

## Chapter 9 Chemical Bonding (Ch 9 Chang, Ch 8 Jespersen)

Lewis in 1916 stated that **atoms combine** to achieve a **more stable electron configuration**.

This is achieved “using” the **valence electrons**.

**Lewis dot structures** have **one dot** for each *valence electron*.

Below are Lewis dot symbols for the **representative elements** and the **noble gases**.

(In general) The number of **unpaired dots** = the number of **bonds** the atom can form in a compound.

1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8	9	10	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
•H																	He:
•Li	•Be•											•B•	•C•	•N•	•O•	•F•	•Ne•
•Na	•Mg•											•Al•	•Si•	•P•	•S•	•Cl•	•Ar•
•K	•Ca•											•Ga•	•Ge•	•As•	•Se•	•Br•	•Kr•
•Rb	•Sr•											•In•	•Sn•	•Sb•	•Te•	•I•	•Xe•
•Cs	•Ba•											•Tl•	•Pb•	•Bi•	•Po•	•At•	•Rn•
•Fr	•Ra•																



## Ionic Bonds and the Formation of Ionic Solids

**Ionic bond** – the **attraction** between the *opposite* charges of **cations** and **anions**.

The energy required for the formation of ionic bonds is supplied largely by the *attraction* between oppositely charged ions.

**Lattice Energy** is the energy required to completely separate a mole of a *solid ionic* compound into its *gaseous ions*.



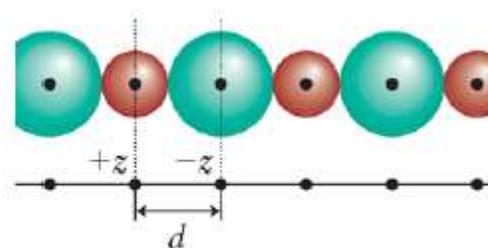
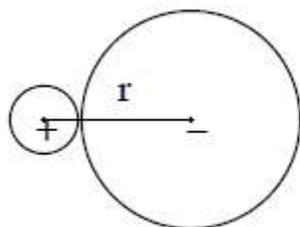
The magnitude of the lattice energy depends on *size of charge*, and *size of ions*.

Coulomb's Law in 1784 described the **Force** interacting between two **charged** particles:

$$\mathbf{F} = k \frac{Q_1 Q_2}{r^2}$$

$$E = \mathbf{F} \times d = k \frac{Q_1 Q_2}{r^2} \times r = k \frac{Q_1 Q_2}{r}$$

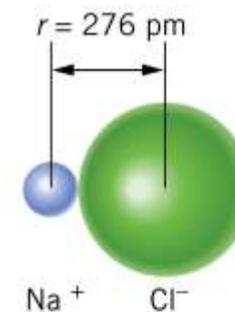
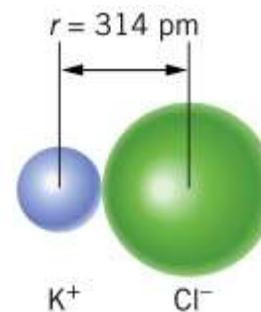
$$\text{Strength of Ionic Bond} = \mathbf{E} = k \frac{q^+ q^-}{r}$$



The **bond** between ions of *opposite charge* is **strongest** when the ions are *small*.

### Lattice Energies of Some Ionic Compounds

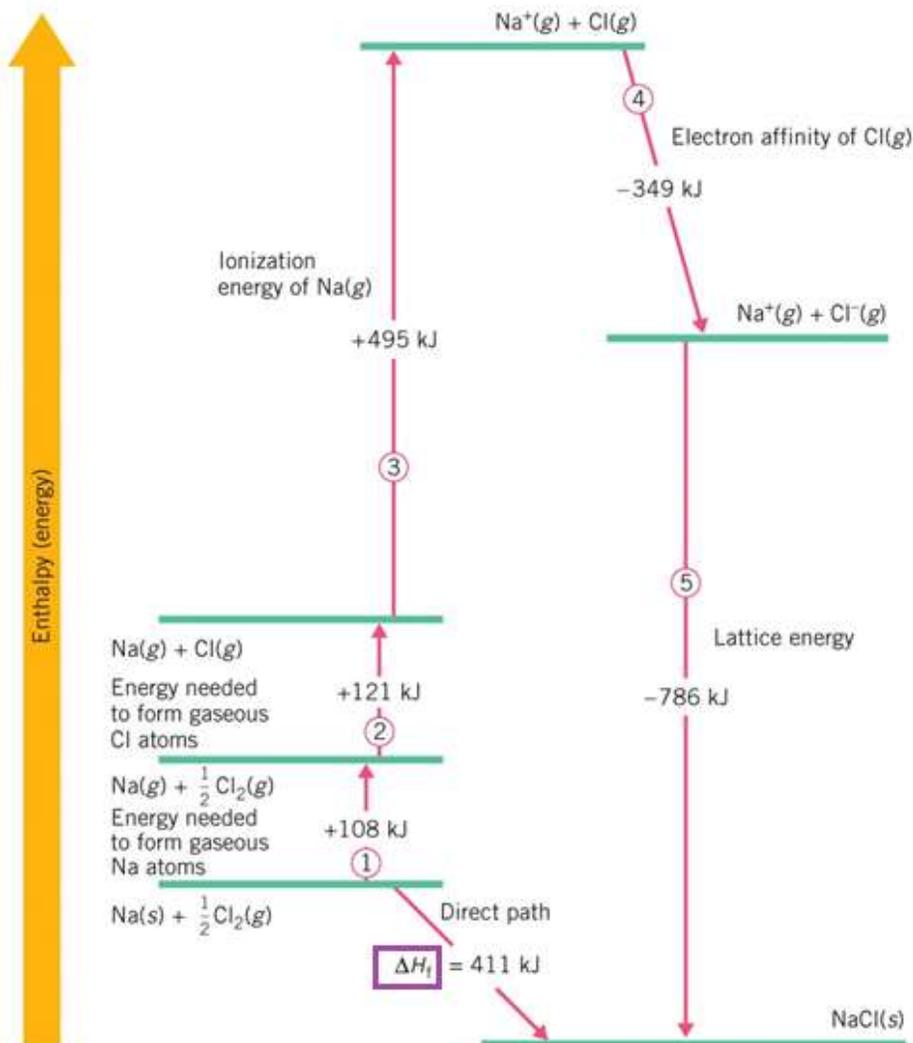
Compound	Ions	Lattice Energy (kJ mol <sup>-1</sup> )
LiCl	Li <sup>+</sup> and Cl <sup>-</sup>	-853
NaCl	Na <sup>+</sup> and Cl <sup>-</sup>	-786
KCl	K <sup>+</sup> and Cl <sup>-</sup>	-715
LiF	Li <sup>+</sup> and F <sup>-</sup>	-1036
CaCl <sub>2</sub>	Ca <sup>2+</sup> and Cl <sup>-</sup>	-2258
AlCl <sub>3</sub>	Al <sup>3+</sup> and Cl <sup>-</sup>	-5492
CaO	Ca <sup>2+</sup> and O <sup>2-</sup>	-3401
Al <sub>2</sub> O <sub>3</sub>	Al <sup>3+</sup> and O <sup>2-</sup>	-15,916



The ionic bond will also become **stronger** as the **charge** on the **ions** becomes *larger*.

	$\text{OH}^-$	$\text{O}^{2-}$
$\text{Na}^+$	900	2481
$\text{Mg}^{2+}$	3006	3791
$\text{Al}^{3+}$	5627	15,916

## Born-Haber Cycles



Previously we learned that **Enthalpy** changes are the same, *regardless of the path taken*.

We can apply this to chemical processes:

$$\Delta H_f = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5$$

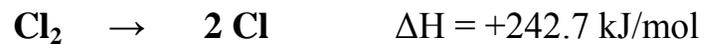
It is important to pay attention to the *details* of each transformation, so as to include **all** the relevant steps.

## The Covalent Bond

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

### Strengths of Covalent Bonds

**Bond enthalpy** is the **enthalpy** change,  $\Delta H$ , for **breaking** a particular **bond** in a mole of **gaseous** substance.



The bond enthalpy is **always** a **positive** quantity.

### Bond Length and Bond Enthalpy

C–C	C=C	C≡C	N–N	N=N	N≡N
1.54 Å	1.34 Å	1.20 Å	1.47 Å	1.24 Å	1.10 Å
348 kJ/mol	614 kJ/mol	839 kJ/mol	163 kJ/mol	418 kJ/mol	941 kJ/mol

As the number of bonds between two atoms *increases*, the bond grows **shorter** and **stronger**.

**Shorter** bonds are **stronger** bonds.

## A Comparison of Ionic and Covalent Compounds

- **Covalent** compounds have relatively *weak intermolecular* forces, resulting in *lower* melting and boiling points compared to **ionic** compounds.
- **Covalent** compounds are often *gases, liquids, or low melting solids*.
- **Ionic** compounds are usually *solids* with *high* melting points.
- **Ionic** compounds give *conducting solutions* when dissolved in water.
- Molten **ionic** compounds conduct *electricity*.

## Polar Covalent Bonds: Electronegativity

**nonpolar covalent** bond – electrons are **shared equally** between atoms.

**polar covalent** bond – one atom *attracts* electrons *more strongly* than the other (**unequal sharing** of the electrons).

**electronegativity** – the ability of an **atom** in a molecule to *attract electrons* to itself.

The most common quantification of EN is the **Pauling scale**.

Increasing electronegativity

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

Notice: **EN increases** → and ↑.

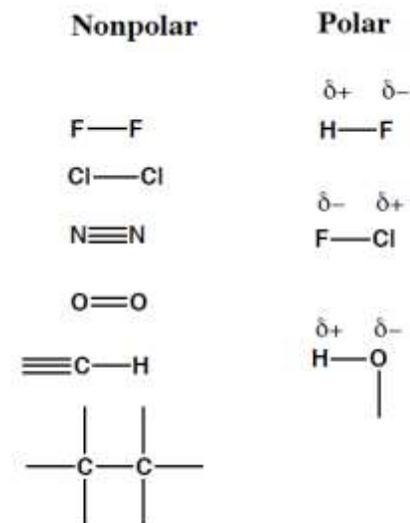
Electrons go *towards* the *more electronegative* element.

## Bond polarity

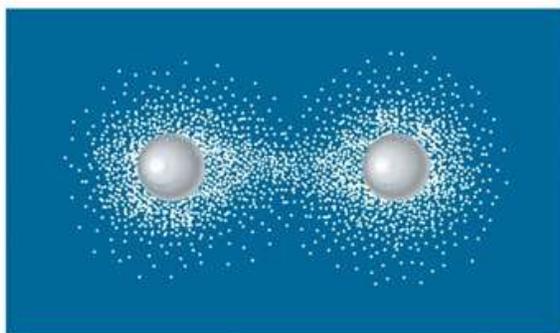
In general:

EN difference < 0.5	⇒ Nonpolar
0.5 < EN difference < 2.0	⇒ Polar
EN difference > 2.0	⇒ Ionic

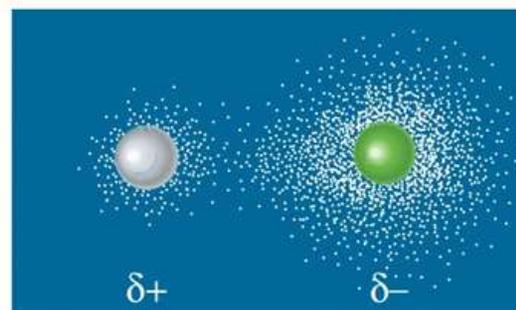
Compound	F <sub>2</sub>	HF	LiF
EN difference	4.0 - 4.0 = 0	4.0 - 2.1 = 1.9	4.0 - 1.0 = 3.0
Type of Bond	Nonpolar covalent	Polar Covalent	Ionic



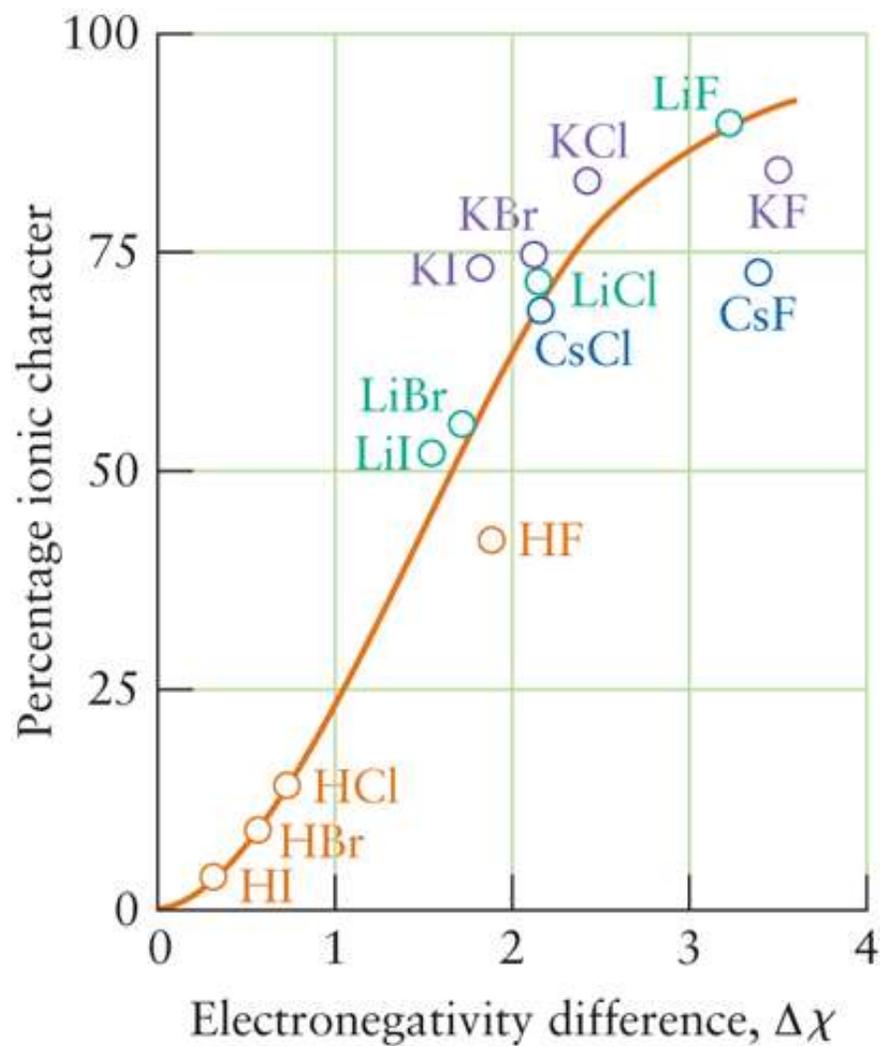
NonPolar  
Electrons shared equally



Polar  
Unequal sharing of electrons

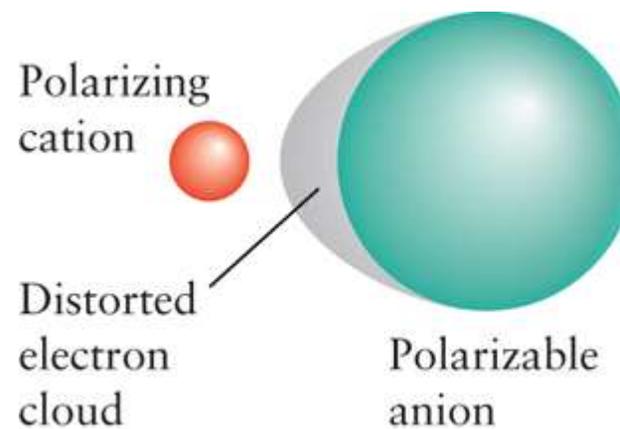


Nonpolar covalent----Polar covalent---- Ionic is a continuous sliding scale:



Be aware that it is a sliding scale, and other factors such as **polarizability** can play a role.

(E.g.  $\text{KCl} \rightarrow \text{KBr} \rightarrow \text{KI}$ )



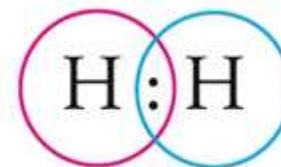
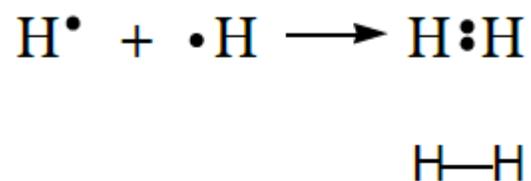
More electrons (*bigger*) means more *polarizable* (increasingly covalent).

## Electron-Dot Structures

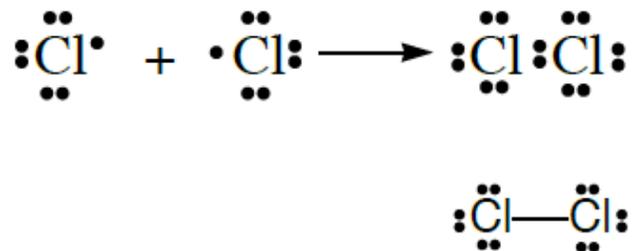


We use our electron dot *symbols* to generate electron dot **molecular** structures.

These are called **Lewis Structures**.



Each Hydrogen acts as if the two electrons are theirs.

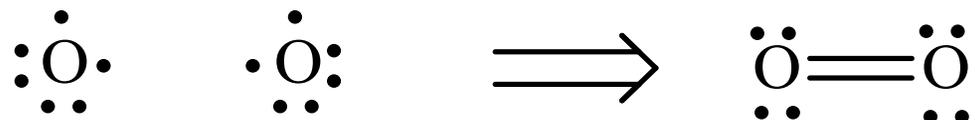


Each **shared pair** of electrons is drawn as a **line**.

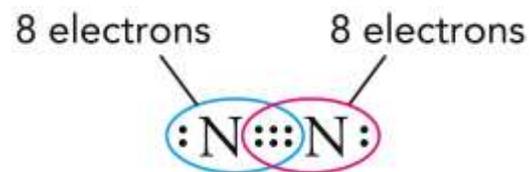
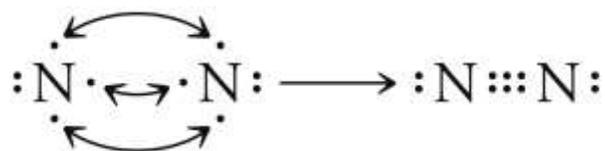
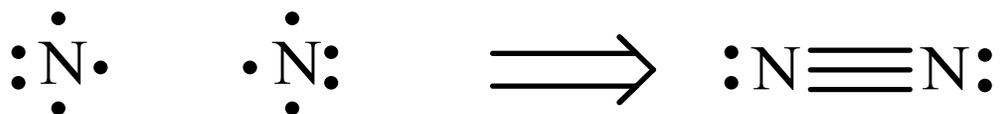
*Non-bonding* or *lone pairs* are left as dots.

## Multiple Bonds

If **two pairs** of electrons are shared, it is a **double bond**.



If **three pairs** of electrons are shared, it is a **triple bond**.



**Octet Rule:** an atom other than hydrogen tends to form bonds until it is surrounded by **eight valence** electrons.

**Main-group elements** tend to undergo reactions that leave them with **eight outer-shell** electrons.

That is, main-group elements react so that they attain a **noble gas electron configuration** with filled **s** and **p sublevels** in their valence electron shells. (*Full* or *closed* shell of electrons).

(Hydrogen only needs one electron to reach its helium-like duplet).

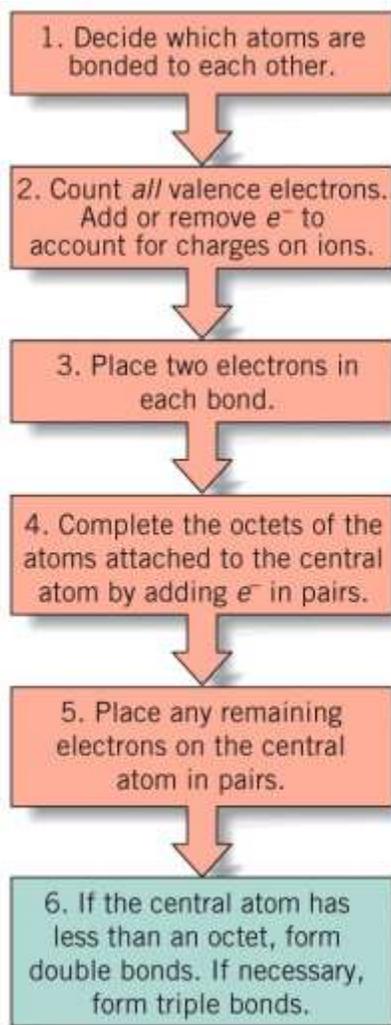
### Lewis Structures

The **Lewis structure** of a **polyatomic** species is obtained when *all* the valence electrons are used to complete the octets (or duplets) of the atoms present by forming *single* or *multiple* bonds, and possibly *non-bonding* electrons.

#### Guide to Drawing Lewis Structures

1. Write the **symbol** for the atoms to show which atoms are attached to which.
2. *Sum* the **valence** electrons from **all** atoms.
3. **Add** one electron for every **negative** charge; **subtract** one electron for every **positive** charge. (This gives you the **total** number of valence electrons).
4. **Connect** the atoms with single **bonds** (**1 bond = 2e<sup>-</sup>**).
5. Use the *remaining* valence electrons to complete the **octets** of the **atoms** bonded **to** the **central atom**.
5. Place any *left-over* electrons on the **central** atom.
6. If there are *not enough* electrons to give the central atom an *octet*, try **multiple** bonds.

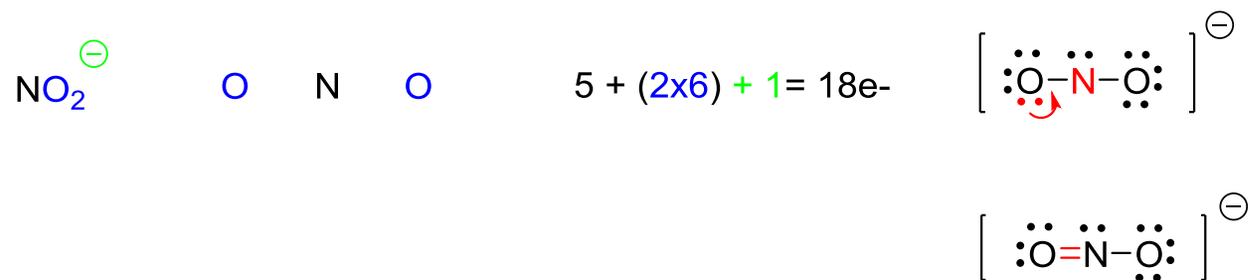
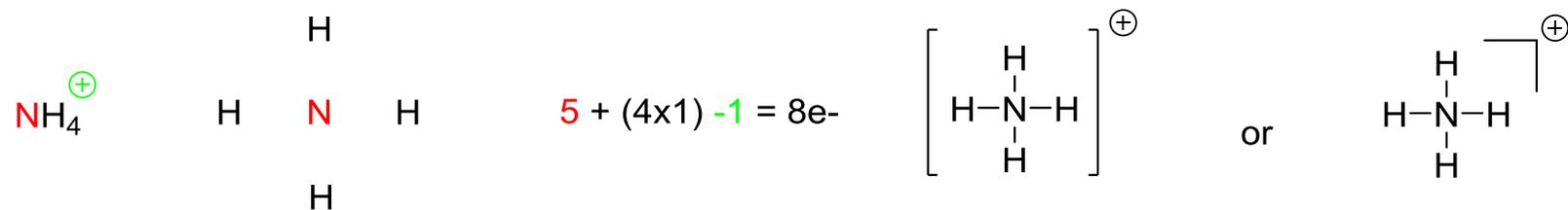
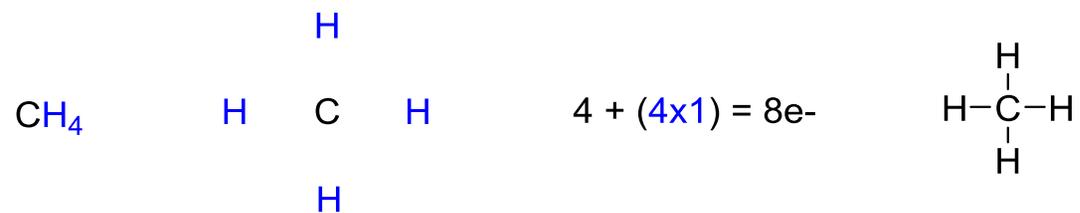
The same information in *Flowchart form*:



Useful hints:

- The *least* electronegative element is usually the **central** atom.
- H and F are *never* central atoms since they form only **one** bond.
- C, N, O and S *may* form **double** bonds.
- N, C and O *may* have **triple** bonds.

## Examples



**Formal Charge** is a way of *keeping count* of electrons, but the charges *may* or *may not* be ‘real’.

(Partial charges  $\delta+$  are ‘real’).

**Formal charge** is the *electrical charge difference* between the **valence** electrons in an *isolated* atom and the number of electrons *assigned* to that atom in a **Lewis structure**.

$$\text{Formal Charge} = (\text{group number}) - (\text{non bonding e}^-) - \frac{1}{2}(\text{shared e}^-)$$

(group number = 1-8)

$$\text{E.g.} \quad \text{N in NH}_3 = 5 - 2 - 3 = 0$$

$$\text{N in NH}_4^+ = 5 - 0 - 4 = +1$$

The **formal charge** gives an indication of the *extent* to which atoms have *gained* or *lost* electrons in the *process* of covalent bond formation.

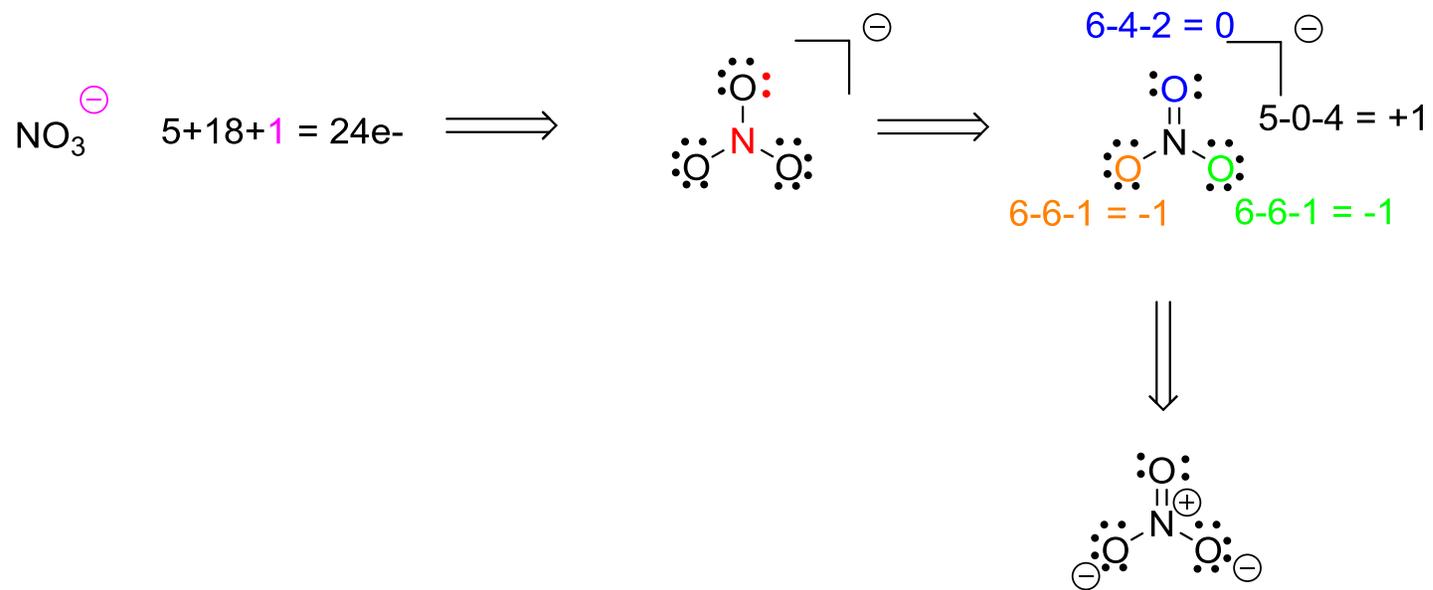
## Formal charges

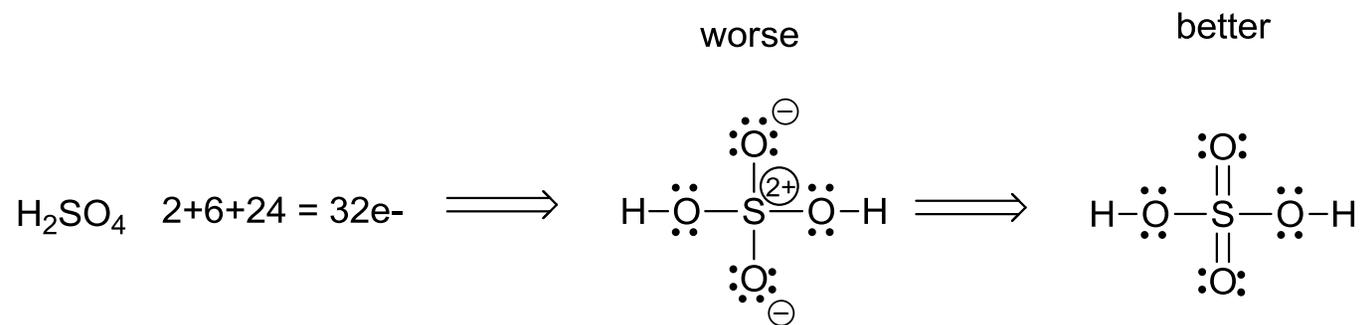
- For **molecules**, the **sum** of the formal charges must add up to **zero** because the molecules are electrically **neutral** species.
- For **cations**, the **sum** of the formal charges must equal the **positive** charge.
- For **anions**, the **sum** of the formal charges must equal the **negative** charge.

## Formal Charges and Lewis Structures

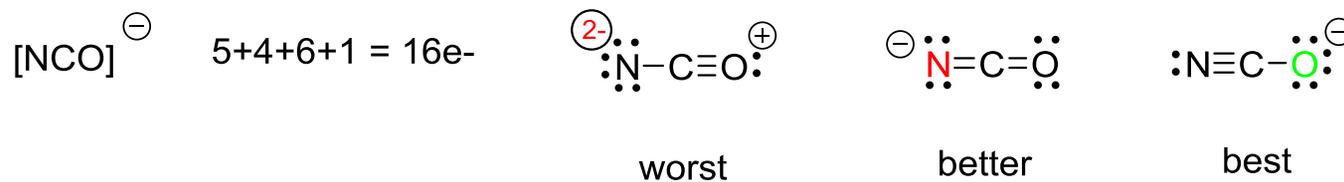
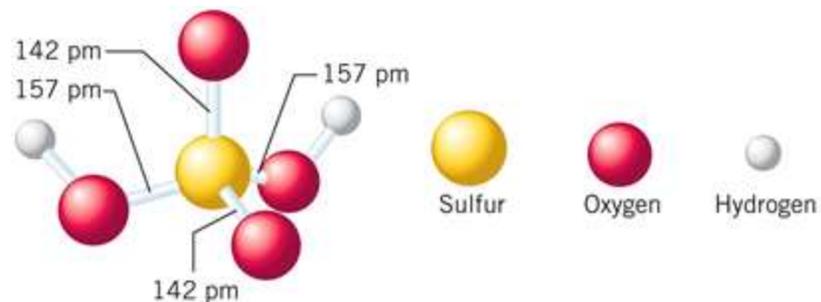
- For **molecules**, a Lewis structure in which there are **no** formal charges is *preferable* to one in which formal charges are present.
- Lewis structures with *large* formal charges (+2, +3 and/or -2, -3 and so on) are **less plausible** than those with small formal charges. (*If there are large charges, try and make more bonds*).
- Among Lewis structures having **similar** distributions of formal charges, the **most plausible** structure is one in which the **negative** formal charges are placed on the *more electronegative* element.







The **measured** bond lengths of (gaseous)  $\text{H}_2\text{SO}_4$  tell us that the Sulfur to Oxygen bonds are *different*. (S–O and S=O).



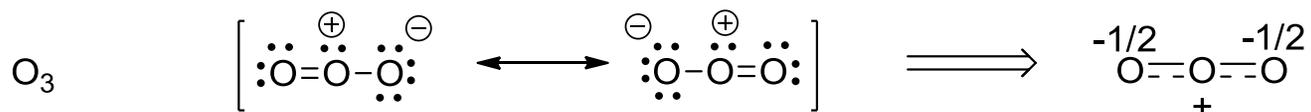
## Common Formal Charges

	Group number or number of valence electrons			
Cl	7 "valence of 1"			
O	6 "valence of 2"			
N	5 "valence of 3"			
C	4 "valence of 4"			

## Electron-Dot Structures and Resonance

For Ozone, we can write two “*correct*” Lewis structures.

But in reality **neither** Lewis structure is **accurate** since the **experimentally measured** O–O bond length is 1.28 Å, but the Lewis structures predict two *different* lengths (O–O is 1.49 Å, and O=O is 1.21 Å).



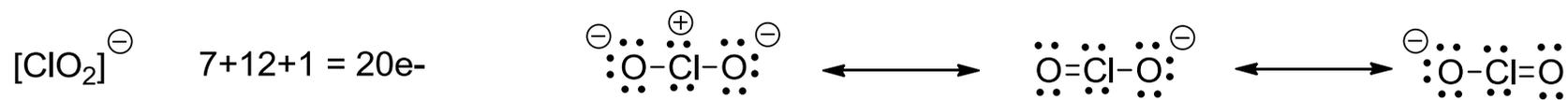
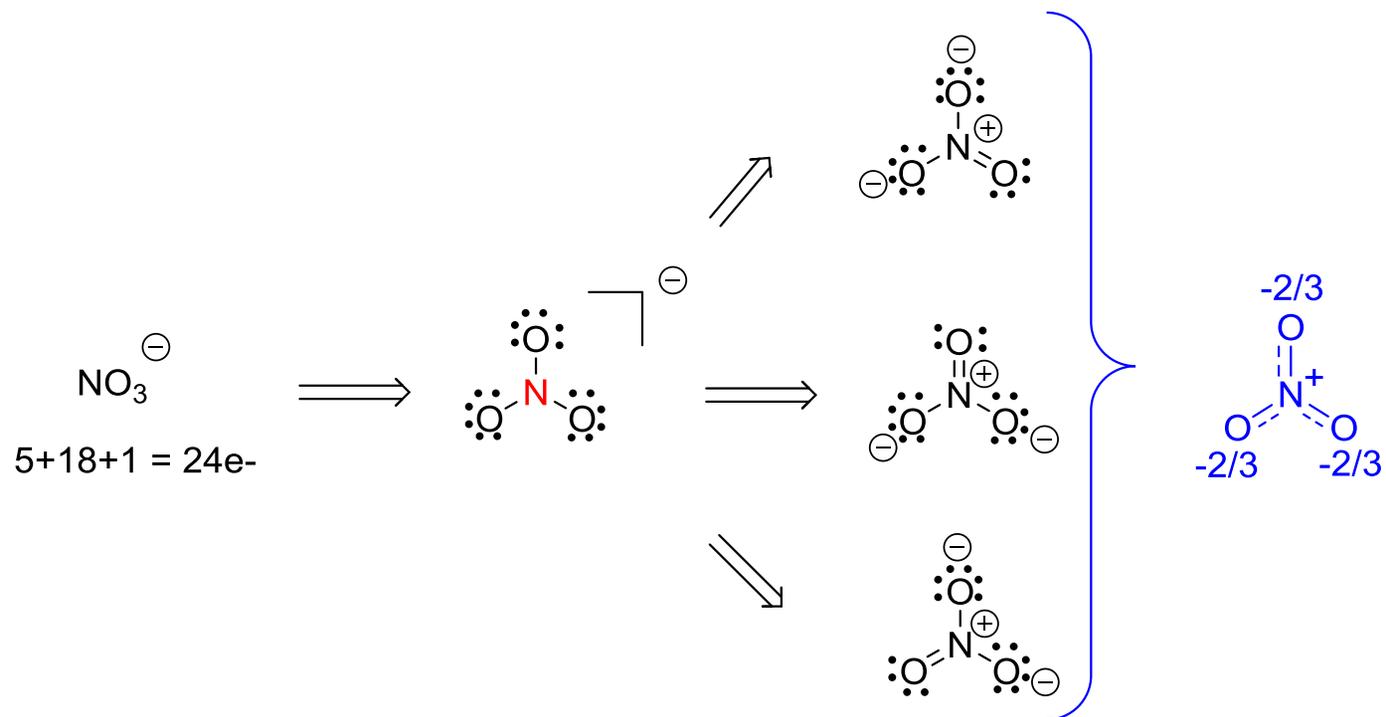
Some species **cannot** be accurately portrayed by a *single* Lewis structure (*non-classical* / *delocalized* structures).

We use **resonance structures** to portray them.

## Resonance Structures

- In each contributing structure, the **nuclei** are in the **same positions**; only the **locations** of **electrons** can **change**.
  - Structures with the *same energy* (equivalent structures) contribute *equally* to the resonance.
  - *Lower energy* structures contribute *more* to the resonance mixture than higher energy structures.
- (**Major** and **minor contributors** to the **overall** structure).

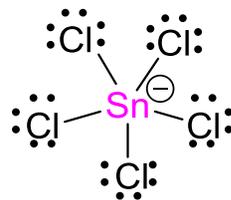
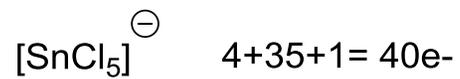
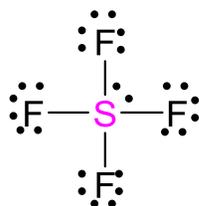
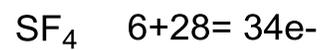
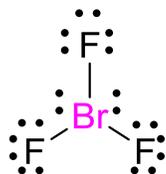
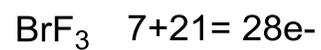
E.g.



## Exceptions to the Octet Rule

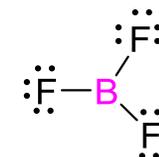
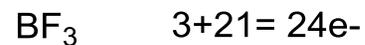
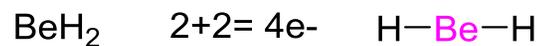
1) Elements of the 3<sup>rd</sup> Row (and beyond) can *expand past* an *octet*.

E.g.



2) "Correct" Lewis structures that predict/explain electron deficient compounds.

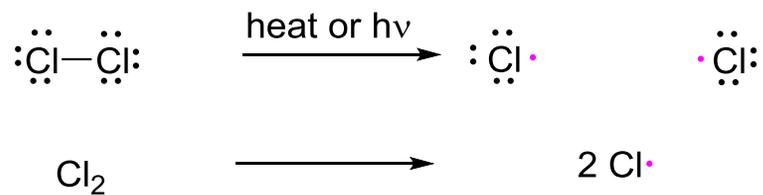
E.g.



3) Odd Numbered Electron Molecules - radicals

A species with at least one unpaired electron is called a radical (*free radical*). These are typically very reactive species.

E.g.



## Bond Enthalpy

A measure of the stability of a molecule is its **bond enthalpy**, which is the **enthalpy** change required to *break* a particular *bond* in 1 mole of *gaseous* molecules.

(Bond enthalpies in solids and liquids are affected by neighboring molecules).

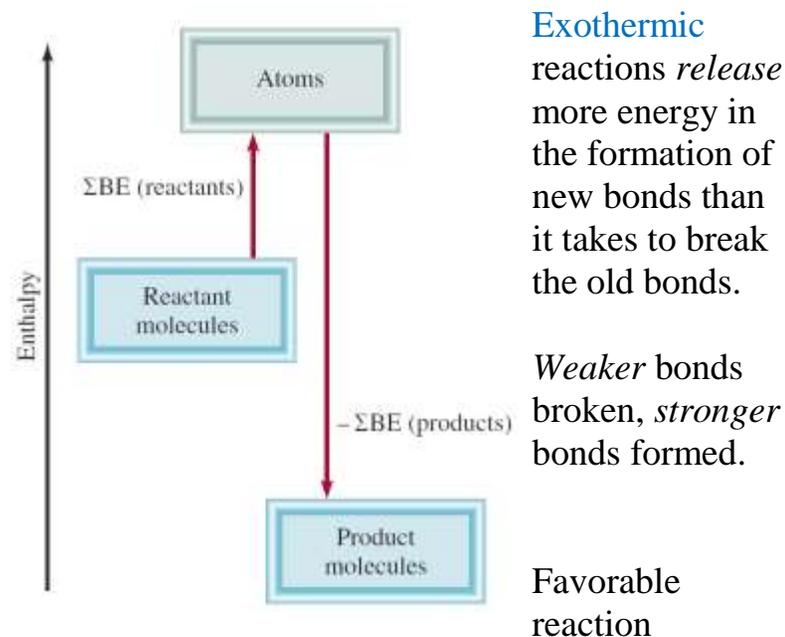
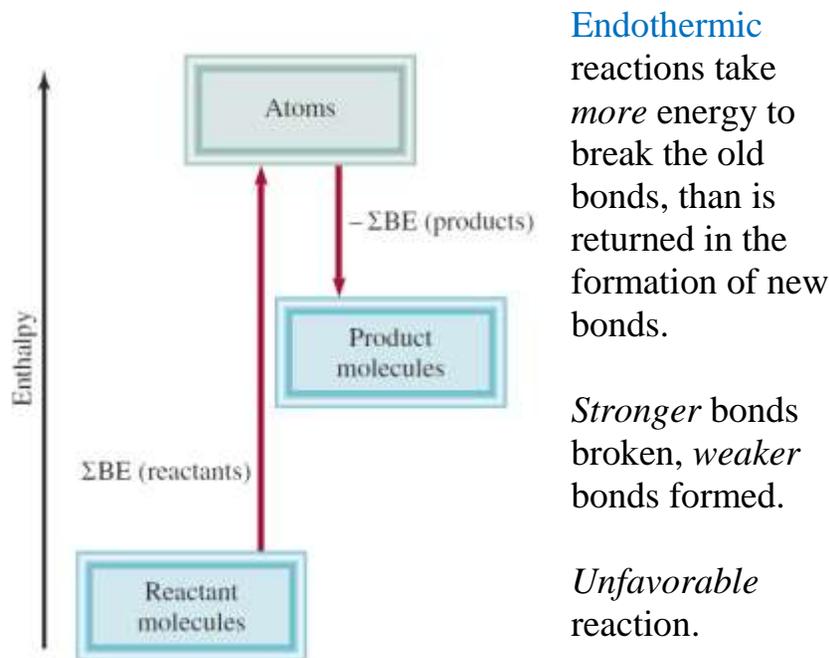
Bond	Bond Enthalpy (kJ/mol)	Bond	Bond Enthalpy (kJ/mol)
H—H	436.4	C—S	255
H—N	393	C=S	477
H—O	460	N—N	193
H—S	368	N=N	418
H—P	326	N=N	941.4
H—F	568.2	N—O	176
H—Cl	431.9	N=O	607
H—Br	366.1	O—O	142
H—I	298.3	O=O	498.7
C—H	414	O—P	502
C—C	347	O=S	469
C=C	620	P—P	197
C≡C	812	P=P	489
C—N	276	S—S	268
C=N	615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

We can *use* these values to determine the **enthalpy change** for a particular chemical reaction.

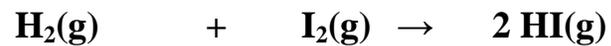
It is just the *difference* between the energy taken to **break old** bonds, and the energy released in **making new** bonds

$$\Delta H^\circ = \Sigma BE_{\text{reactants}} - \Sigma BE_{\text{products}}$$

= Total energy input – Total energy released



**Problem:** Calculate the enthalpy of reaction for the process:



$$\text{Bonds broken} = \text{H-H} = 436.4 \text{ kJ/mol}$$

$$\text{I-I} = 151.0$$

$$\text{Bonds formed} = 2 \text{ H-I} = 2 \times 298.3 = 596.6 \text{ kJ/mol}$$

$$\Delta H^\circ = \Sigma BE_{\text{reactants}} - \Sigma BE_{\text{products}}$$

$$= (436.4 + 151.0) - 596.6$$

$$= -9.2 \text{ kJ/mol}$$