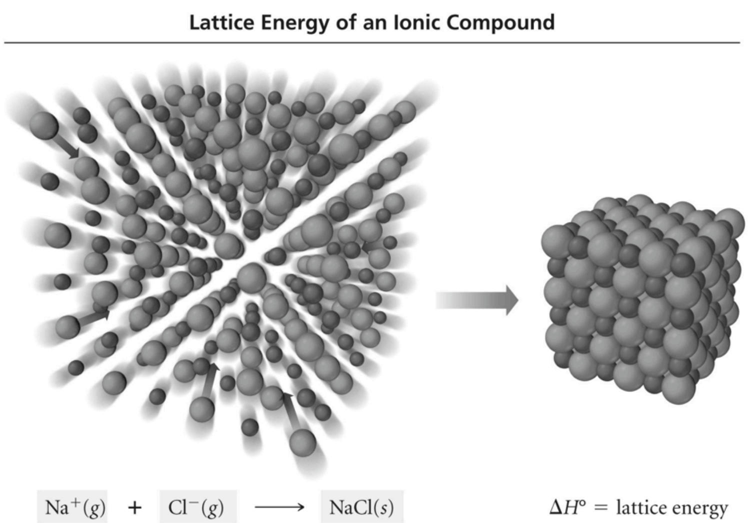
$Na(g) \rightarrow Na^{+}(g) + e^{-}$ $\qquad I_1 = +496$ kJ/mol

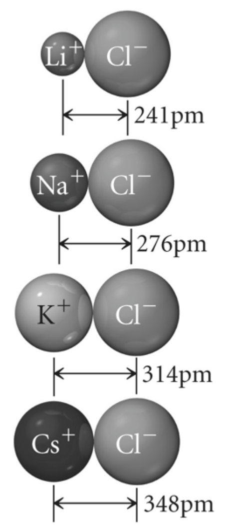
$Cl(g) + e^{-} \rightarrow Cl^{-}(g)$ $\qquad EA_1 = –349$ kJ/mol

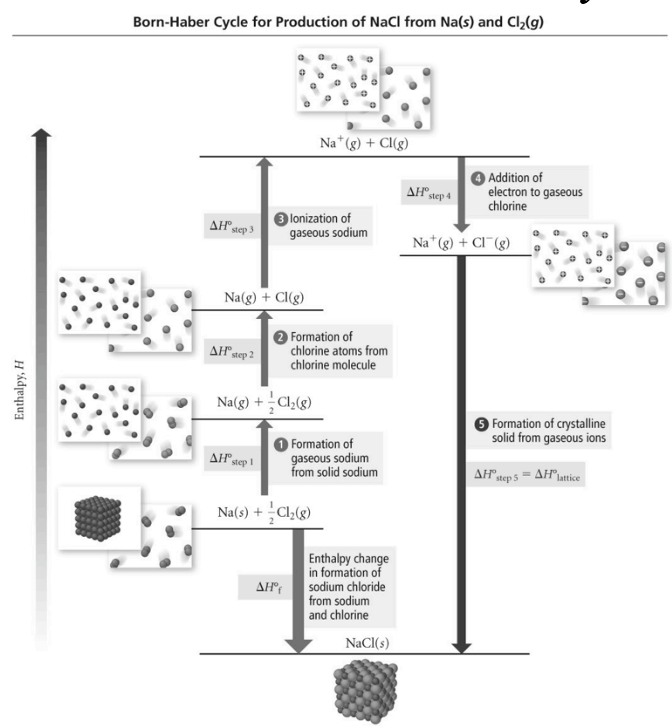
From the data above, it doesn't appear that the formation of NaCl from its elements is energetically favored. However …

… the ***enthalpy of formation*** of the ionic compound is more important than either the first ionization energy or electron affinity.

The overall enthalpy change can be calculated using a step-wise procedure called the ***Born–Haber cycle***.







$$\Delta H^{\circ}_{f} = \Delta H^{\circ}_{\text{step 1}} + \Delta H^{\circ}_{\text{step 2}} + \Delta H^{\circ}_{\text{step 3}} + \Delta H^{\circ}_{\text{step 4}} + \overbrace{\Delta H^{\circ}_{\text{step 5}}}^{\text{Lattice energy}}$$

Lewis Structures of Simple Molecules

A ***Lewis structure*** is a combination of Lewis symbols that represents the formation of covalent bonds between atoms.

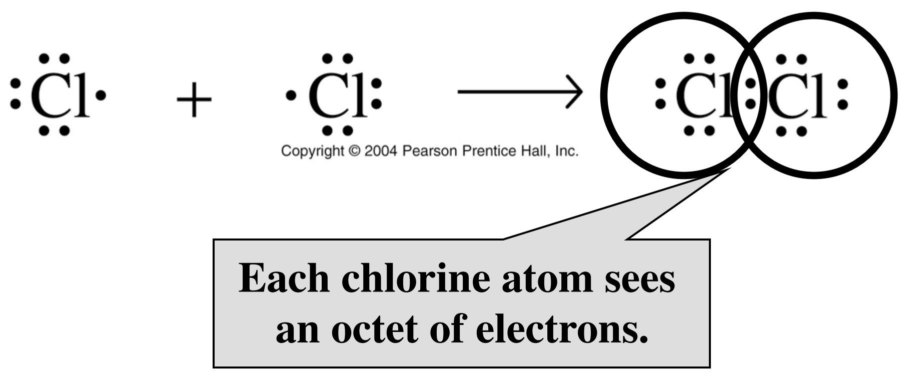
In most cases, a Lewis structure shows the bonded atoms with the electron configuration of a noble gas; that is, the atoms obey the *octet rule*. (H obeys the *duet rule*.)

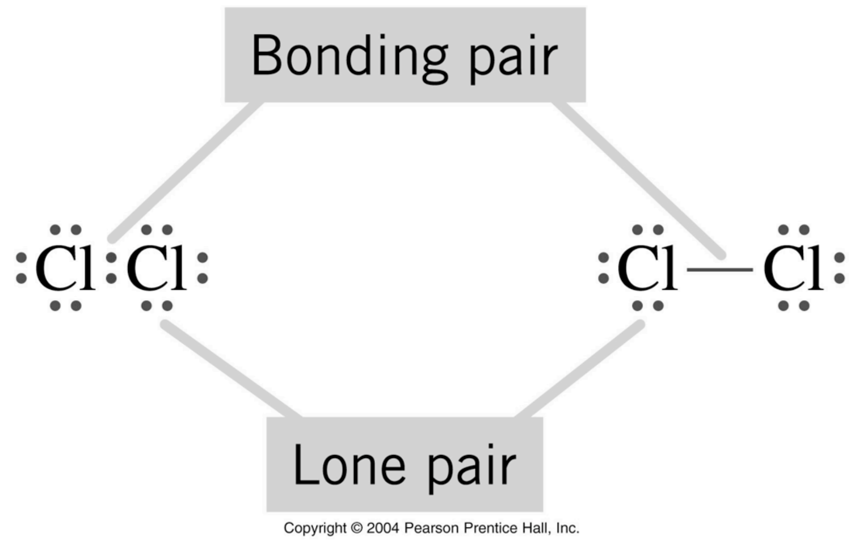
The shared electrons can be counted for each atom that shares them, so each atom may have a noble gas configuration.

The shared pairs of electrons in a molecule are called ***bonding pairs***.

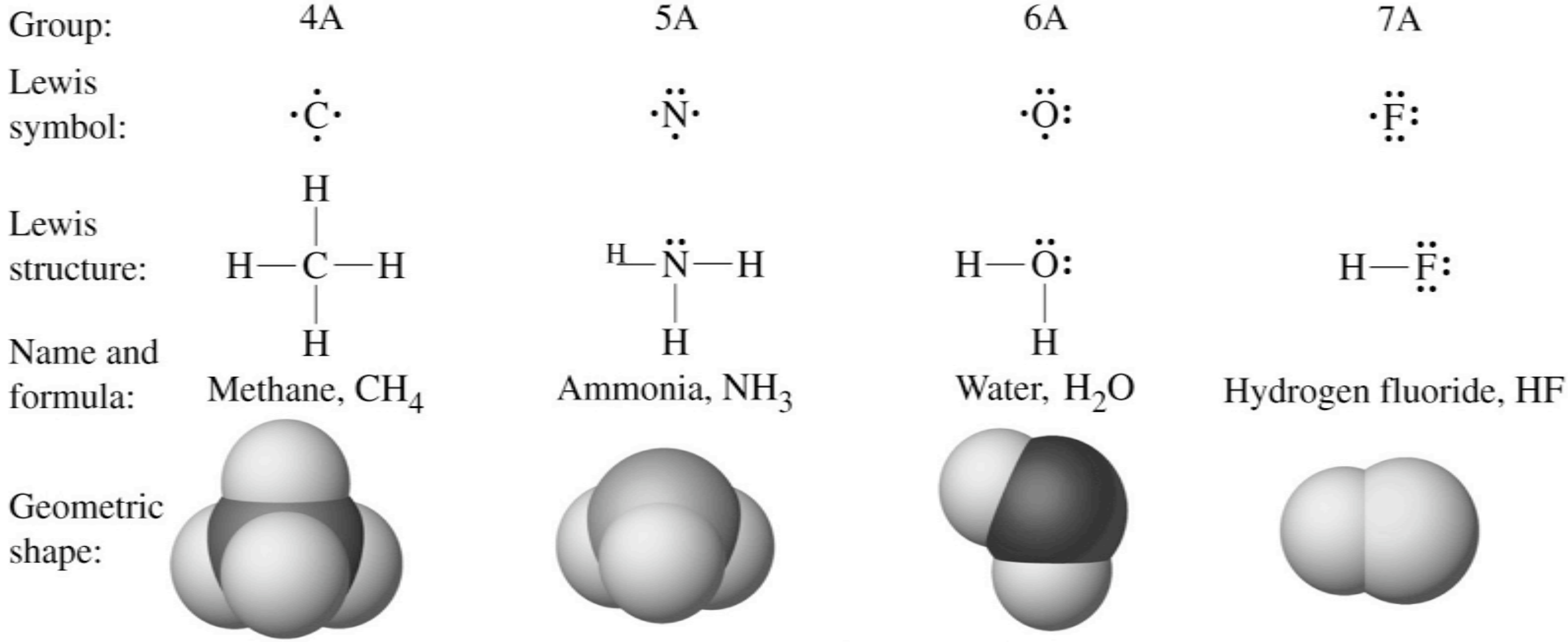
In common practice, the bonding pair is represented by a dash (—).

The other electron pairs, which are not shared, are called ***nonbonding pairs***, or **lone pairs**.

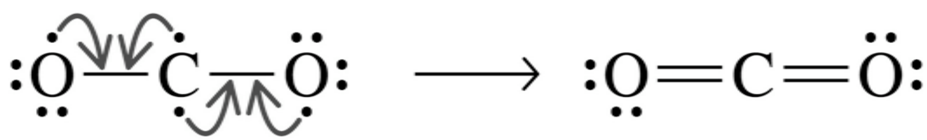


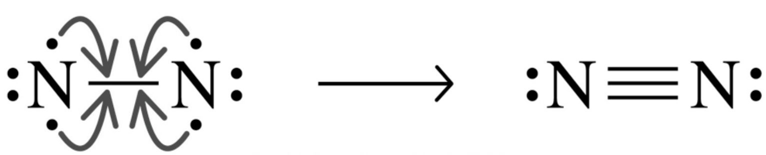


Some Illustrative Compounds

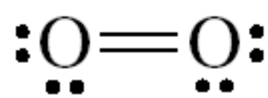


The covalent bond in which one pair of electrons is shared is called a ***single bond***. Multiple bonds can also form:





•Lewis structures are a useful ***tool***, but they do not always represent molecules correctly, even when the Lewis structure is plausible.



Polar Covalent Bonds and Electronegativity

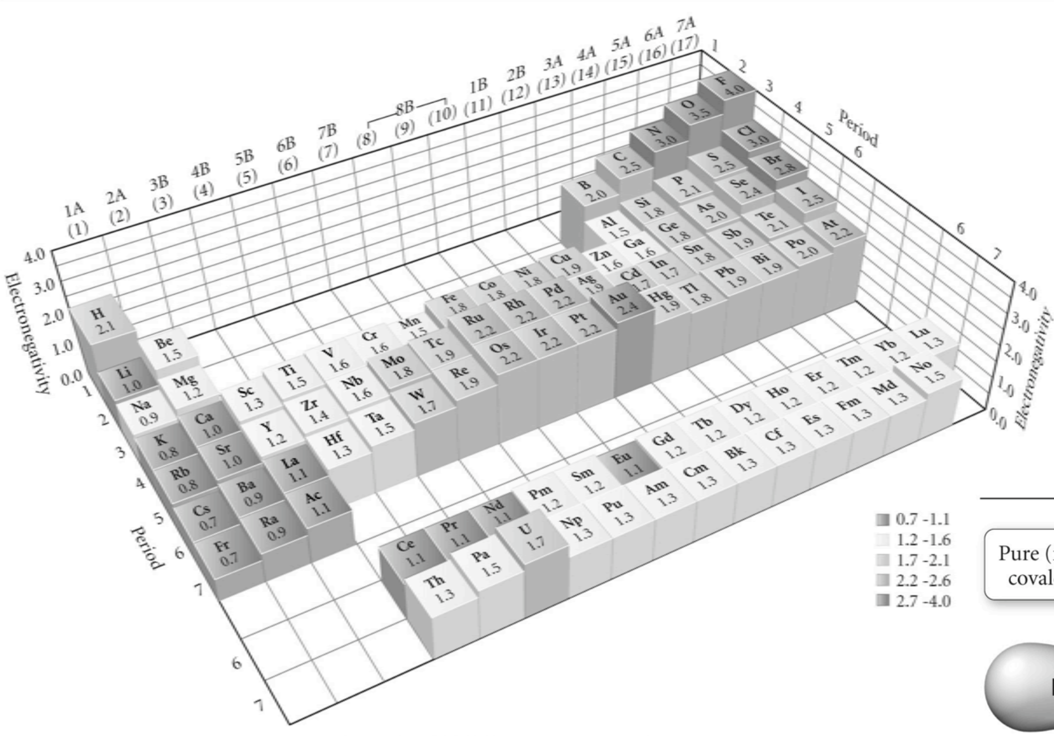
Electronegativity (**EN**) is a measure of the ability of an atom to attract its bonding electrons to itself.

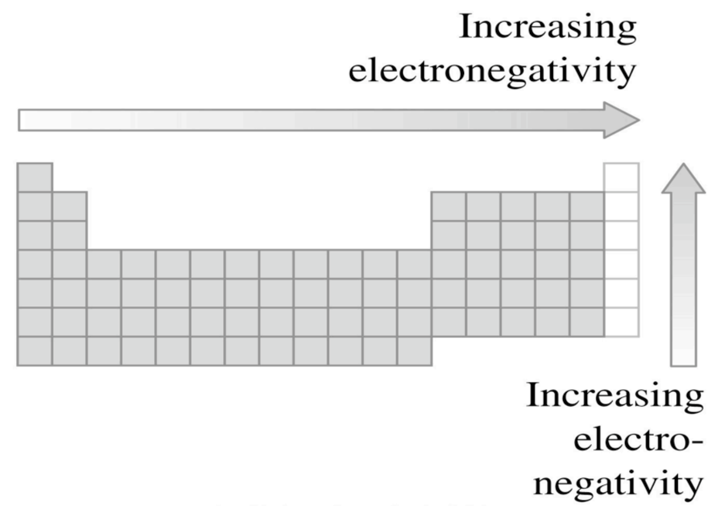
EN is related to ionization energy and electron affinity.

The greater the EN of an atom in a molecule, the more strongly the atom attracts the electrons in a covalent bond.

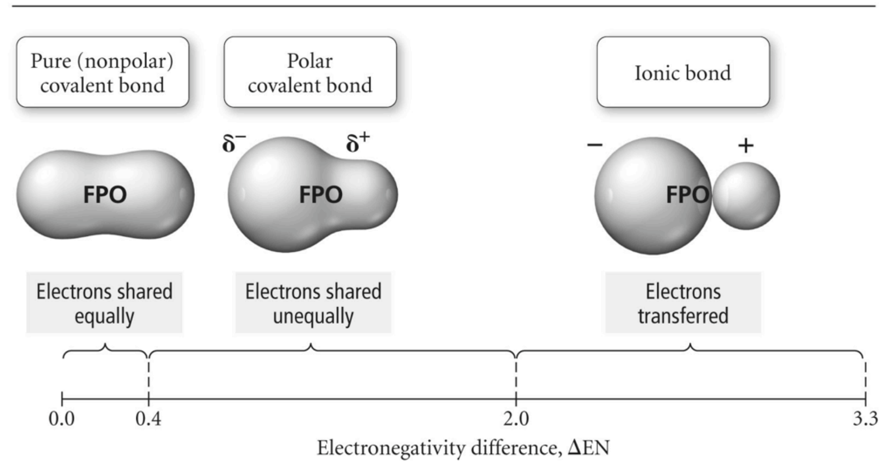
Pauling's Electronegativities

Trends in Electronegativity



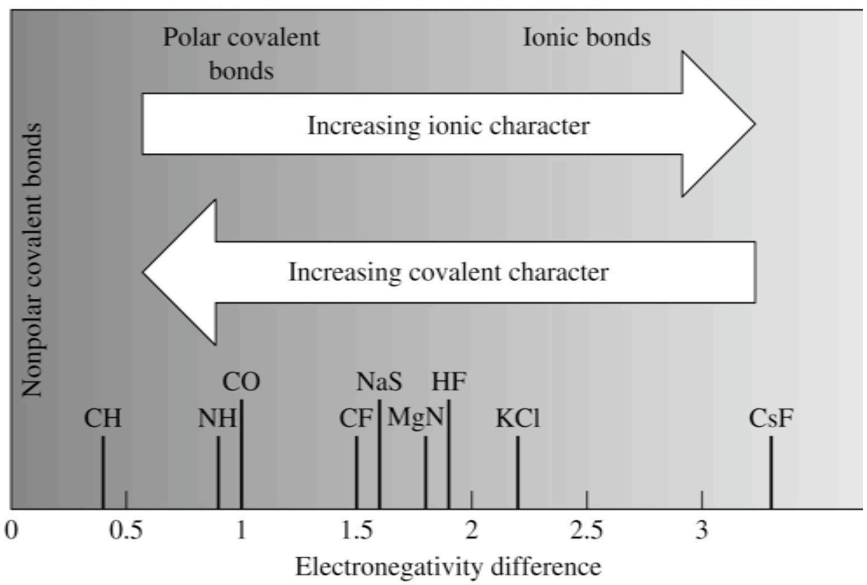


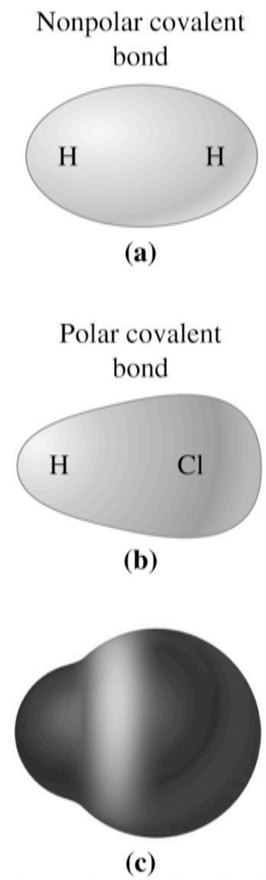
The Continuum of Bond Types



Electronegativity Difference and Bond Type

Identical atoms have the same electronegativity and share a bonding electron pair ***equally***.
The bond is a **nonpolar** covalent bond.
When electronegativities differ significantly, electron pairs are shared ***unequally***.
The electrons are drawn closer to the atom of higher electronegativity; the bond is a **polar** covalent bond.
With still larger differences in electronegativity, electrons may be completely transferred from metal to nonmetal atoms to form **ionic bonds**.





Use electronegativity values to arrange the following bonds in order of increasing polarity: Br—Cl, Cl—Cl, Cl—F, H—Cl, I—Cl

$$\overset{\delta+}{\mathrm{H}}-\overset{\delta-}{\mathrm{Cl}}$$

$$\mathrm{H}-\mathrm{Cl}$$

Writing Lewis Structures: Skeletal Structures

The skeletal structure shows the arrangement of atoms.

Hydrogen atoms are ***terminal atoms*** (bonded to only one other atom).

The ***central atom*** of a structure usually has the ***lowest*** electronegativity.

In oxoacids ($HClO_4$, HNO_3, etc.) hydrogen atoms are usually bonded to ***oxygen*** atoms.

Molecules and polyatomic ions usually have compact, symmetrical structures.

Writing Lewis Structures: A Method

Determine the total number of valence electrons.

Write a plausible skeletal structure and connect the atoms by single dashes (covalent bonds).

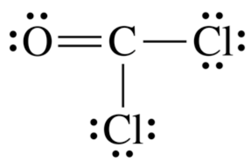
Place pairs of electrons as lone pairs around the terminal atoms to give each terminal atom (except H) an octet.

Assign any remaining electrons as lone pairs around the central atom.

If necessary (if there are not enough electrons), move one or more lone pairs of electrons from a terminal atom to form a multiple bond to the central atom.

NF_3 $COCl_2$ ClO_3^-

Formal charge is the difference between the number of valence electrons in a free (uncombined) atom and the number of electrons assigned to that atom when bonded to other atoms in a Lewis structure.
Formal charge is a ***hypothetical*** quantity; a useful tool.
Usually, the ***most plausible*** Lewis structure is one with no formal charges.
When formal charges are required, they should be as small as possible.
Negative formal charges should appear on the most electronegative atoms.
Adjacent atoms in a structure should not carry formal charges of the same sign.



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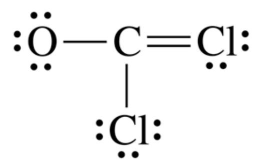

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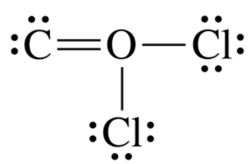
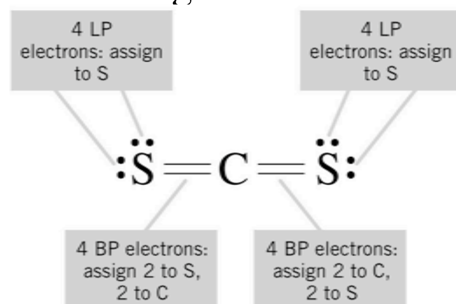
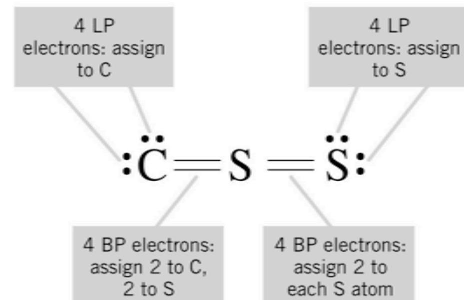


(c)



	S	C	S
Valence electrons	6	4	6
Electrons assigned	6	4	6
Formal charge	0	0	0

(a)

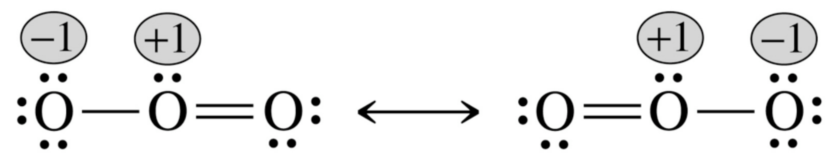


	C	S	S
Valence electrons	4	6	6
Electrons assigned	6	4	6
Formal charge	−2	+2	0

(b)

Resonance: Delocalized Bonding

When a molecule or ion can be represented by two or more plausible Lewis structures that differ ***only in the distribution of electrons***, the true structure is a composite, or hybrid, of them.
The different plausible structures are called ***resonance structures***.
The actual molecule or ion that is a hybrid of the resonance structures is called a ***resonance hybrid***.
Electrons that are part of the resonance hybrid are spread out over several atoms and are referred to as being ***delocalized***.



SO_3

Molecules that Don't Follow the Octet Rule

Molecules with an ***odd number*** of valence electrons have at least one of them unpaired and are called ***free radicals***.

Some molecules have ***incomplete octets***. These are usually compounds of Be, B, or Al; they generally have some unusual bonding characteristics, and are often quite reactive.

Some compounds have ***expanded valence shells***, which means that the central atom has more than eight electrons around it.

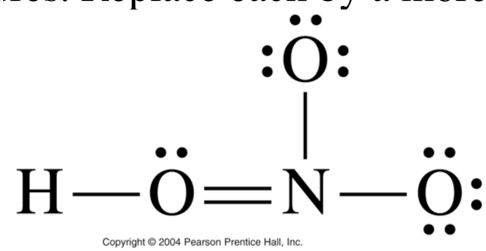
A central atom can have expanded valence if it is in the third period or lower (i.e., S, Cl, P).

BrF_5

Indicate the error in each of the following Lewis structures. Replace each by a more acceptable structure(s).

a.

b.



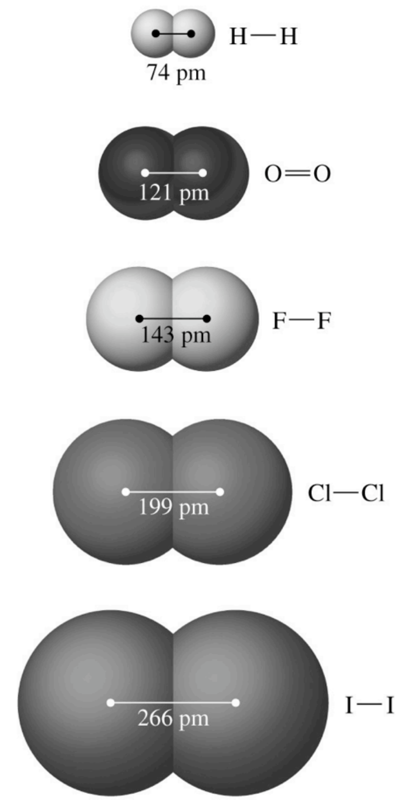
Bond Order and Bond Length

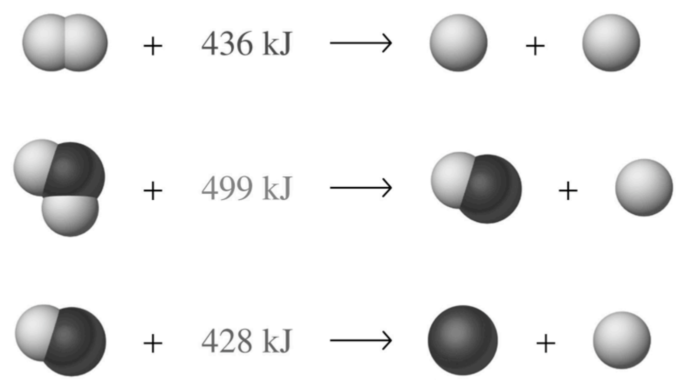
Bond order is the number of shared electron pairs in a bond.
A single bond has BO = 1, a double bond has BO = 2, etc.
Bond length is the distance between the nuclei of two atoms joined by a covalent bond.
Bond length depends on the particular atoms in the bond and on the bond order.
Bond-dissociation energy (***D***) is the energy required to break one mole of a particular type of covalent bond in a *gas*-phase compound.
Energies of some bonds can differ from compound to compound, so we use an ***average*** bond energy.

Table 9.1 Some Representative Bond Lengths and Bond Energies

Bond	Bond Length, pm	Bond Energy,[a] kJ/mol	Bond	Bond Length, pm	Bond Energy,[a] kJ/mol
H—H	74	436	C—O	143	360
H—C	110	414	C=O	120	736[b]
H—N	100	389	C—Cl	178	339
H—O	97	464	N—N	145	163
H—S	132	368	N=N	123	418
H—F	92	565	N≡N	110	946
H—Cl	127	431	N—O	136	222
H—Br	141	364	N=O	120	590
H—I	161	297	O—O	145	142
C—C	154	347	O=O	121	498
C=C	134	611	F—F	143	159
C≡C	120	837	Cl—Cl	199	243
C—N	147	305	Br—Br	228	193
C=N	128	615	I—I	266	151
C≡N	116	891			

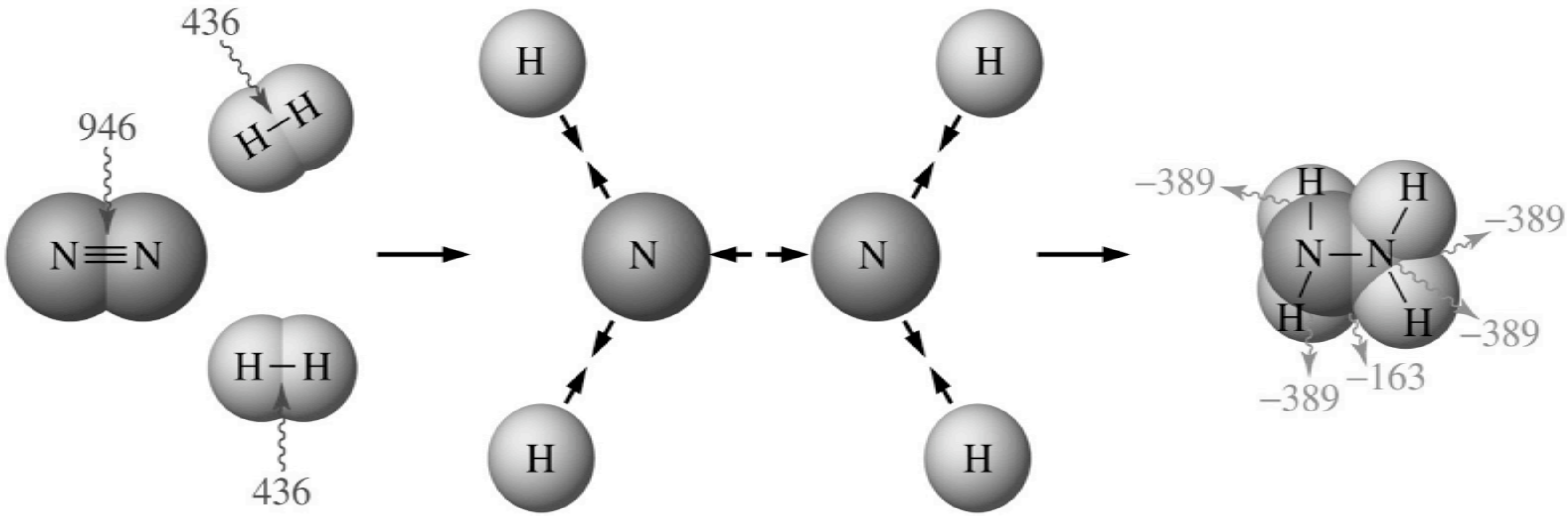
[a] Bond-dissociation energy for the bonds in diatomic molecules (H_2, HF, HCl, HBr, HI, N_2, O_2, F_2, Cl_2, Br_2 and I_2) and average bond energies for the other bonds.
[b] The value for the CO bond in CO_2 is considerably different: 799 kJ/mol.





Calculations Involving Bond Energies

For the reaction $N_2(g) + 2\,H_2(g) \rightarrow N_2H_4(g)$ to occur …



$$\Delta H = (+946\text{ kJ}) + 2(+436\text{ kJ}) + (-163\text{ kJ}) + 4(-389\text{ kJ})$$

$$\Delta H_{rxn} = \sum(\underbrace{\Delta H\text{'s bonds broken}}_{\text{Positive}}) + \sum(\underbrace{\Delta H\text{'s bonds formed}}_{\text{Negative}})$$