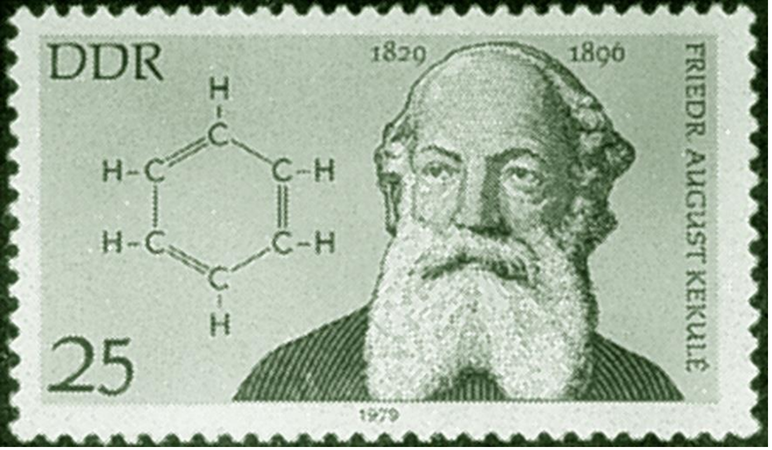
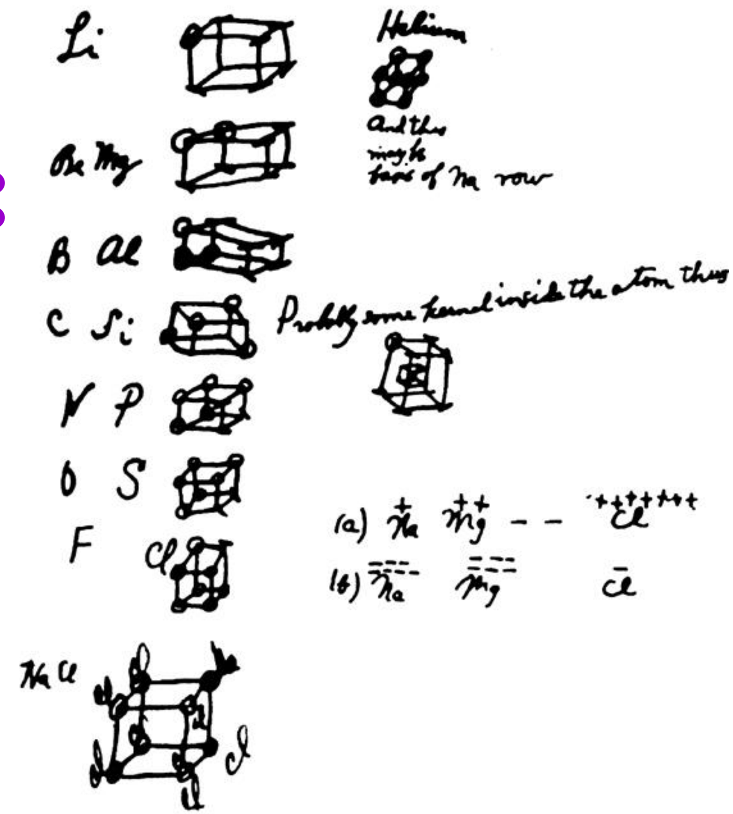


Chemical Bonding I: Basic Concepts

Chapter 9



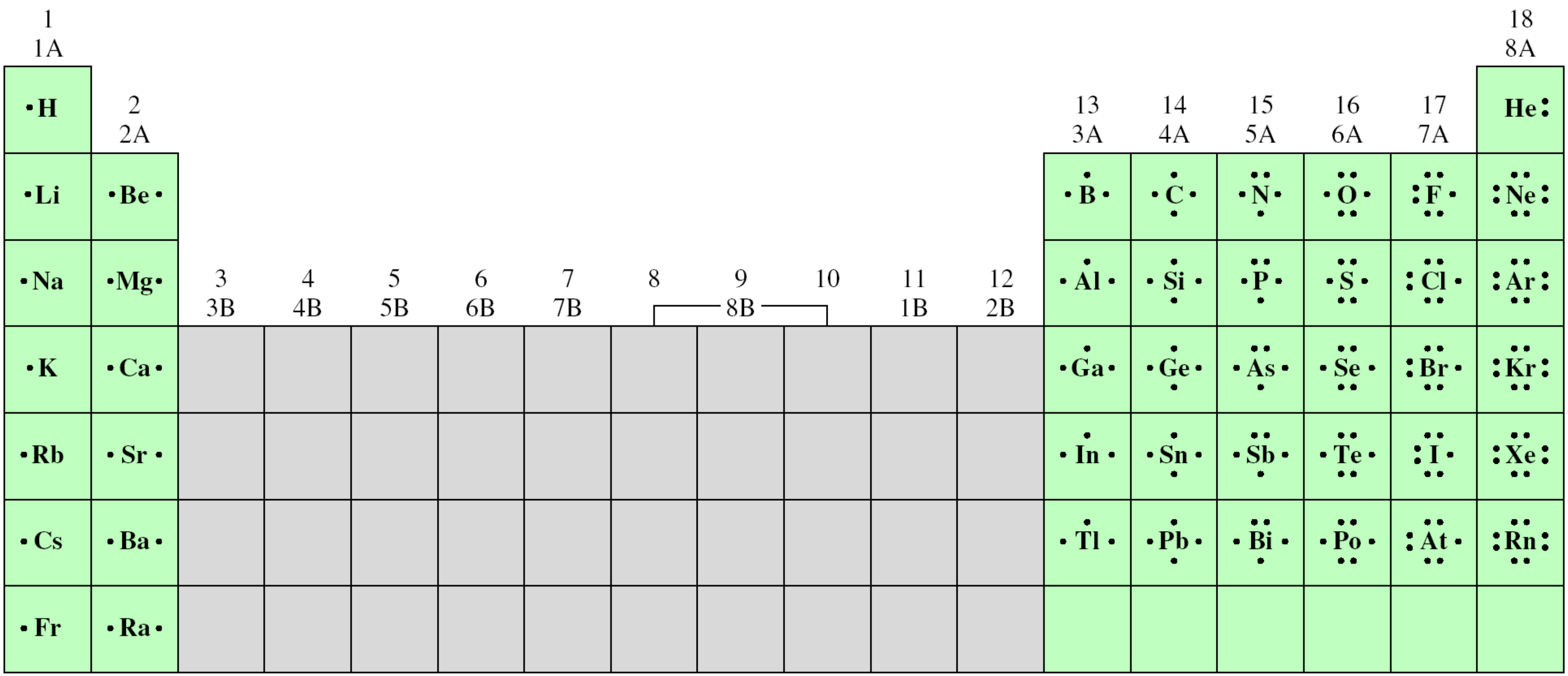
Valence Electrons

Valence electrons are the outer shell electrons of an atom.

The valence electrons are the electrons that particpate in chemical bonding.

Group	e^- configuration	# of valence e^-
1A	ns^1	1
2A	ns^2	2
3A	ns^2np^1	3
4A	ns^2np^2	4
5A	ns^2np^3	5
6A	ns^2np^4	6
7A	ns^2np^5	7

Lewis Dot Symbols for the Representative Elements & Noble Gases



The Ionic Bond

Ionic bond is the electrostatic force that holds ions together in an ionic compound.

$$\cdot\mathrm{Li} + \cdot\ddot{\underset{\cdot\cdot}{\mathrm{F}}}: \longrightarrow \mathrm{Li}^+\,:\ddot{\underset{\cdot\cdot}{\mathrm{F}}}:^-$$

$1s^22s^1$ $1s^22s^22p^5$ [He] $1s^2$ [Ne] $1s^22s^22p^6$

$$\cdot\mathrm{Li} \longrightarrow \mathrm{Li}^+ + e^-$$

$$e^- + \cdot\ddot{\underset{\cdot\cdot}{\mathrm{F}}}: \longrightarrow :\ddot{\underset{\cdot\cdot}{\mathrm{F}}}:^-$$

$$\mathrm{Li}^+ + :\ddot{\underset{\cdot\cdot}{\mathrm{F}}}:^- \longrightarrow \mathrm{Li}^+\,:\ddot{\underset{\cdot\cdot}{\mathrm{F}}}:^-$$

Electrostatic (Lattice) Energy

Lattice energy (U) is the energy required to completely separate one mole of a solid ionic compound into gaseous ions.

$$E = k\frac{Q_+Q_-}{r}$$

E is the potential energy

Q_+ is the charge on the cation

Q_- is the charge on the anion

r is the distance between the ions

Lattice energy increases as ***Q increases*** and/or as ***r decreases***.

Compound	Lattice Energy (kJ/mol)	
MgF_2	2957	*Q*: +2,-1
MgO	3938	*Q*: +2,-2
LiF	1036	r F^- < r Cl^-
LiCl	853	

TABLE 9.1 Lattice Energies and Melting Points of Some Alkali Metal and Alkaline Earth Metal Halides and Oxides

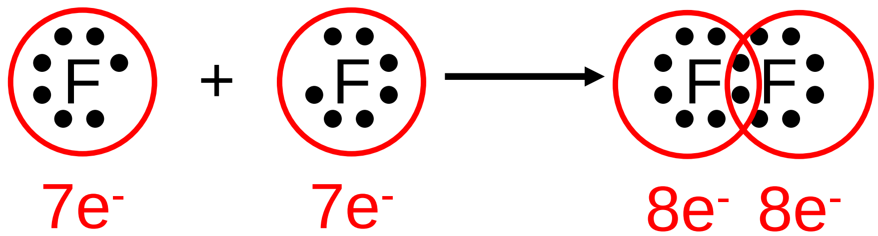
Compound	Lattice Energy (kJ/mol)	Melting Point (°C)
LiF	1017	845
LiCl	828	610
LiBr	787	550
LiI	732	450
NaCl	788	801
NaBr	736	750
NaI	686	662
KCl	699	772
KBr	689	735
KI	632	680
$MgCl_2$	2527	714
Na_2O	2570	Sub*
MgO	3890	2800

*Na_2O sublimes at 1275°C.

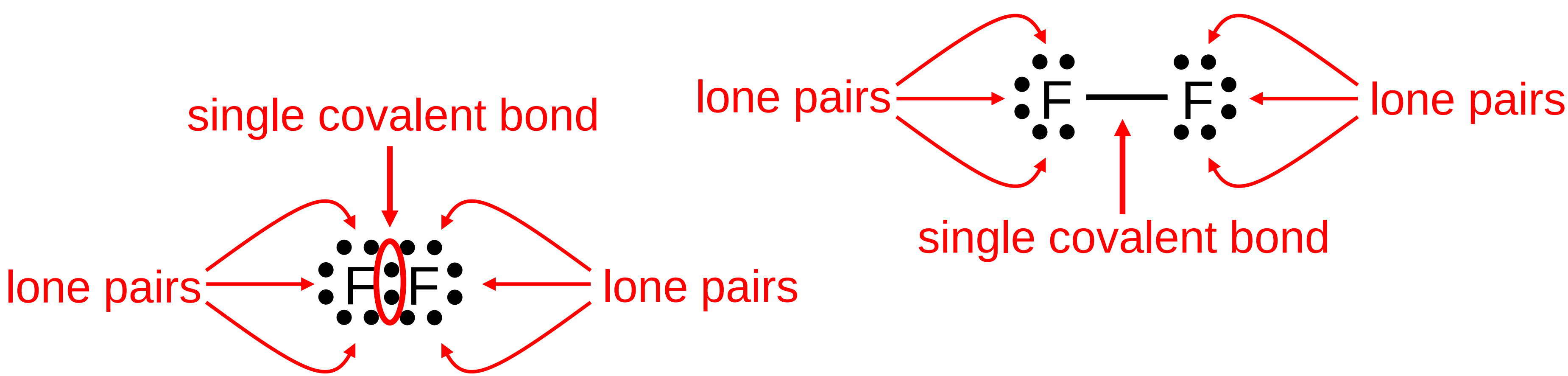
Covalent Bond

A ***covalent bond*** is a chemical bond in which two or more electrons are shared by two atoms.

Why should two atoms share electrons?

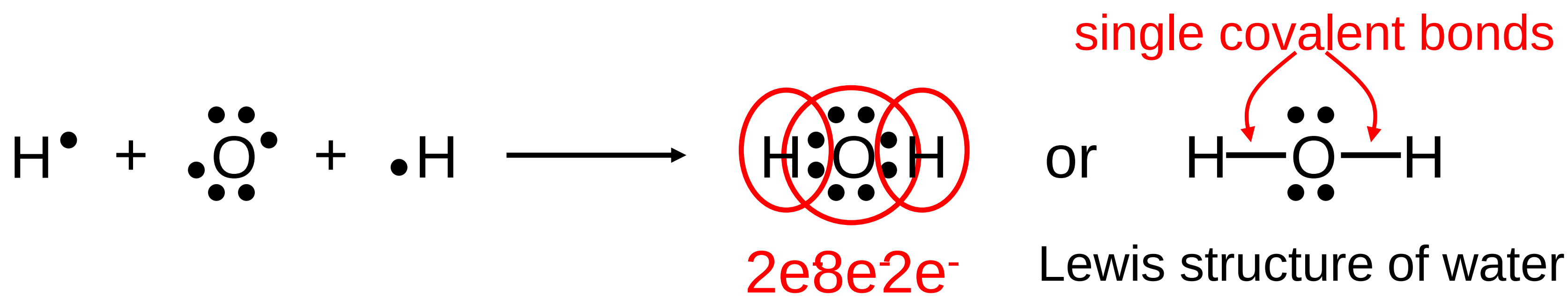


Lewis structure of F_2

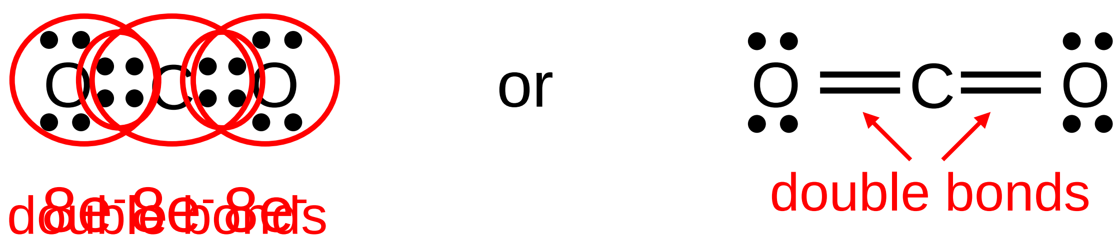


Covalent Bond: Single, Double & Triple Bonds

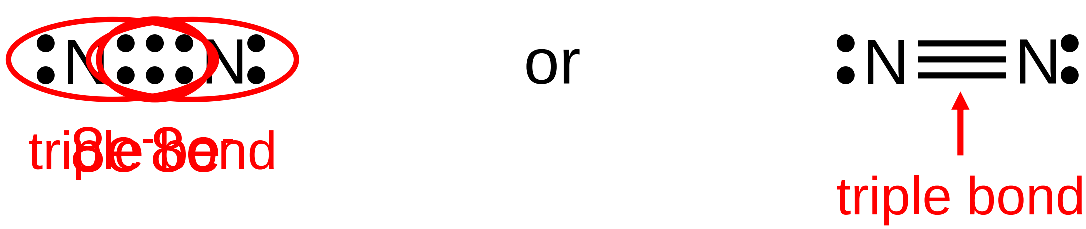
Single bond – two atoms share one pair of electron



Double bond – two atoms share two pairs of electron



Triple bond – two atoms share three pairs of electron



Lengths of Covalent Bonds

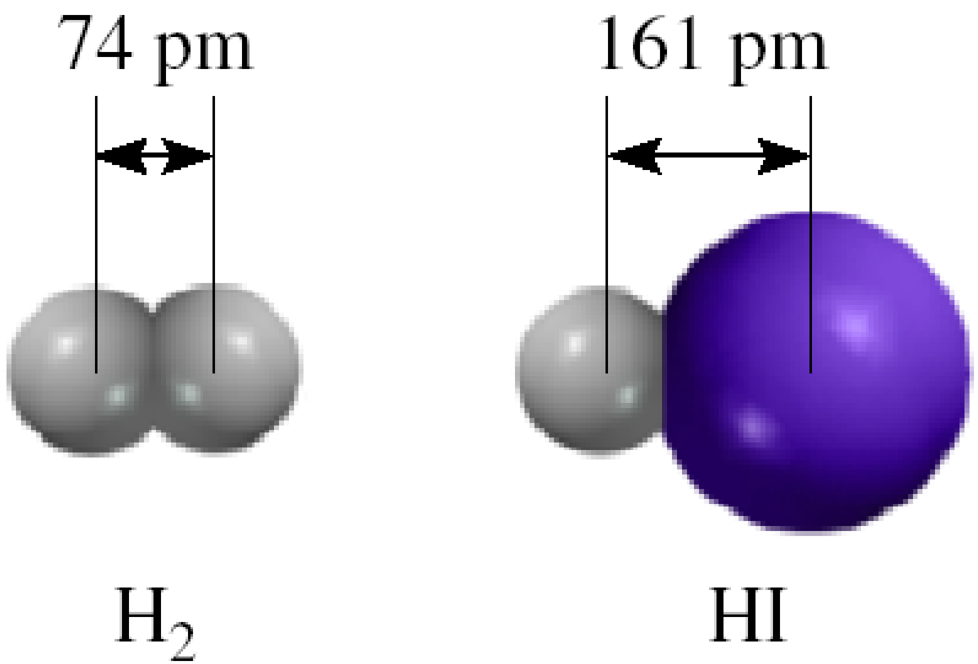


TABLE 9.2

Average Bond Lengths of Some Common Single, Double, and Triple Bonds

Bond Type	Bond Length (pm)
C—H	107
C—O	143
C═O	121
C—C	154
C═C	133
C≡C	120
C—N	143
C═N	138
C≡N	116
N—O	136
N═O	122
O—H	96

Bond Lengths

Triple bond < Double Bond < Single Bond

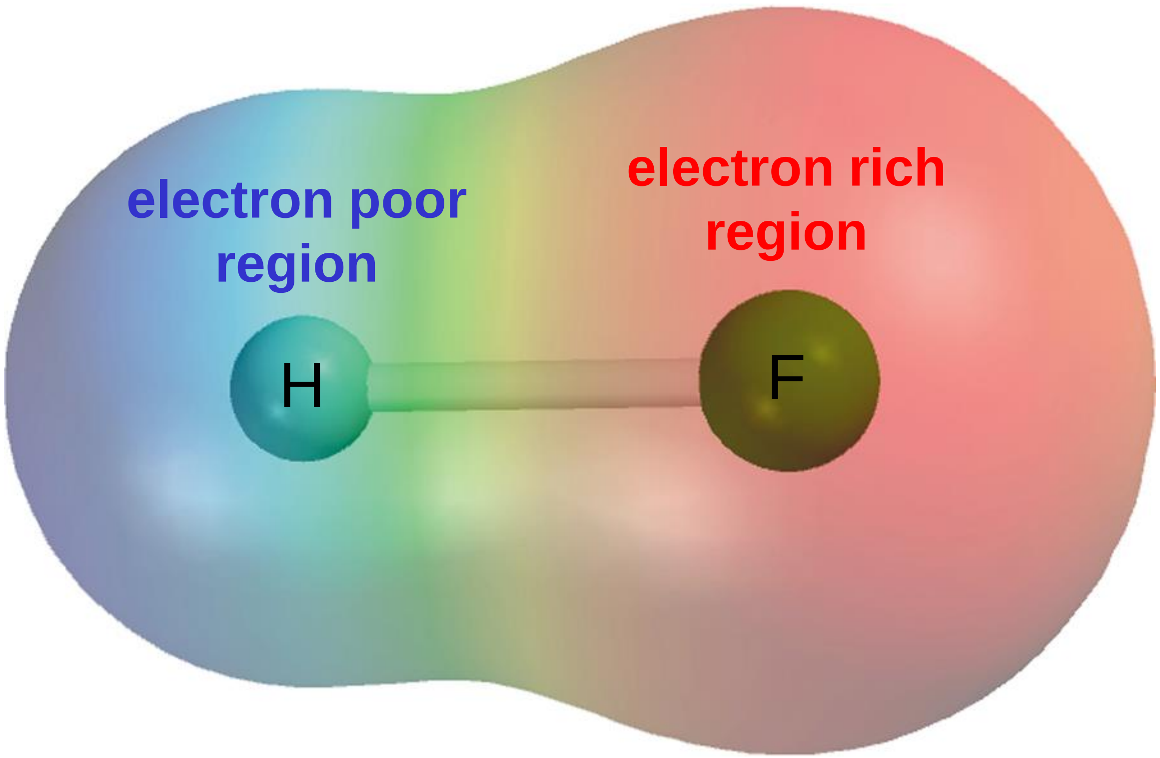
TABLE 9.3 Comparison of Some General Properties of an Ionic Compound and a Covalent Compound

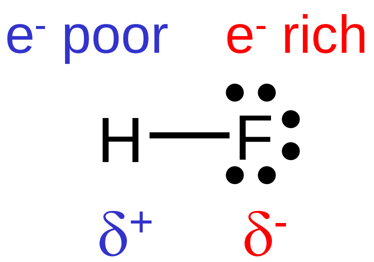
Property	NaCl	CCl_4
Appearance	White solid	Colorless liquid
Melting point (°C)	801	−23
Molar heat of fusion* (kJ/mol)	30.2	2.5
Boiling point (°C)	1413	76.5
Molar heat of vaporization* (kJ/mol)	600	30
Density (g/cm^3)	2.17	1.59
Solubility in water	High	Very low
Electrical conductivity		
Solid	Poor	Poor
Liquid	Good	Poor

*Molar heat of fusion and molar heat of vaporization are the amounts of heat needed to melt 1 mole of the solid and to vaporize 1 mole of the liquid, respectively.

Polar Covalent Bond or Polar Bond

Polar covalent bond or ***polar bond*** is a covalent bond with greater electron density around one of the two atoms.





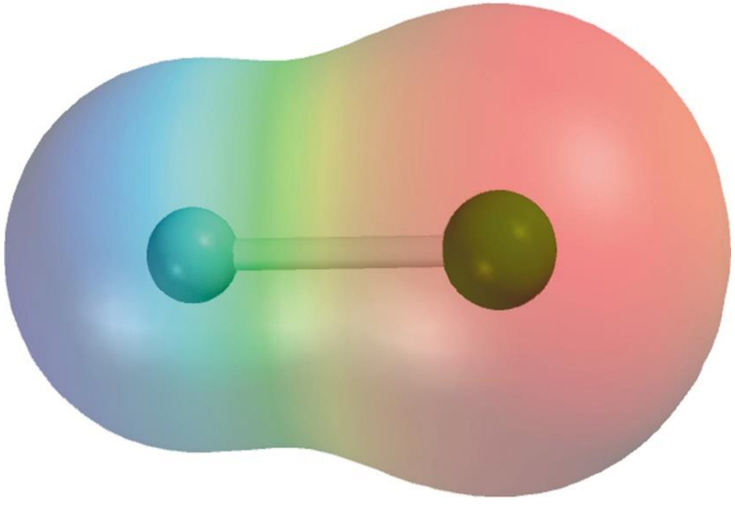
Electronegativity

Electronegativity is the ability of an atom to attract toward itself the electrons in a chemical bond.

Electron Affinity - **measurable**, Cl is highest

$$X_{(g)} + e^- \longrightarrow X^-_{(g)}$$

Electronegativity - **relative**, F is highest



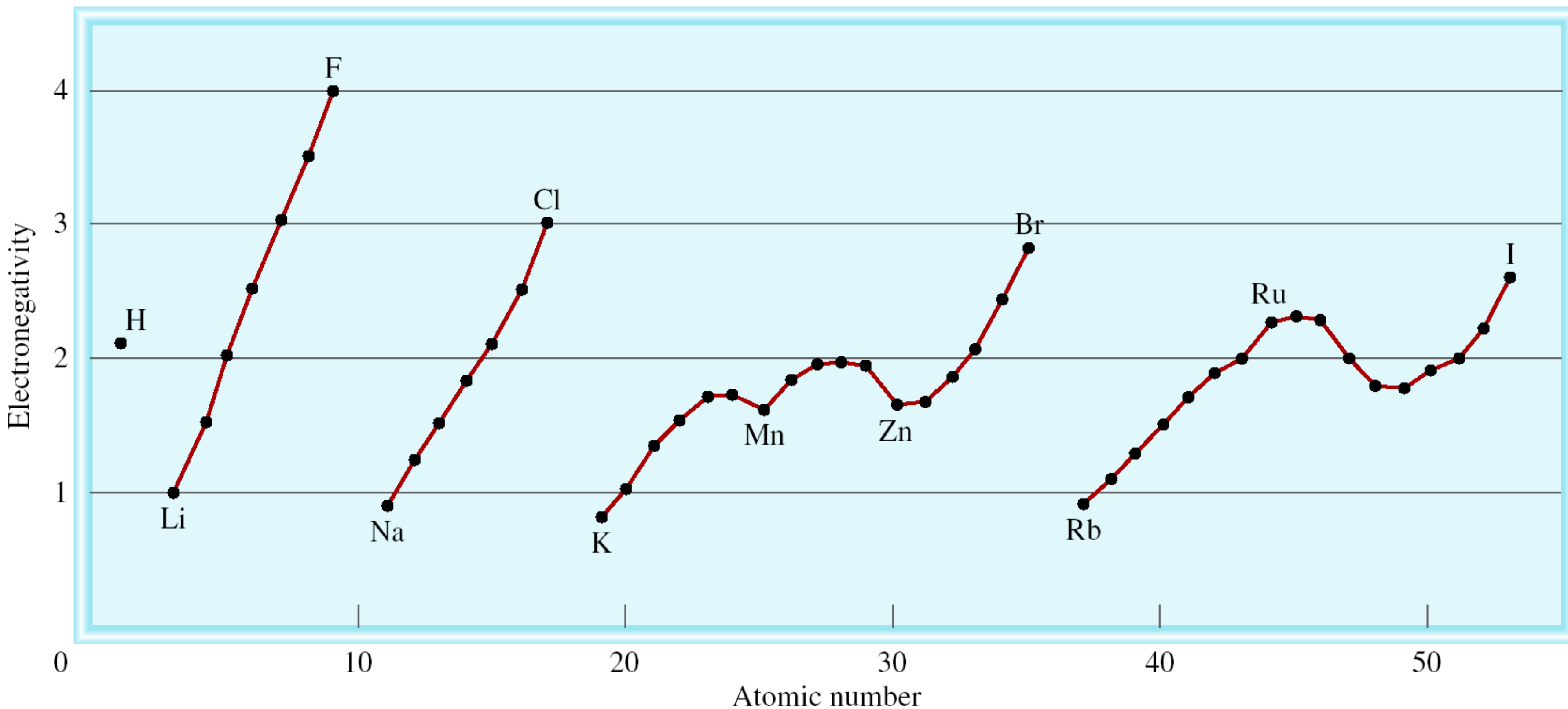
The Electronegativities of Common Elements

Increasing electronegativity

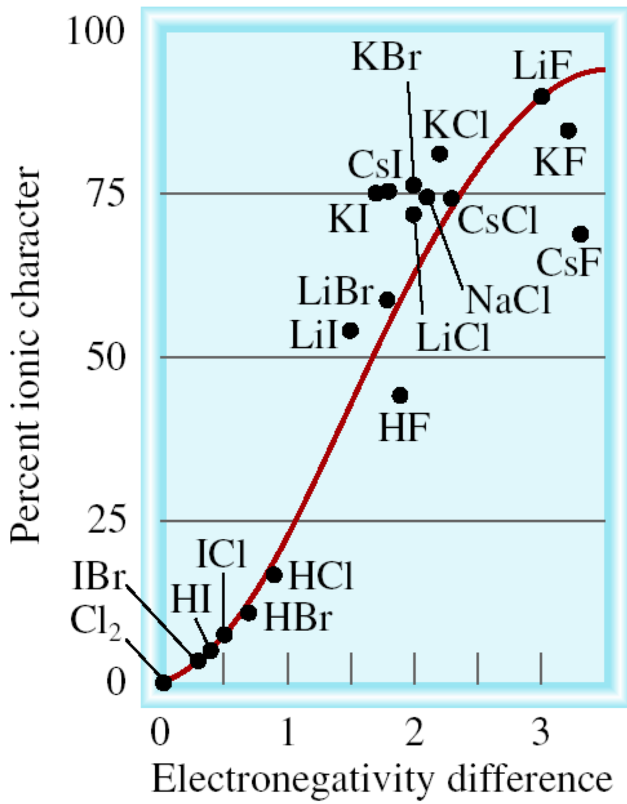
Increasing electronegativity

1A	2A	3B	4B	5B	6B	7B	8B	8B	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																

Variation of Electronegativity with Atomic Number



Classification of bonds by difference in electronegativity



Difference	Bond Type
0	Covalent
≥ 2	Ionic
0 < and <2	Polar Covalent

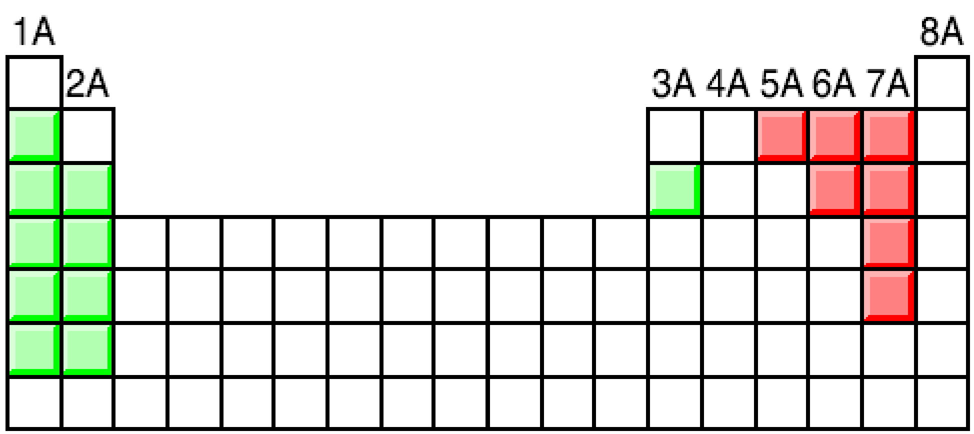
Increasing difference in electronegativity →

Covalent → Polar Covalent → Ionic

share e^- partial transfer of e^- transfer of e^-

Classify the following bonds as ionic, polar covalent, or covalent: The bond in CsCl; the bond in H_2S; and the NN bond in H_2NNH_2.

Cs – 0.7	Cl – 3.0	3.0 – 0.7 = 2.3	Ionic
H – 2.1	S – 2.5	2.5 – 2.1 = 0.4	Polar Covalent
N – 3.0	N – 3.0	3.0 – 3.0 = 0	Covalent



Writing Lewis Structures

1. Draw skeletal structure of compound showing what atoms are bonded to each other. Put least electronegative element in the center.
2. Count total number of valence electrons. Add 1 for each negative charge. Subtract 1 for each positive charge.
3. Complete an octet for all atoms ***except*** hydrogen.
4. If structure contains too many electrons, form double and triple bonds on central atom as needed.

Write the Lewis structure of nitrogen trifluoride (NF_3).

Step 1 – N is less electronegative than F, put N in center

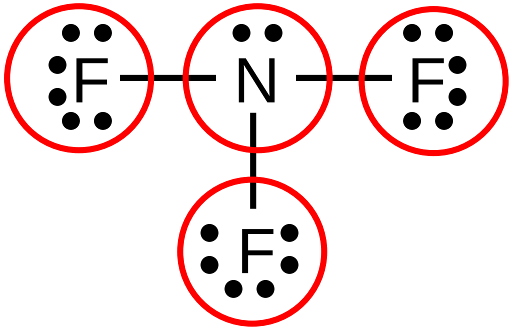
Step 2 – Count valence electrons N - 5 ($2s^22p^3$) and F - 7 ($2s^22p^5$)

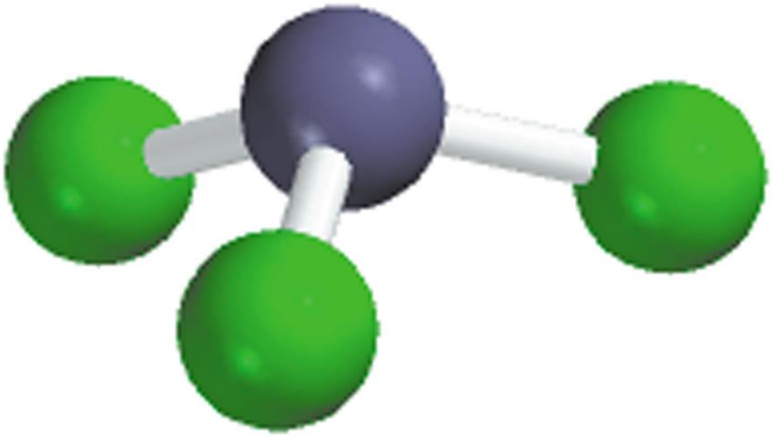
5 + (3 x 7) = 26 valence electrons

Step 3 – Draw single bonds between N and F atoms and complete octets on N and F atoms.

Step 4 - Check, are # of e^- in structure equal to number of valence e^- ?

3 single bonds (3x2) + 10 lone pairs (10x2) = 26 valence electrons





Write the Lewis structure of the carbonate ion (CO_3^{2-}).

Step 1 – C is less electronegative than O, put C in center

Step 2 – Count valence electrons C - 4 ($2s^22p^2$) and O - 6 ($2s^22p^4$)
-2 charge – $2e^-$

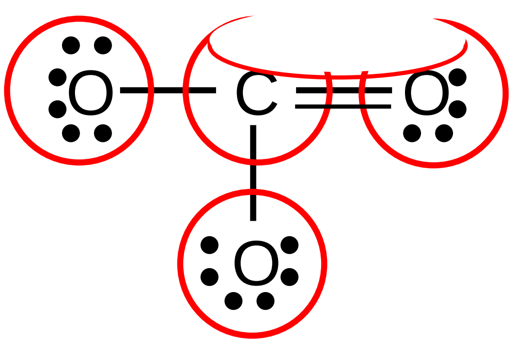
4 + (3 x 6) + 2 = 24 valence electrons

Step 3 – Draw single bonds between C and O atoms and complete octet on C and O atoms.

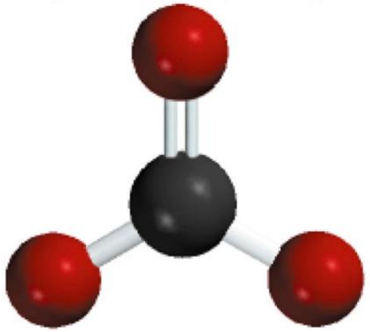
Step 4 – Check, are # of e^- in structure equal to number of valence e^- ?

3 single bonds (3x2) + 10 lone pairs (10x2) = 26 valence electrons

Step 5 – Too many electrons, form double bond and re-check # of e^-

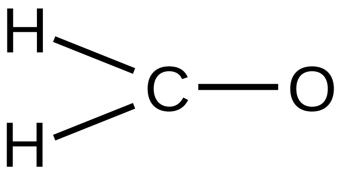


2 single bonds (2x2) =	4
1 double bond =	4
8 lone pairs (8x2) =	16
Total =	24



Formal Charge of an Atom

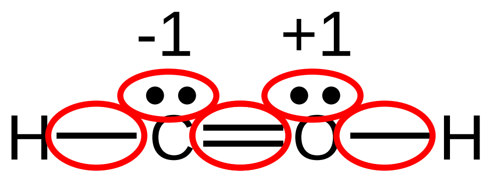
Two possible skeletal structures of formaldehyde (CH_2O)



An atom's ***formal charge*** is the difference between the number of valence electrons in an isolated atom and the number of electrons assigned to that atom in a Lewis structure.

$$\text{formal charge on an atom in a Lewis structure} = \text{total number of valence electrons in the free atom} - \text{total number of nonbonding electrons} - \frac{1}{2}\left(\text{total number of bonding electrons}\right)$$

The sum of the formal charges of the atoms in a molecule or ion must equal the charge on the molecule or ion.



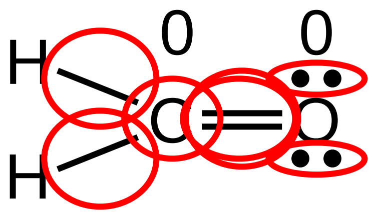
$$\begin{array}{r} C - 4\ e^- \\ O - 6\ e^- \\ 2H - 2\times1\ e^- \\ \hline 12\ e^- \end{array}$$

$$\begin{array}{r} \text{2 single bonds (2x2) = } 4 \\ \text{1 double bond = } 4 \\ \text{2 lone pairs (2x2) = } 4 \\ \hline \text{Total = } 12 \end{array}$$

formal charge on an atom in a Lewis structure = total number of valence electrons in the free atom - total number of nonbonding electrons - $\frac{1}{2}$ (total number of bonding electrons)

formal charge on C = 4 -2 -½ x 6 = -1

formal charge on O = 6 -2 -½ x 6 = +1



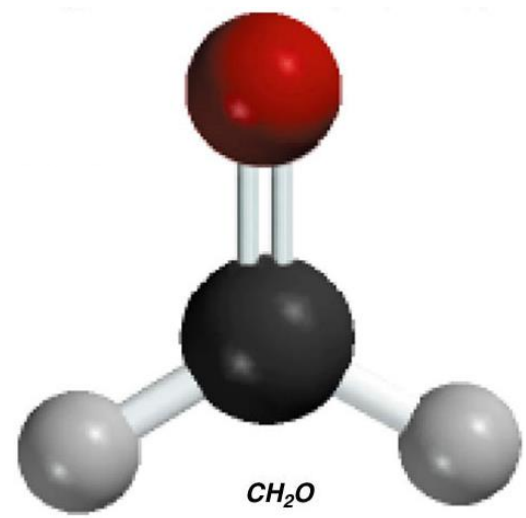
$$\begin{array}{r} C - 4\ e^- \\ O - 6\ e^- \\ 2H - 2x1\ e^- \\ \hline 12\ \ e^- \end{array}$$

$$\begin{array}{r} \text{2 single bonds (2x2) =}\ \ 4 \\ \text{1 double bond =}\ \ 4 \\ \text{2 lone pairs (2x2) =}\ \ 4 \\ \hline \text{Total = 12} \end{array}$$

$$\text{formal charge on an atom in a Lewis structure} = \text{total number of valence electrons in the free atom} - \text{total number of nonbonding electrons} - \frac{1}{2}\left(\text{total number of bonding electrons}\right)$$

formal charge on C $= 4 - 0 - ½ \times 8 = 0$

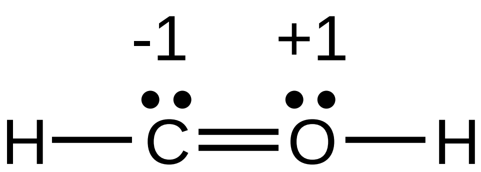
formal charge on O $= 6 - 4 - ½ \times 4 = 0$

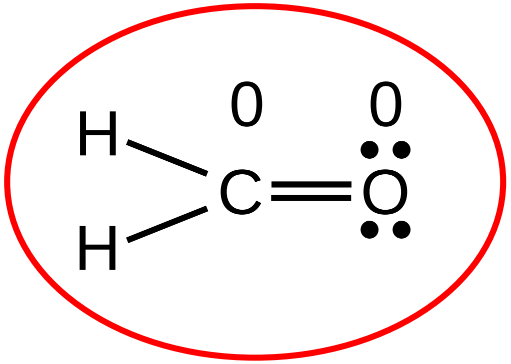


Formal Charge and Lewis Structures

1. For neutral molecules, a Lewis structure in which there are no formal charges is preferable to one in which formal charges are present.
2. Lewis structures with large formal charges are less plausible than those with small formal charges.
3. Among Lewis structures having similar distributions of formal charges, the most plausible structure is the one in which negative formal charges are placed on the more electronegative atoms.

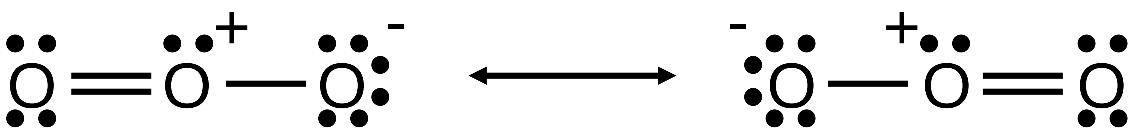
Which is the most likely Lewis structure for CH_2O?

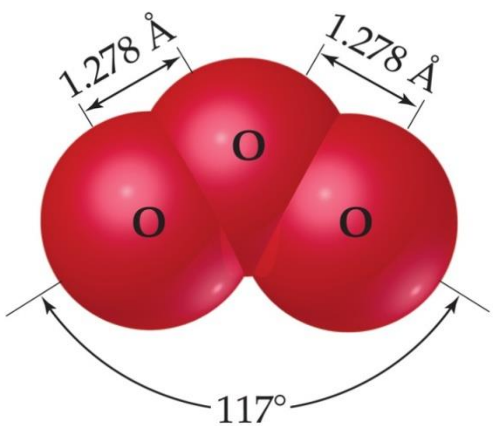


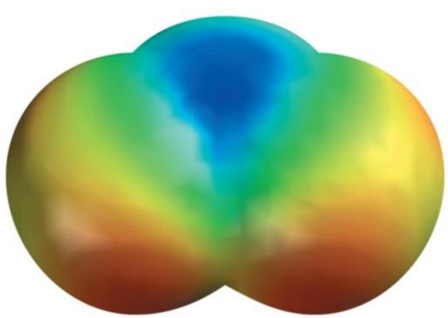


Resonance Structures

A ***resonance structure*** is one of two or more Lewis structures for a single molecule that cannot be represented accurately by only one Lewis structure.

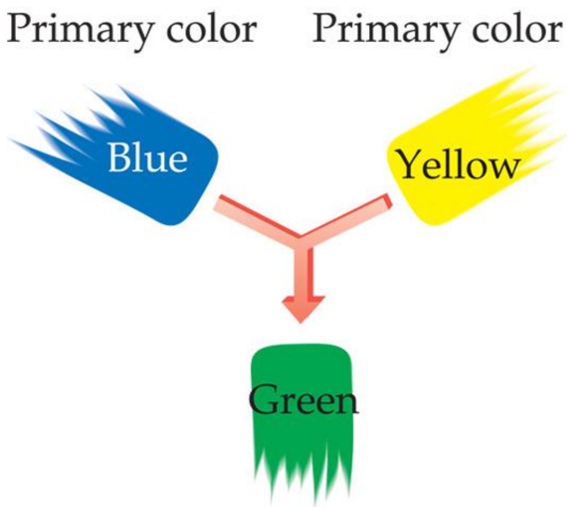




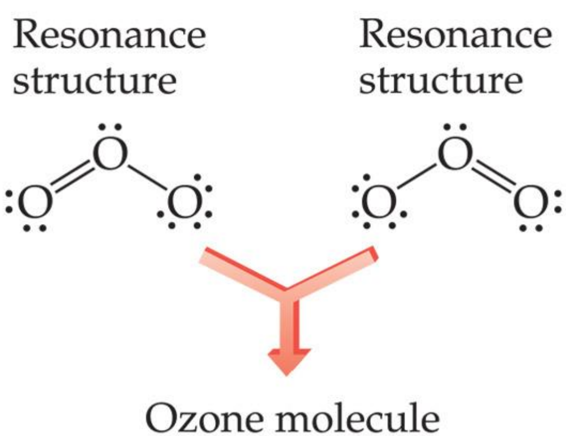


- But this is at odds with the true, observed structure of ozone, in which…
  - …both O-O bonds are the same length.
  - …both outer oxygens have a charge of -1/2.

Resonance Structures



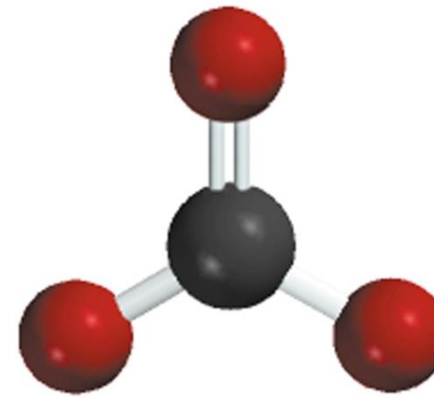
…just as green is a synthesis of blue and yellow…

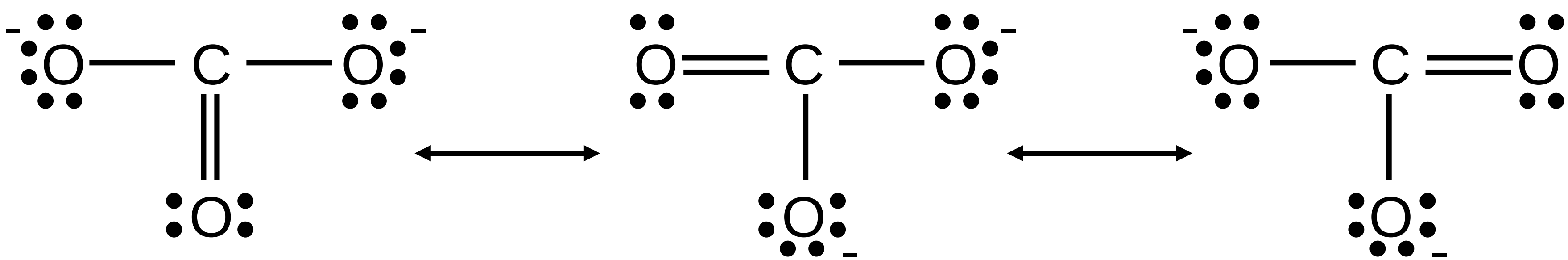


…ozone is a synthesis of these two resonance structures.

Resonance Structures

What are the resonance structures of the carbonate (CO_3^{2-}) ion?





Exceptions to the Octet Rule

The Incomplete Octet

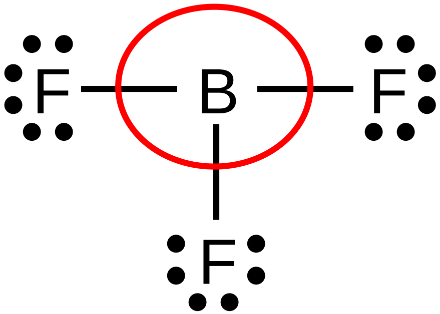
BeH_2

Be – 2e$^-$
2H – 2x1e$^-$
4e$^-$

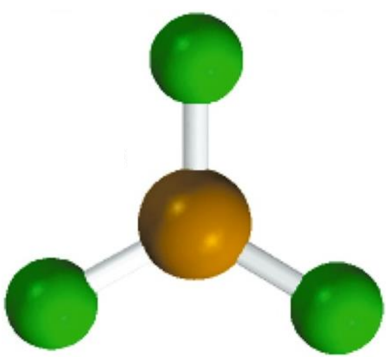
H — Be — H

BF_3

B – 3e$^-$
3F – 3x7e$^-$
24e$^-$



3 single bonds (3x2) = 6
9 lone pairs (9x2) = 18
Total = 24

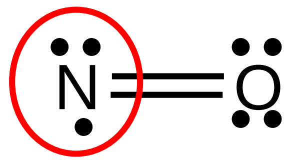


Exceptions to the Octet Rule

Odd-Electron Molecules

NO

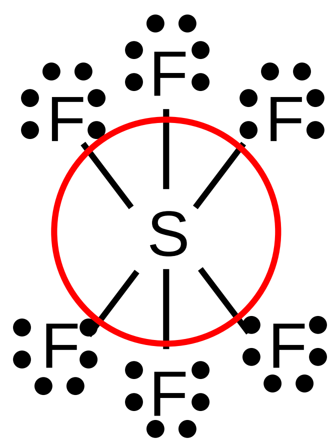
$$\begin{array}{r} N - 5e^- \\ O - 6e^- \\ \hline 11e^- \end{array}$$



The Expanded Octet (central atom with principal quantum number n > 2)

SF_6

$$\begin{array}{r} S - 6e^- \\ 6F - 42e^- \\ \hline 48e^- \end{array}$$



6 single bonds (6x2) = 12
18 lone pairs (18x2) = 36
Total = 48

Bond Enthalpy

The enthalpy change required to break a particular bond in one mole of gaseous molecules is the ***bond enthalpy***.

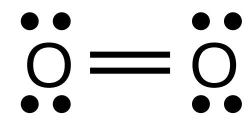
Bond Enthalpy

$H_{2\,(g)} \longrightarrow H_{(g)} + H_{(g)} \quad \Delta H^{o} = 436.4 \text{ kJ}$

$Cl_{2\,(g)} \longrightarrow Cl_{(g)} + Cl_{(g)} \quad \Delta H^{o} = 242.7 \text{ kJ}$

$HCl_{(g)} \longrightarrow H_{(g)} + Cl_{(g)} \quad \Delta H^{o} = 431.9 \text{ kJ}$

$O_{2\,(g)} \longrightarrow O_{(g)} + O_{(g)} \quad \Delta H^{o} = 498.7 \text{ kJ}$



$N_{2\,(g)} \longrightarrow N_{(g)} + N_{(g)} \quad \Delta H^{o} = 941.4 \text{ kJ}$

Bond Enthalpies

Single bond < Double bond < Triple bond

Average Bond Enthalpy

Average ***bond enthapy*** in polyatomic molecules

$$H_2O_{(g)} \longrightarrow H_{(g)} + OH_{(g)} \quad \Delta H^0 = 502\ kJ$$

$$OH_{(g)} \longrightarrow H_{(g)} + O_{(g)} \quad \Delta H^0 = 427\ kJ$$

$$\text{Average OH bond enthalpy} = \frac{502 + 427}{2} = 464\ kJ$$

Bond Enthalpies of Diatomic Molecules and Average Bond Enthalpies in polyatomic molecules

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

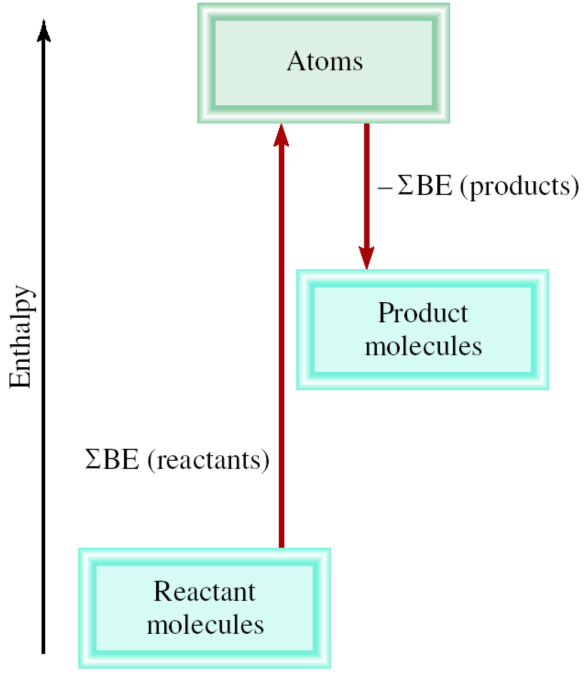
Bond	Bond Enthalpy (kJ/mol)	Bond	Bond Enthalpy (kJ/mol)
H—H	436.4	C—S	255
H—N	393	C═S	477
H—O	460	N—N	193
H—S	368	N═N	418
H—P	326	N≡N	941.4
H—F	568.2	N—O	176
H—Cl	431.9	N═O	607
H—Br	366.1	O—O	142
H—I	298.3	O═O	498.7
C—H	414	O—P	502
C—C	347	O═S	469
C═C	620	P—P	197
C≡C	812	P═P	489
C—N	276	S—S	268
C═N	615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

*Bond enthalpies for diatomic molecules (in color) have more significant figures than bond enthalpies for bonds in polyatomic molecules because the bond enthalpies of diatomic molecules are directly measurable quantities and not averaged over many compounds.
†The C═O bond enthalpy in CO_2 is 799 kJ/mol.

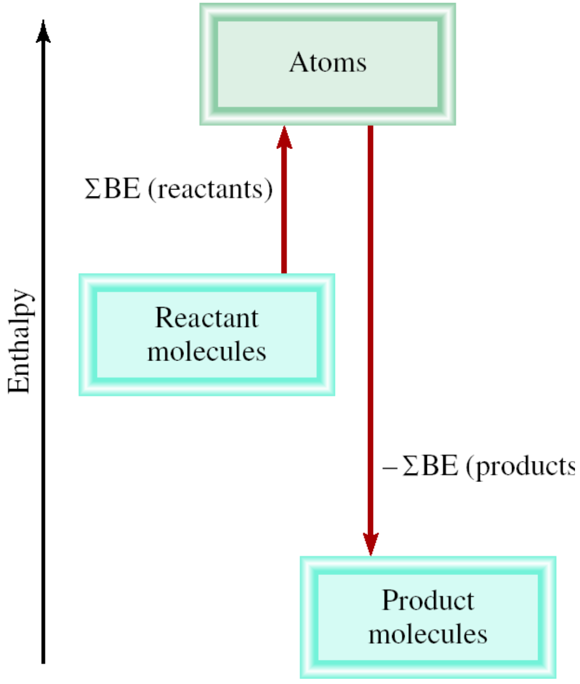
Bond Enthalpies (BE) and Enthalpy changes in reactions

Imagine reaction proceeding by breaking all bonds in the reactants and then using the gaseous atoms to form all the bonds in the products.

$$\Delta H^o = \text{total energy input} - \text{total energy released}$$
$$= \Sigma BE(\text{reactants}) - \Sigma BE(\text{products})$$

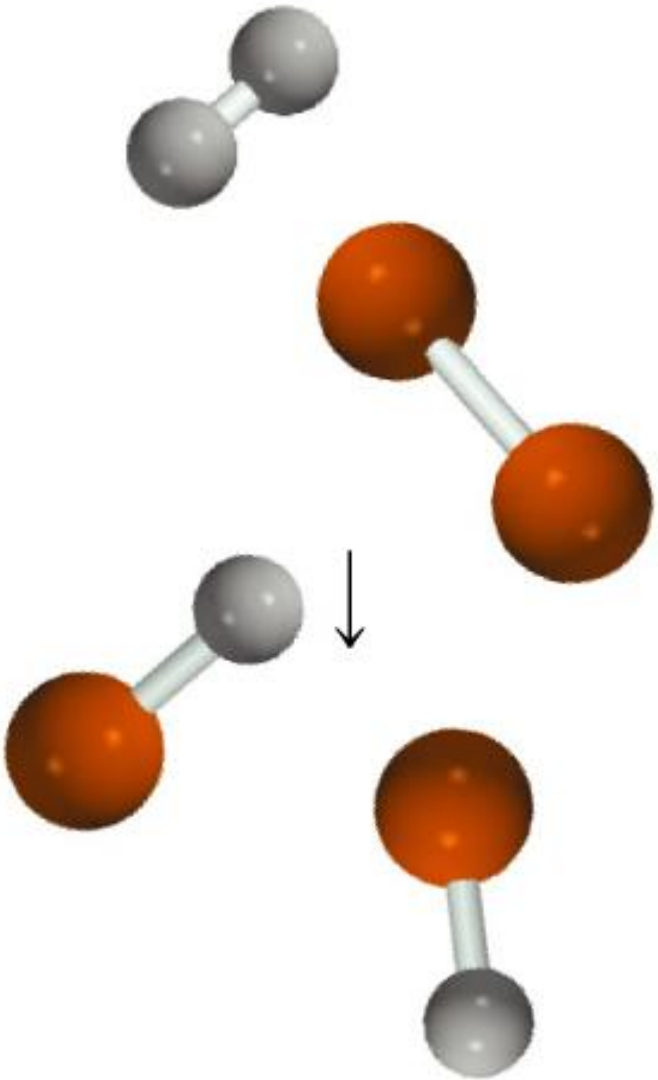


endothermic

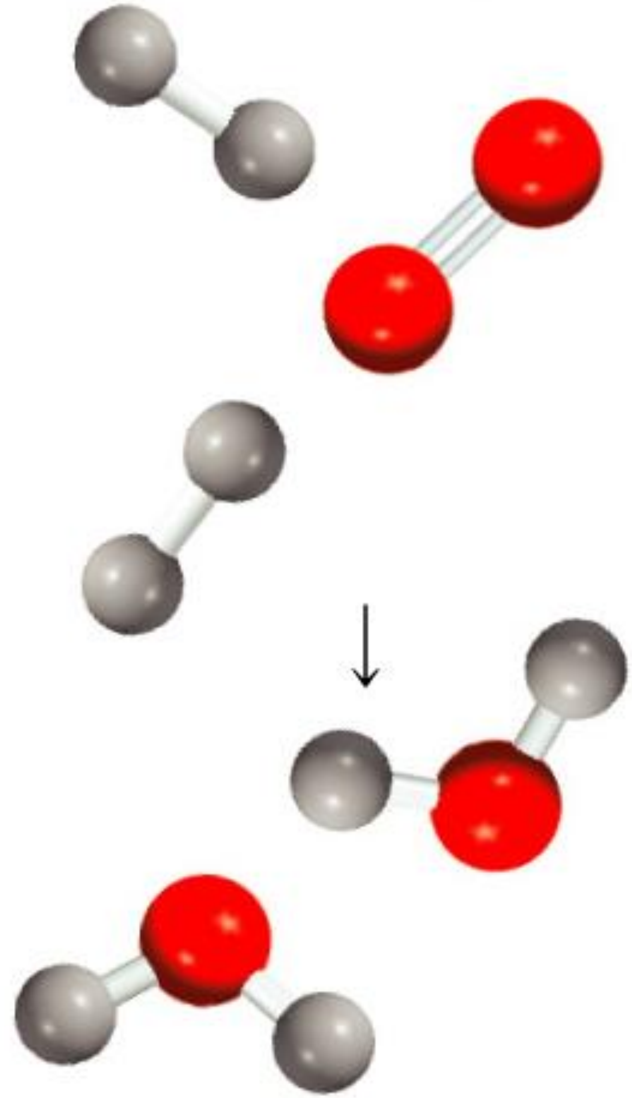


exothermic

$H_2\ (g) + Cl_2\ (g) \longrightarrow 2HCl\ (g)$



$2H_2\ (g) + O_2\ (g) \longrightarrow 2H_2O\ (g)$



Use bond enthalpies to calculate the enthalpy change for:

$$H_{2\,(g)} + F_{2\,(g)} \longrightarrow 2HF_{\,(g)}$$

$$\Delta H^o = \Sigma BE(\text{reactants}) - \Sigma BE(\text{products})$$

Type of bonds broken	Number of bonds broken	Bond enthalpy (kJ/mol)	Enthalpy change (kJ/mol)
H—H	1	436.4	436.4
F—F	1	156.9	156.9

Type of bonds formed	Number of bonds formed	Bond enthalpy (kJ/mol)	Enthalpy change (kJ/mol)
H—F	2	568.2	1136.4

$$\Delta H^o = 436.4 + 156.9 - 2 \times 568.2 = -543.1 \text{ kJ/mol}$$