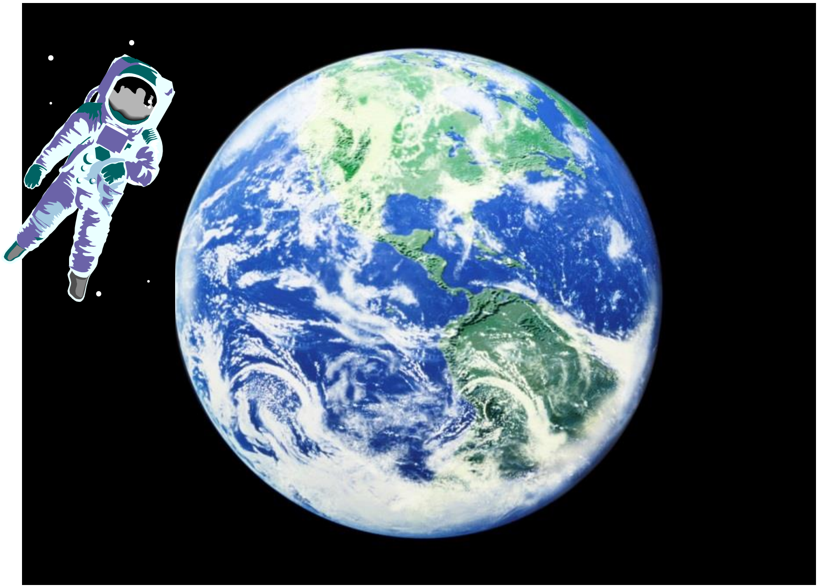
Chemical Bonds

Bonds between Atoms



Each atoms is unique due to their differing;

- **Sizes;**
- **Electron Affinities;**
- **Ionization Energies.**

As the gravitational force varies with size and distance, atoms, like planets, have similar unique and variable inherent strengths and forces that influence other atoms.

Atoms minimize these **imbalances** by forming bonds.

Bonds between Atoms

Atoms strive to **fill** their outer shells with electrons just like a noble gas does.

In a generalized-way atoms can achieve satisfaction by forming two types of bonds: ionic and covalent

Ionic is **gaining** & **losing** electrons
Covalent is **sharing** electrons

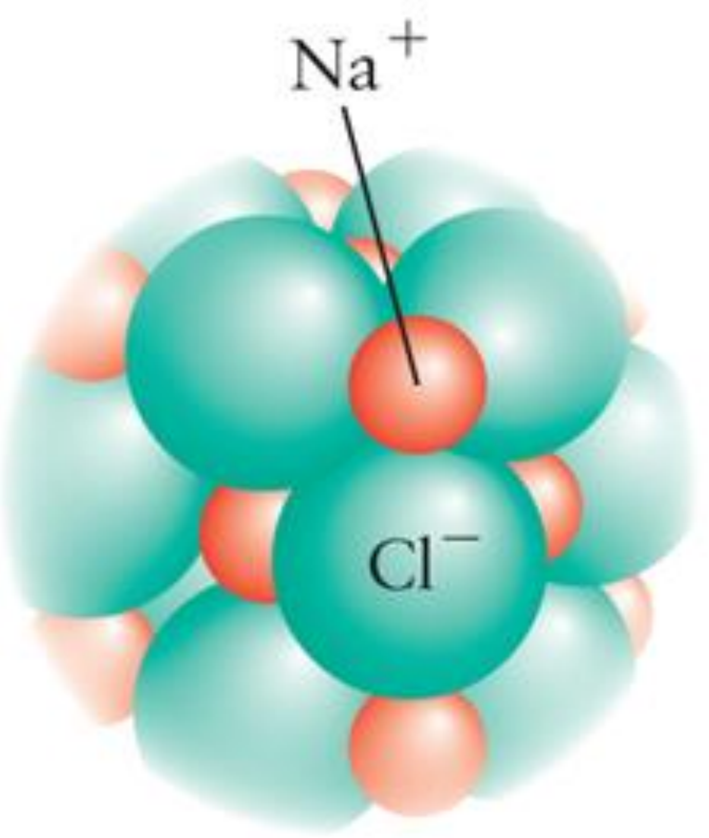
The resulting bond is **lower** in energy than the separate atoms.

If electrons transfer from one or more atoms, the entire compound is held together by **electrostatic attractions** between all the ions.

This attraction is called an **ionic bond**.

Note: the energy is lower when Na^+ and Cl^- ions bind than separated sodium and chlorine atoms.

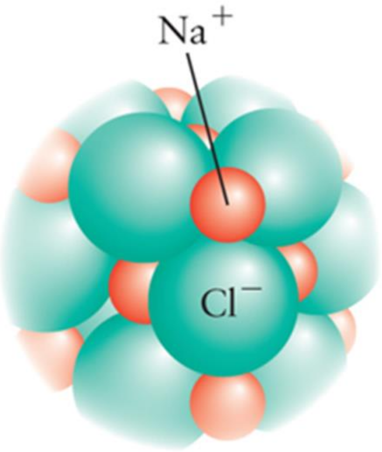
The new partnership is lower in energy than the separate Atoms.



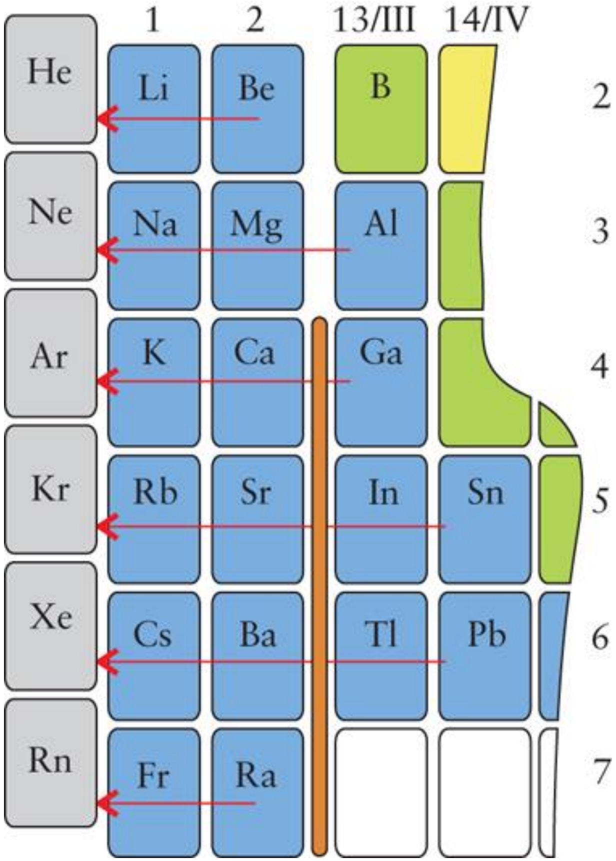
Binary ionic compound form between s-block **metal**, and a **nonmetallic** element.

Cation and anions stack themselves into alternating sodium ions with chloride ions, oppositely charged ions are lined up in all three dimensions.

An example of an ionic **crystalline solid.**



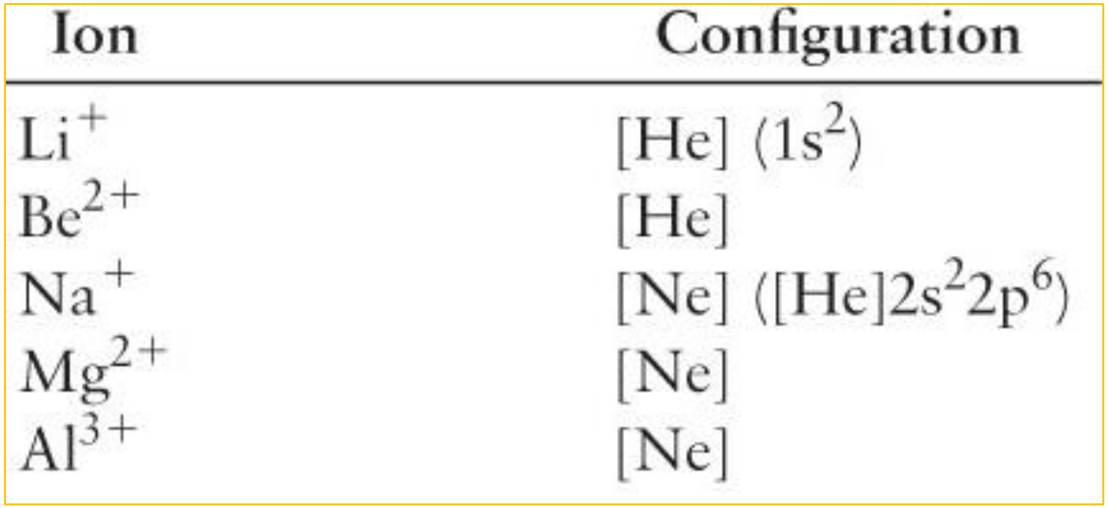
Metals



S-block metals form cations, by <u>losing electrons</u> to their **noble-gas core** or octet of electrons.

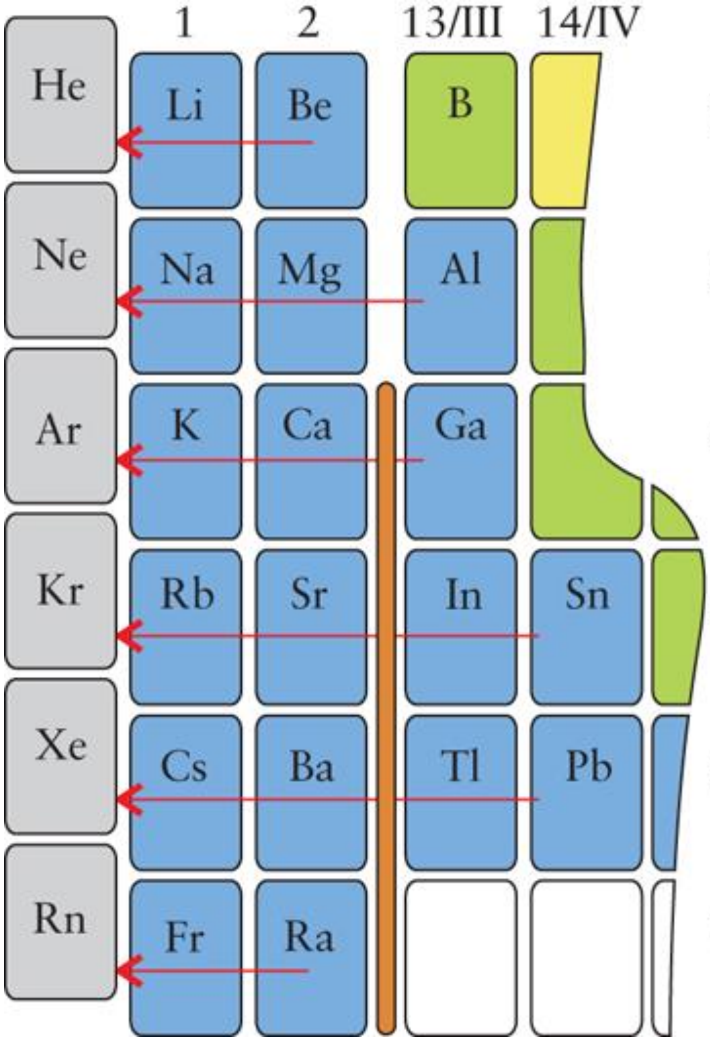
Al forms the Al^{3+} ending with [Ne] electron configuration by the loss of it’s *s* and *p* electrons

noble-gas core



Ion	Configuration
Li^{+}	[He] $(1s^2)$
Be^{2+}	[He]
Na^{+}	[Ne] $([He]2s^2 2p^6)$
Mg^{2+}	[Ne]
Al^{3+}	[Ne]

Ga^{3+} 4p block **d electrons** remain



Metallic elements, in Period 4 and later, **lose** their s- and p-electrons.

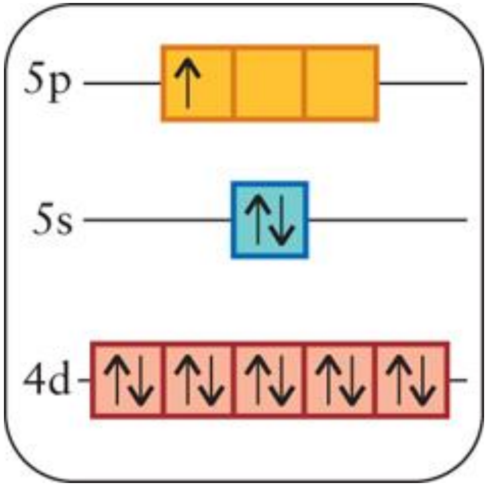
Ga^{3+}, $[Ar]3d^{10}$

The **d electrons** of the p-block atoms **are gripped tightly** by the nucleus and **cannot be lost**.

Write the electron configurations of In^+ and In^{3+}

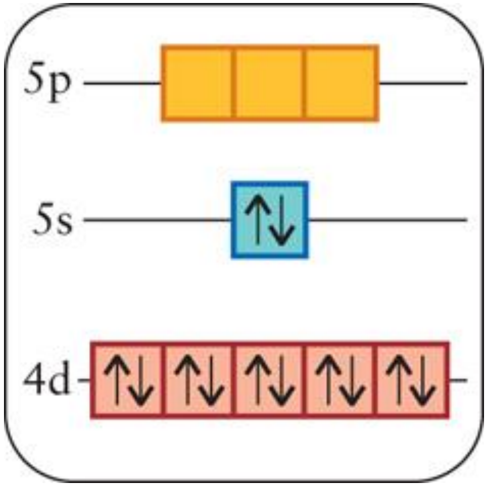
Remove electrons from the valence-shell *p*-orbitals **first**, then from the *s*-orbitals

Determine the configuration of the neutral atom.

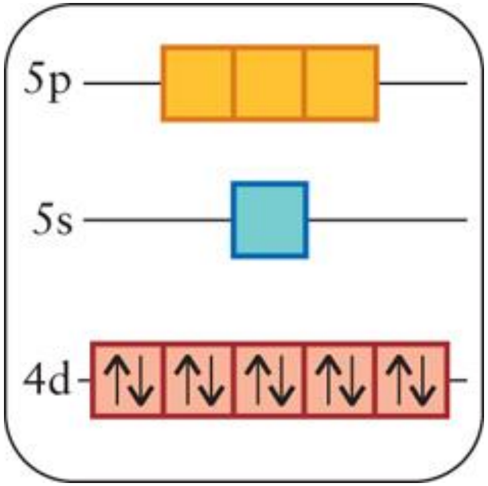


$[Kr]4d^{10}5s^{2}5p^{1}$

Remove the outermost electron. In^+ $[Kr]4d^{10}5s^{2}$



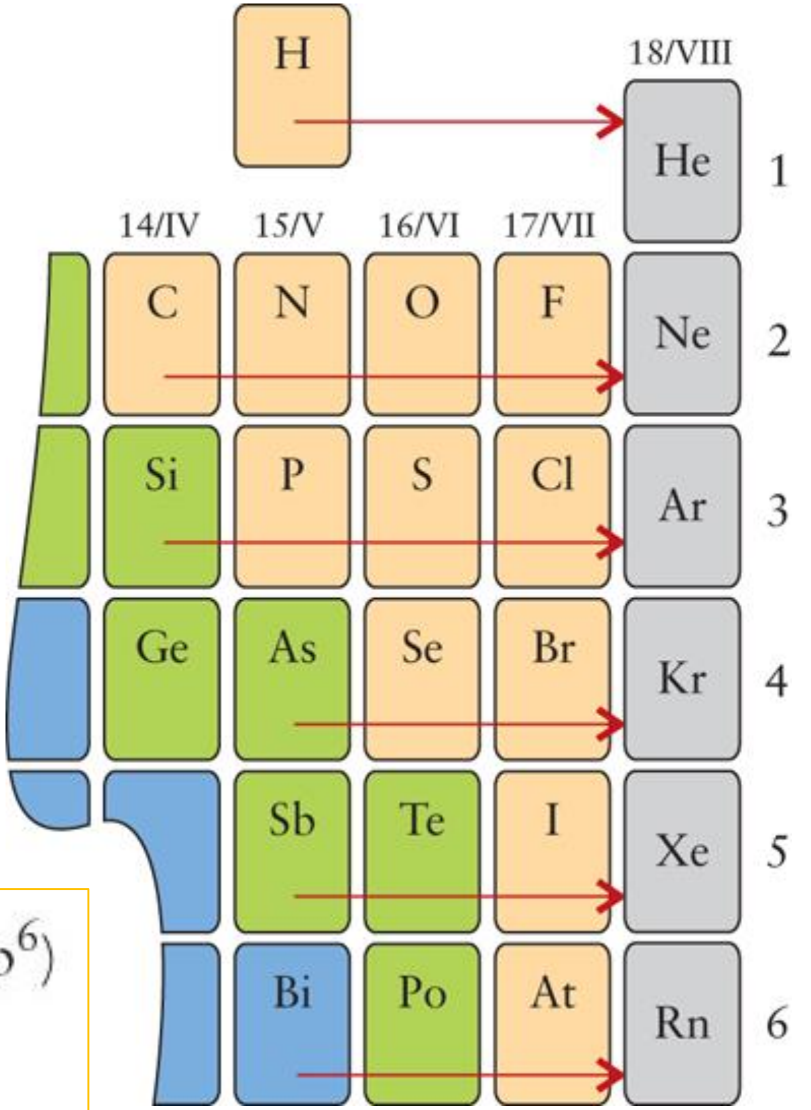
Remove the next two outermost electron. In^{3+} $[Kr]4d^{10}$

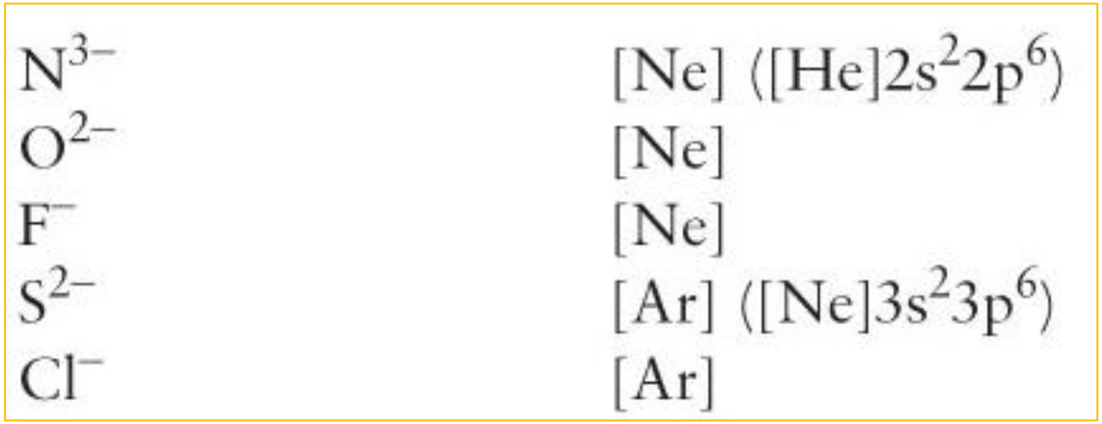


Nonmetals **rarely lose electrons** because their **ionization** and **electron affinity** energies are too high.

Instead, nonmetal atom **acquire electrons** to fill their outer shell

N [He]2$s^2$2p^3 plus 3 e^- to N^{3-}[Ne]



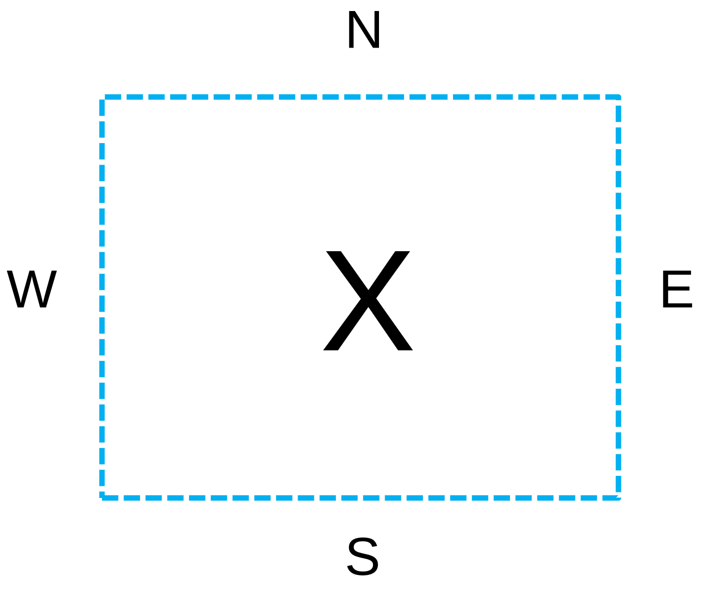


N^{3-}	[Ne] ([He]$2s^22p^6$)
O^{2-}	[Ne]
F^-	[Ne]
S^{2-}	[Ar] ([Ne]$3s^23p^6$)
Cl^-	[Ar]

G. N. Lewis

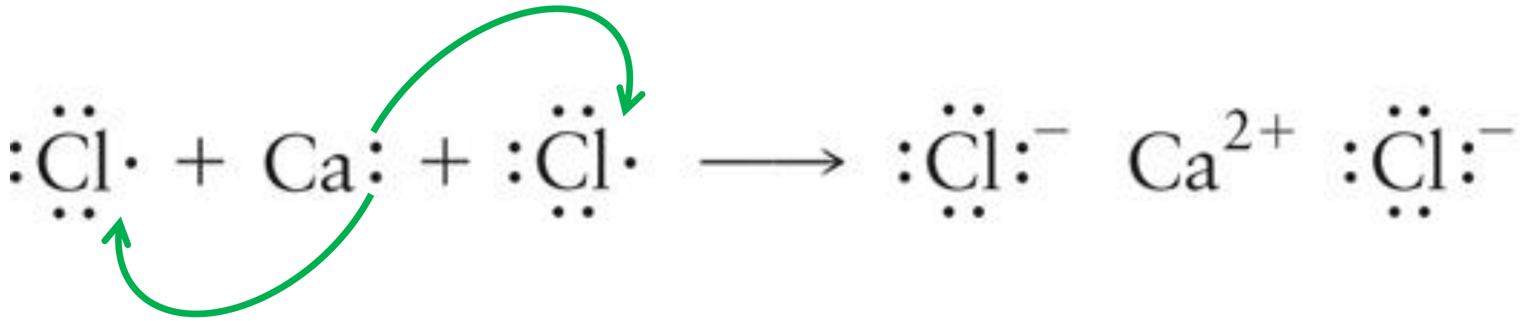
A **single dot** represents a **valence electron** (*outer most electrons in the last shell*) in the atom.

A **pair of dots** represents two paired electrons sharing an orbital.



Each symbol is thought of as having four sides, a north, south, east, and west position, where valance electrons are shown as dots

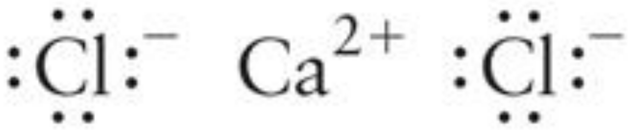
An ionic formula starts by **removing** valance electrons from the metal and **transferring** them to the **nonmetal atom** to complete its valence shell.



$$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}\cdot + Ca: + :\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}\cdot \longrightarrow :\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:^{-} \quad Ca^{2+} \quad :\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:^{-}$$

The **calcium** atom loses its two valence electrons.

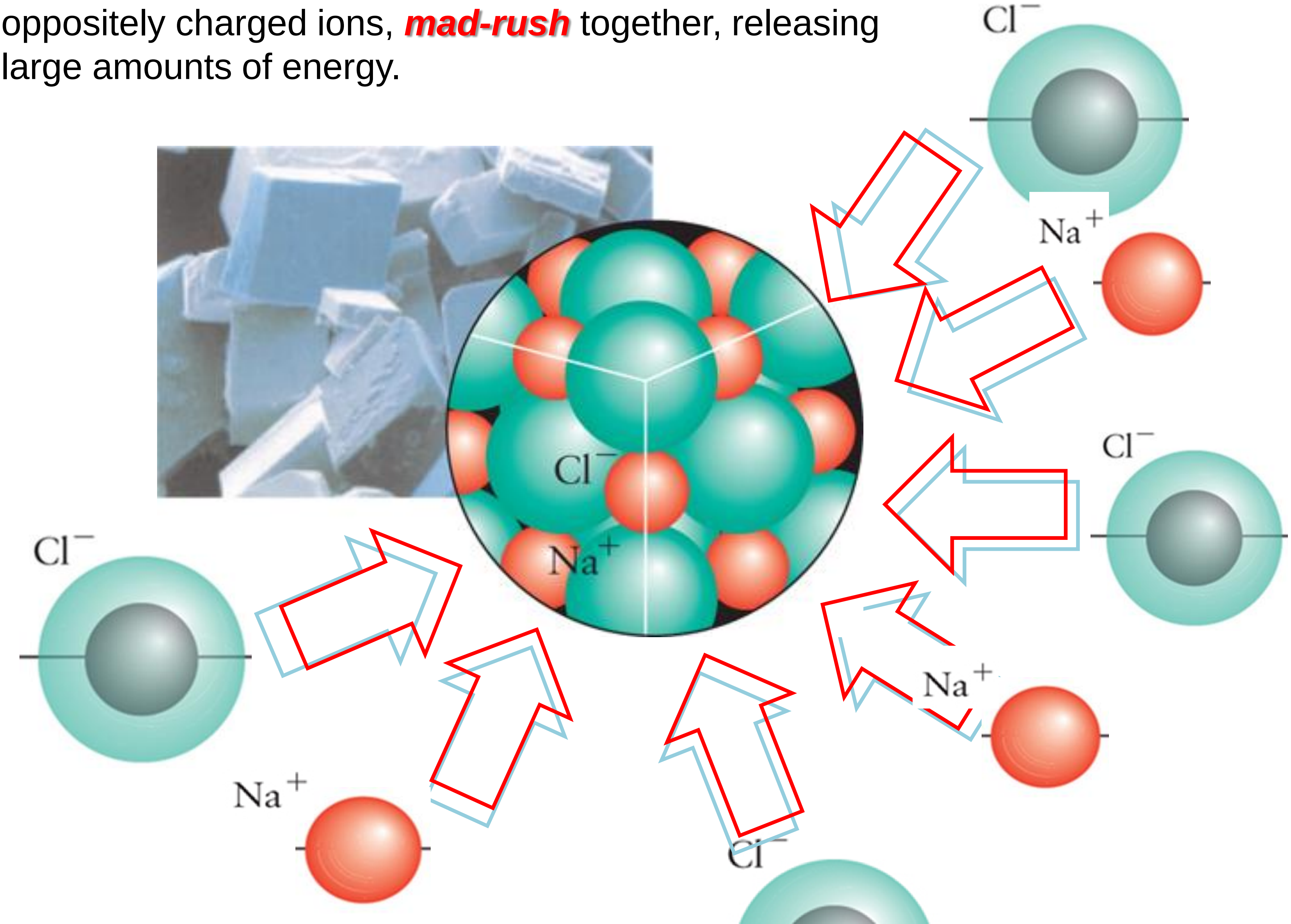
Each **chlorine** atom has one vacancy electron so it forms one bond.

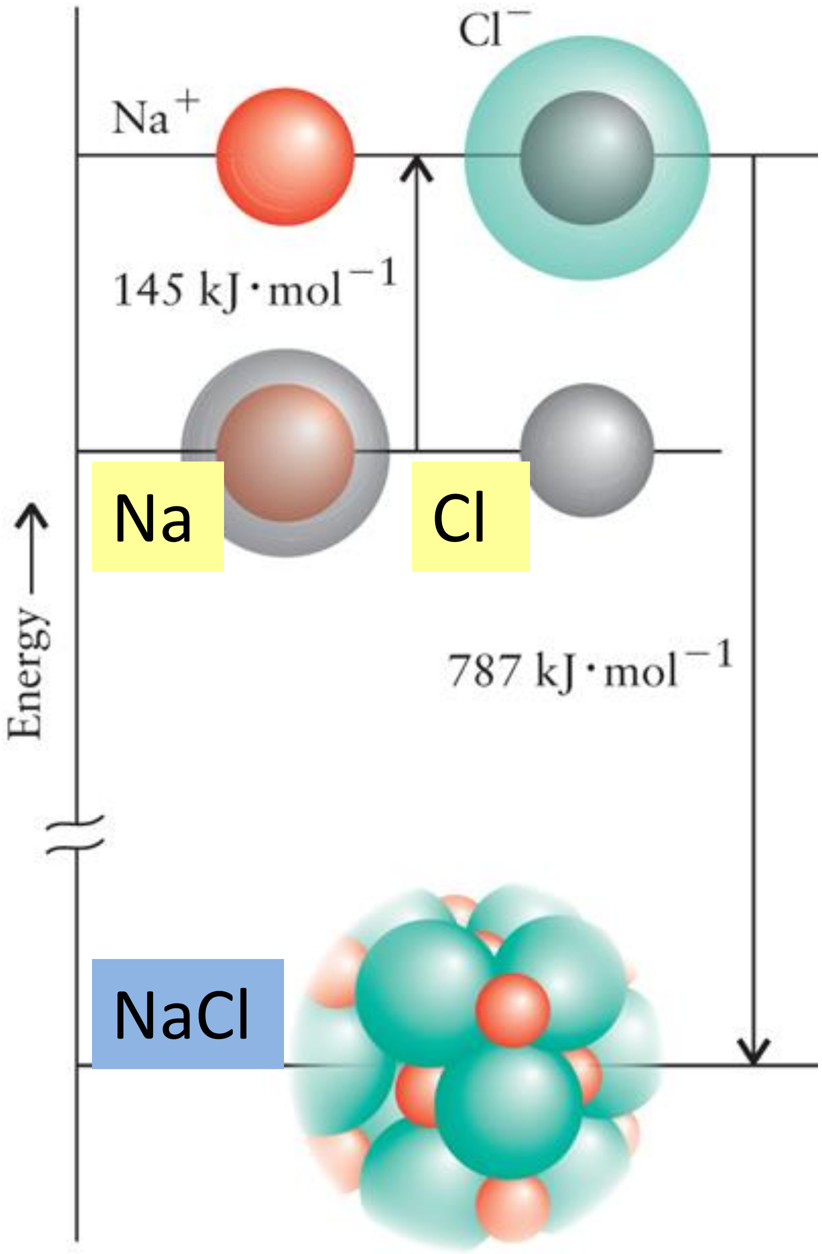


Two chloride ions (Cl^-) ***balances the charge*** for **each** calcium ion (Ca^{2+}) resulting in the formula $CaCl_2$; the overall charges is zero.

There are **no** $CaCl_2$ molecules, only **crystals** of three-dimensional arrays of $CaCl_2$ ions held by the vast array of opposite charges spread throughout the crystal-hence $CaCl_2$ is called a formal unit.

Crystal formation starts when large numbers of oppositely charged ions, ***mad-rush*** together, releasing large amounts of energy.





A **crystal** of sodium chloride has lower energy than separated sodium and chlorine atoms.

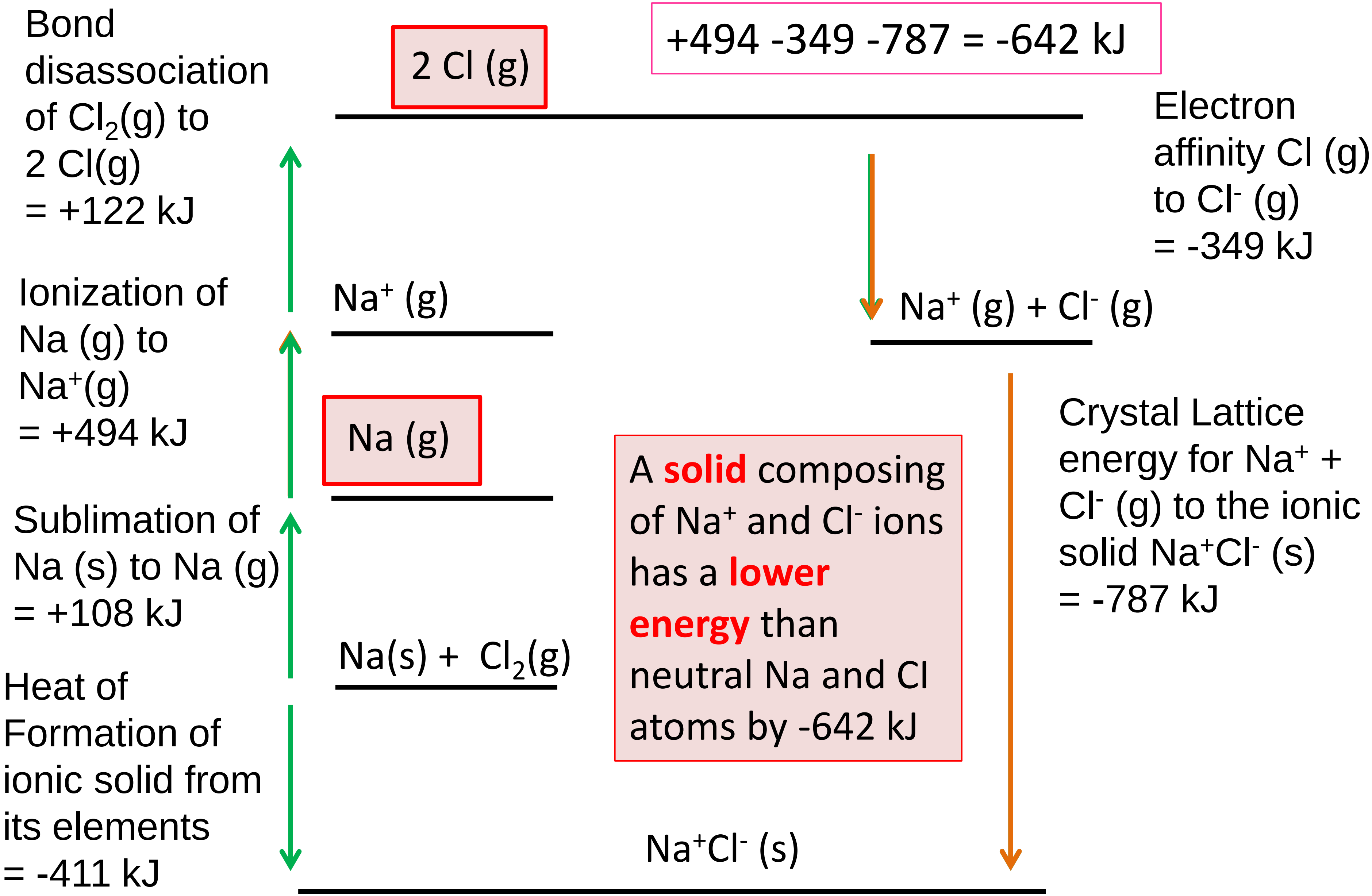
Formation of the solid takes place in three steps:

1. Sodium atoms release electrons;

2. These electrons attach to chlorine atoms;

3. Newly formed cations and anions clump together as a crystal.

Crystal Lattice is stability gained when ions form ionic solid



$+494 -349 -787 = -642$ kJ

Bond disassociation of $Cl_2(g)$ to $2\ Cl(g)$ = +122 kJ

Ionization of Na (g) to $Na^+(g)$ = +494 kJ

Sublimation of Na (s) to Na (g) = +108 kJ

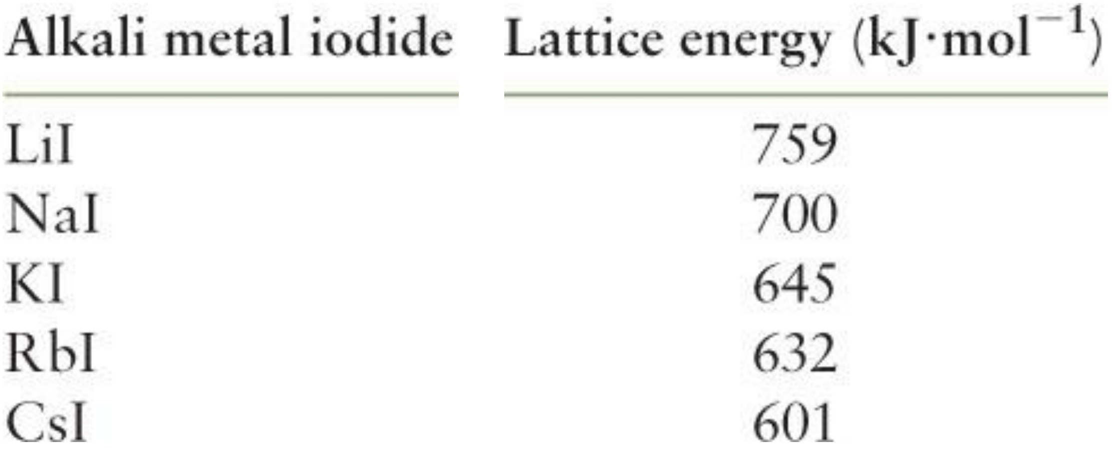
Heat of Formation of ionic solid from its elements = -411 kJ

Electron affinity Cl (g) to Cl^- (g) = -349 kJ

Crystal Lattice energy for $Na^+ + Cl^-$ (g) to the ionic solid Na^+Cl^- (s) = -787 kJ

A **solid** composing of Na^+ and Cl^- ions has a **lower energy** than neutral Na and Cl atoms by -642 kJ

Lattice energy is a "**global**" characteristic of the **entire** crystal, a net lowering of energy in the entire crystal (once the cations and anions clump together as a crystal).



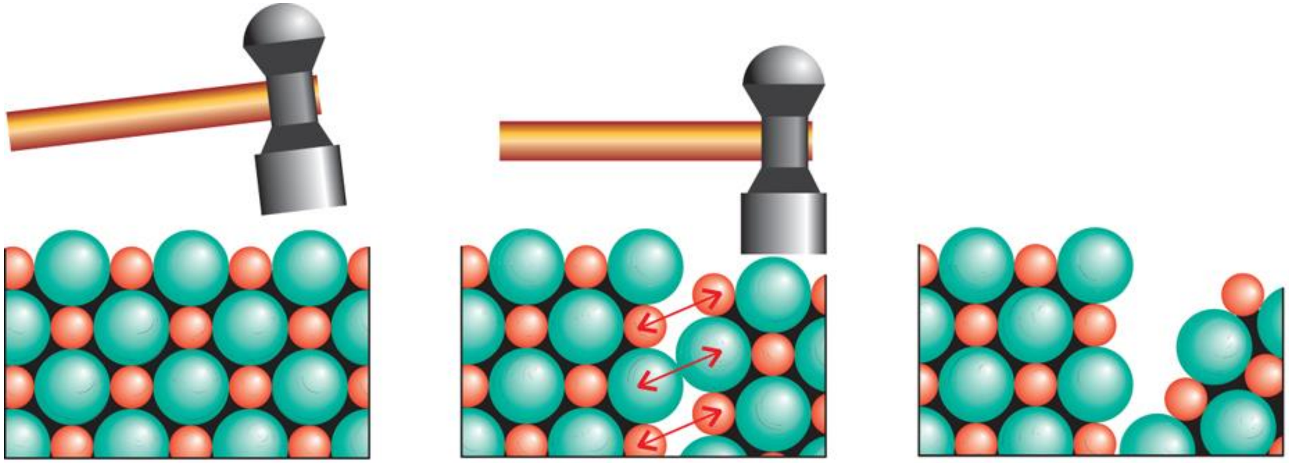
Alkali metal iodide	Lattice energy (kJ·mol^{-1})
LiI	759
NaI	700
KI	645
RbI	632
CsI	601

A **high lattice energy** value indicates **a stronger ion pair** which produces a more tightly bonded solid.

Coulomb's Potential Energy measure the strength between individual ion pairs

The **strong attraction** (Coulomb's Potential Energy) between oppositely charged ions accounts for the typical properties of ionic solids:

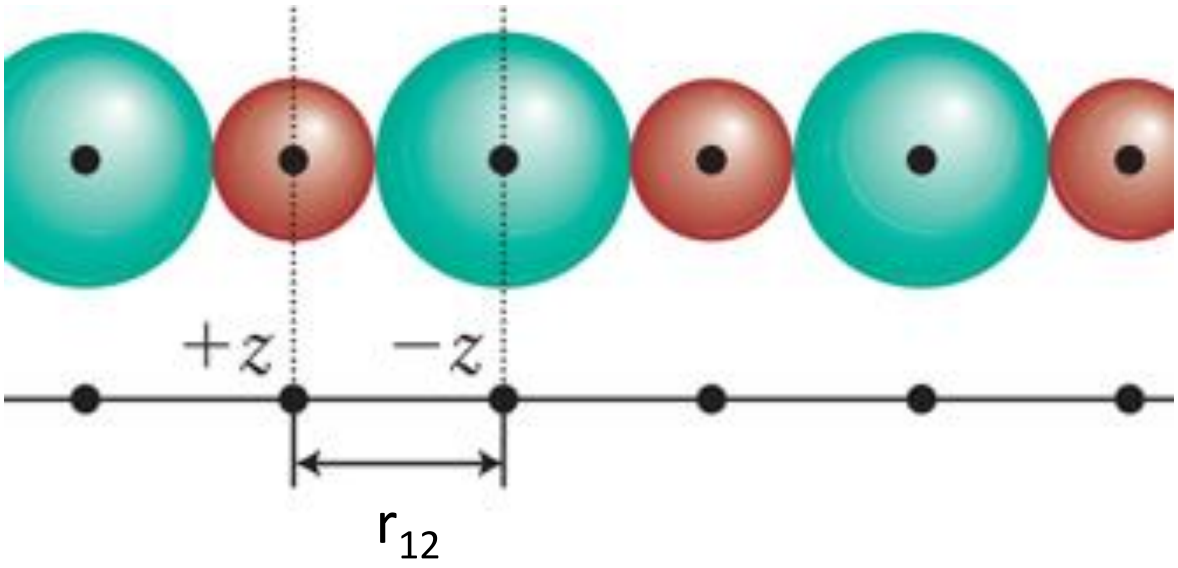
- **high melting points** and
- **brittleness**.



Coulomb's Potential Energy measure the ion-ion force

$$E_{P,12} = \frac{z_1 z_2 e^2}{4\pi\varepsilon_0 r_{12}}$$

As r_{12}↑ **E**↓



- e is the fundamental charge (the absolute value of the charge of an electron),
- z_1 and z_2 are the charge numbers of the two ions, as either + 1, or -1.
- r_{12} is the distance between the centers of the ions, and
- $\mathcal{E}_0$ is the vacuum permittivity.

Coulomb's Potential Energy measure the ion-ion force

Avogadro’s constant

$$E_P = -A\frac{z^2 N_A e^2}{4\pi\varepsilon_0 d}$$

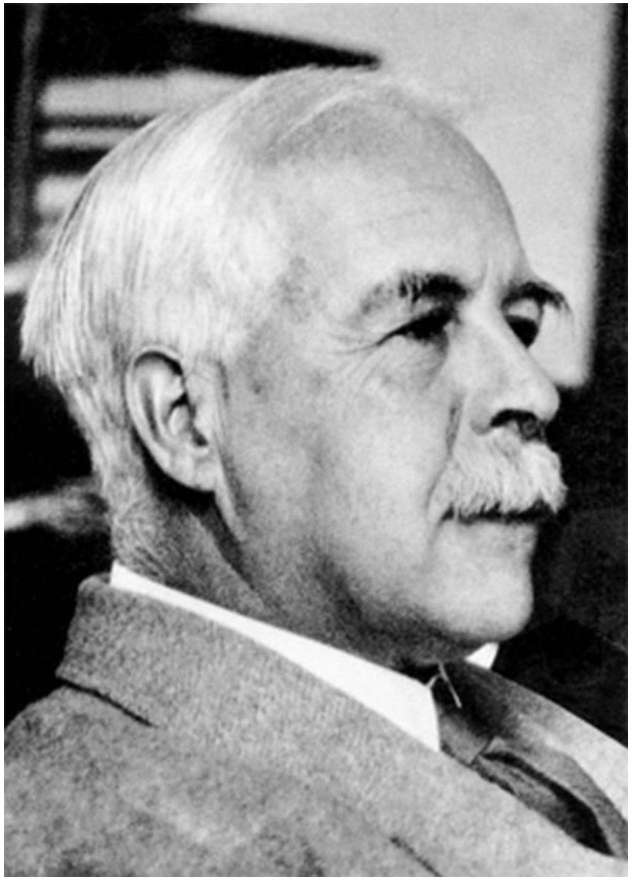
		A
CsCl	cesium chloride	1.763
CaF_2	fluorite	2.519
NaCl	rock salt	1.748
TiO_2	rutile	2.408

Negative means: there is a net lowering of energy, the attraction between opposite charges overcomes the repulsion between like charges.

“A” is called the Madelung constant. It depends on how the ions are arranged about one another.

Larger Madelung constants are smaller, highly charged ions that **pack closely together**.

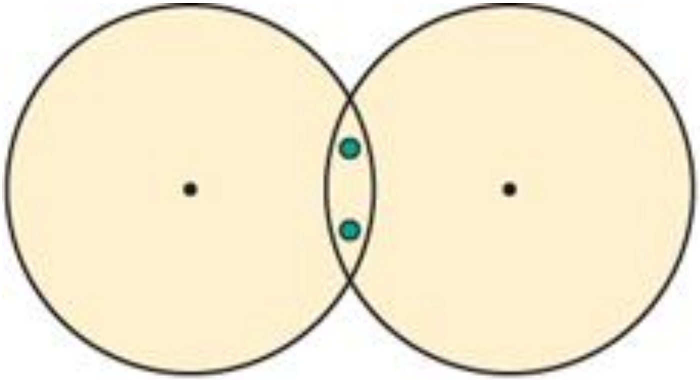
This lead to stronger interactions with high charged, small radii tightly packed crystals.



Covalent Bonds form between **two nonmetals** that **do not form into ions**.

The nature of nonmetal bonds *puzzled* scientists until 1916, when **G.N. Lewis** published his explanation.

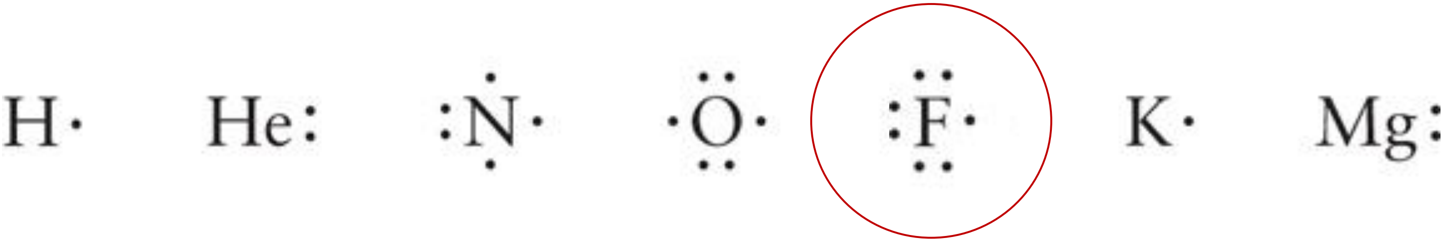
A brilliant insight, before anyone knew anything about quantum mechanics.



Shared electron pair

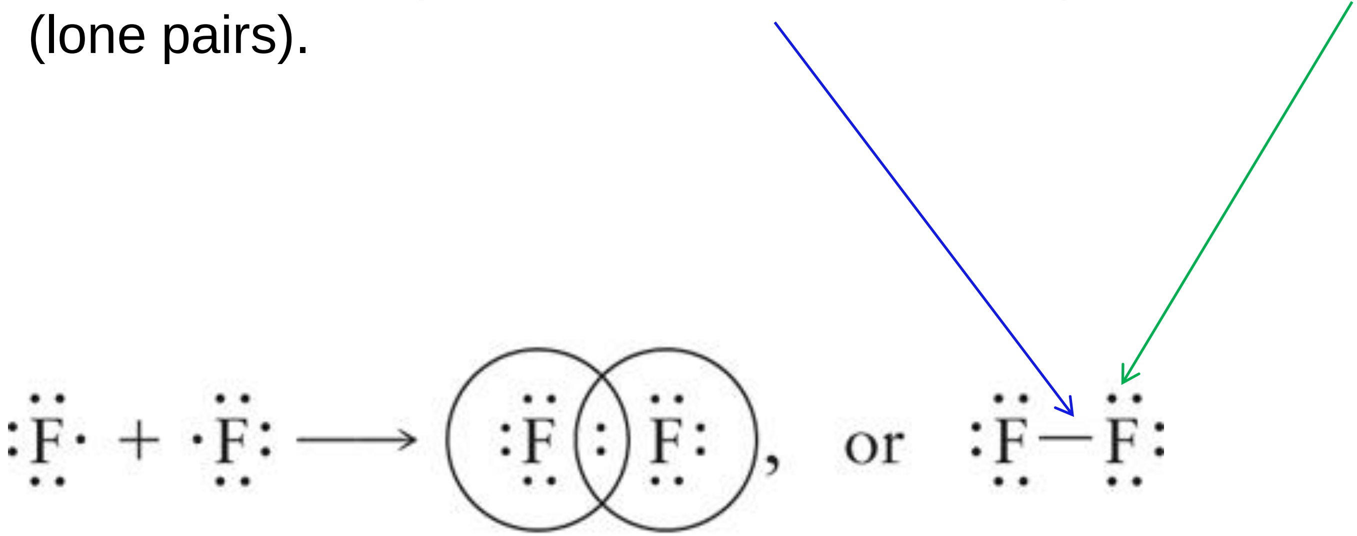
No Columbic interactions

Lewis: Share to an Octet



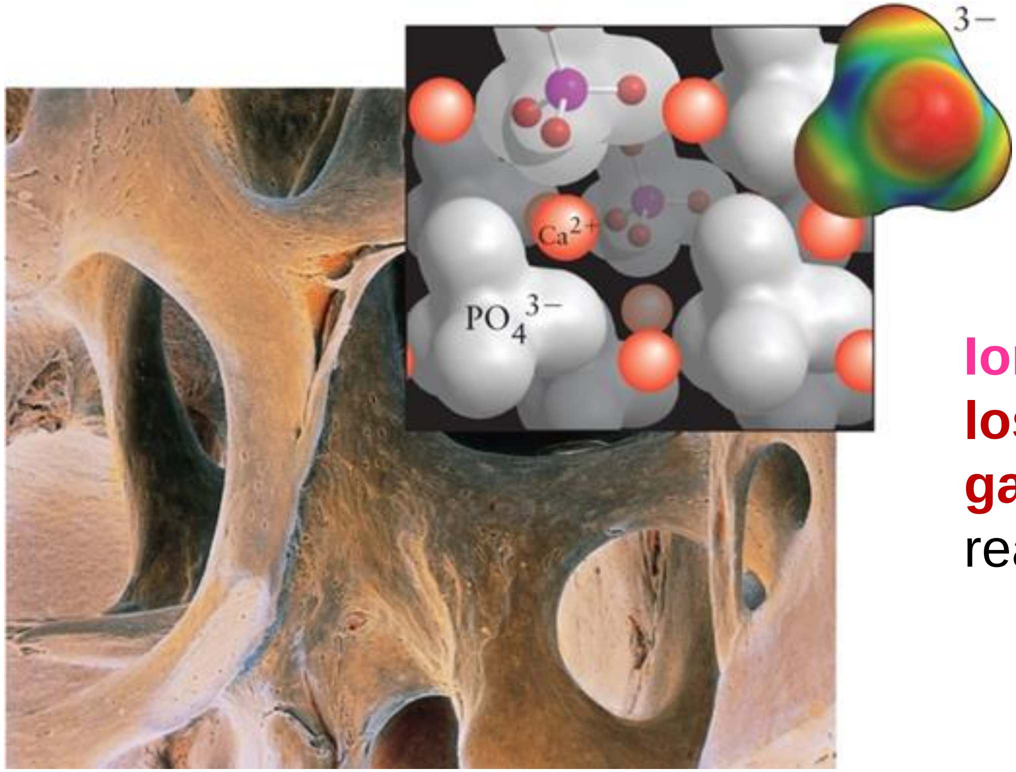
A fluorine atom can achieve an octet by accepting a share in an electron from another fluorine atom.

The **octet** (or duplet) shows **lines** (bonding pairs) and **dots** (lone pairs).



Covalent bonds form by atoms **sharing** electrons until they reach a ***noble-gas configuration***.

Lewis called this principle the **octet rule**, reaching a ***noble-gas configuration***



Ionic bonds form when one element **loses** electrons and the other atom **gains** electrons, until both atoms reach a ***noble-gas configuration***.

Rules to Write Dot Structures

1. Write a skeleton molecule with the lone atom in the middle (Hydrogen can never be in the middle).

2. Find the number of electrons needed (N)
    (8 x number of atoms, 2 x number of H atoms)

1. Find the number of electrons you have (valence e$^-$'s) (H)

2. Subtract to find the number of bonding electrons (N-H=B)

3. Subtract again to find the number of non-bonding electrons (H-B=NB)

4. Insert minimum number of bonding electrons in the skeleton between atoms only. Add more bonding if needed until you have B bonding electrons.

5. Insert needed non-bonding electrons around (not between) atoms so that all atoms have 8 electrons around them. The total should be the same as NB in 5 above.

Water H_2O

1. S H O H

2. N
$2 \times 2 = 4$ for Hydrogen
$1 \times 8 = 8$ for Oxygen
$4+8 = 12$ needed electrons

12 N

3. H
$2 \times 1 = 2$ for Hydrogen
$1 \times 6 = 6$ for Oxygen
You have 8 available electrons

- 8 H

4. B
$12 - 8 = 4$ bonding electrons

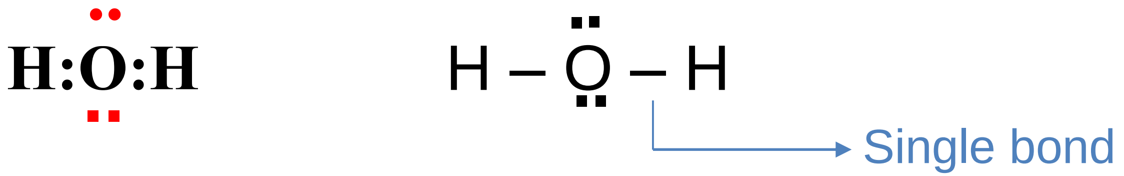
- 4 B

5. NB
$8 - 4 = 4$ non-bonding electrons

4 NB

6.

H:O:H



Single bond

Carbon dioxide CO_2

1. S O C O

2. N

1 x 8 = 8 for Carbon
2 x 8 = 16 for Oxygen
8+16=24 needed electrons

24 N

3. H

1 x 4 = 4 for Carbon
2 x 6 = 12 for Oxygen
You have 16 available electrons

- 16 H

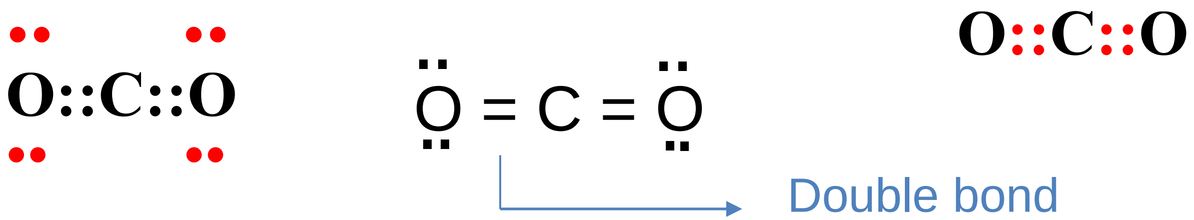
4. B 24 - 16 = 8 bonding electrons

5. NB 16 – 8 = 8 non-bonding electrons

- 8 B

8 NB

6.



Acetylene C_2H_2

1. S

H C C H

2. N

$2 \times 8 = 16$ for Carbon
$2 \times 2 = 4$ for Hydrogen
$16+4 = 20$ needed electrons

20 N

3. H

$2 \times 4 = 8$ for Carbon
$2 \times 1 = 2$ for Hydrogen
You have 10 available electrons

- 10 H

4. B

$20 - 10 = 10$ bonding electrons

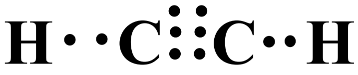
5. NB

$10 - 10 = 0$ non-bonding electrons

- 10 B

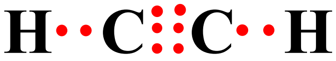
0 NB

6.



$H-C\equiv C-H$

Triple bond



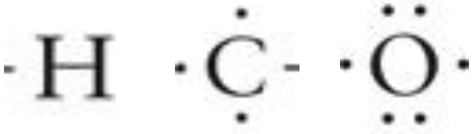
Practice

Write the Lewis structure for the:

NH_4^+

CN^-

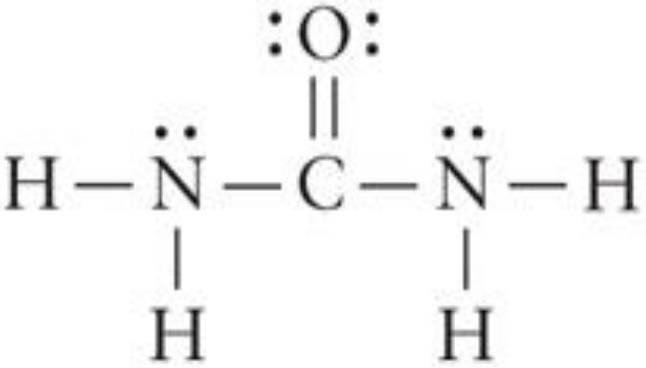
Remember **simple** Lewis Dot diagrams



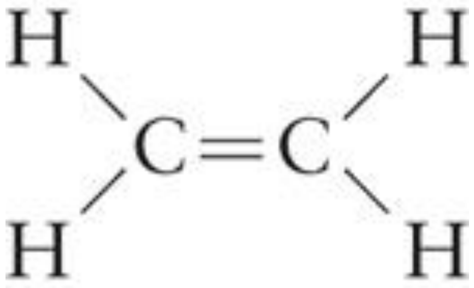
1 bond, 4 bonds, 2 bonds to complete their octet

Molecules have **symmetry**

Urea, $(NH_2)_2CO$



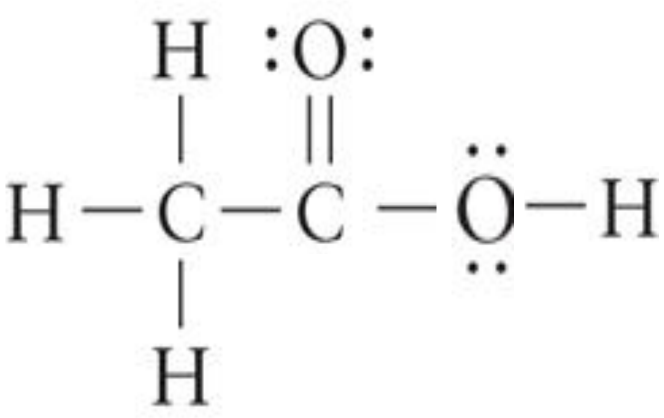
C_2H_4

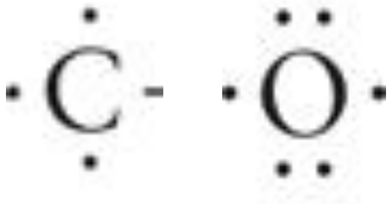


Read the formula for order of atom attachment

CH_3COOH

acetic acid



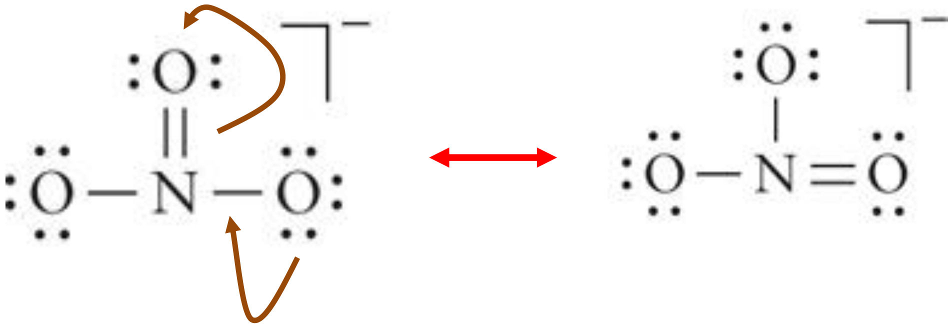


Carbons makes 4 bonds and oxygen makes 2 bonds to complete the octet.

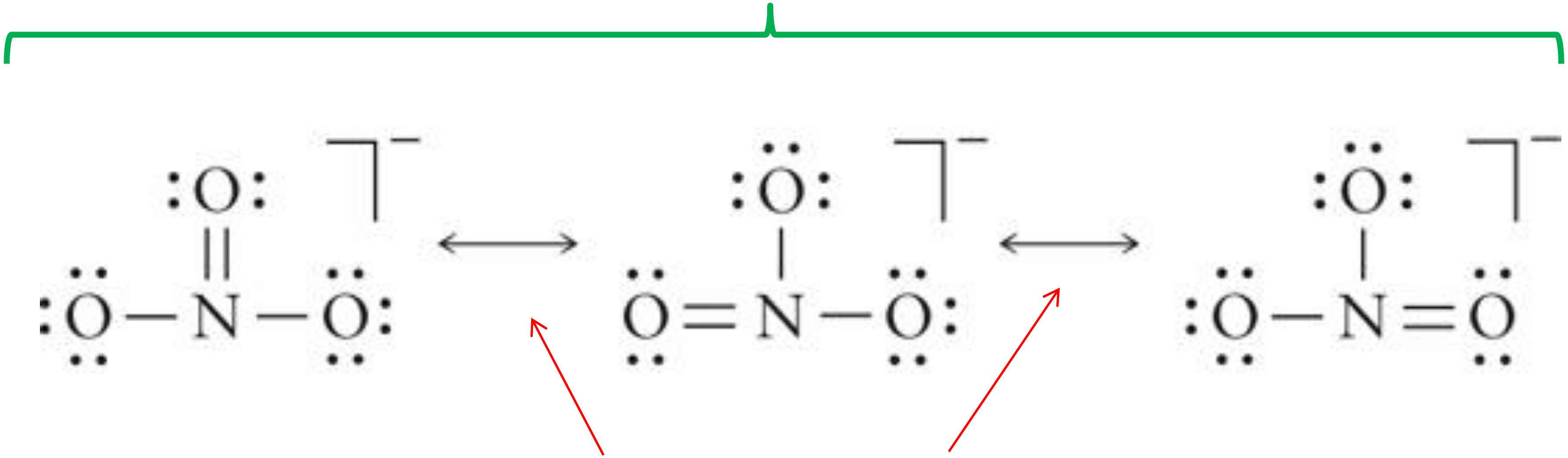
Resonance Structures

Delocalized electrons ***hop*** from one atom to another; no discretion as long as it's the *same atom pair*.

Nitrate ion, NO_3^-

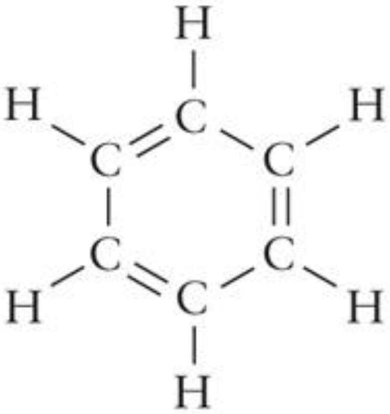


Resonance Structures



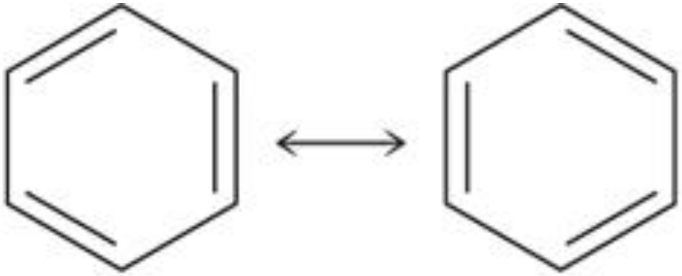
Resonance arrows

Kekulé aromatic structures



Kekulé structure

Kekulé structure, stick form



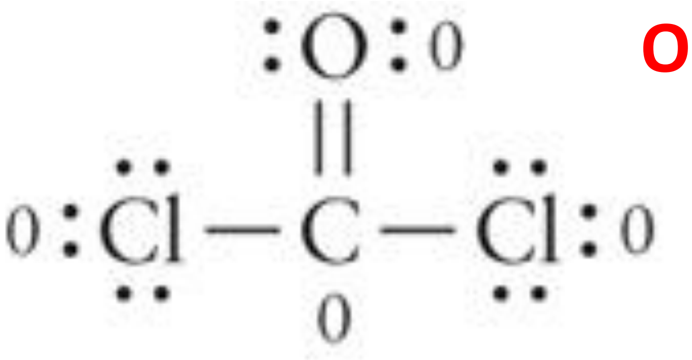
Benzene resonance structure

Final, “**blended**” structure for Benzene

Formal Charge

$$Formal\ Charge = V - \left(L + \frac{1}{2}B\right)$$

V: valance e$^-$
L: lone pair e$^-$
B: bonding e$^-$



O 6 - (4 + ½ 4) = 0

Cl 7 - (6 + ½ 2) = 0

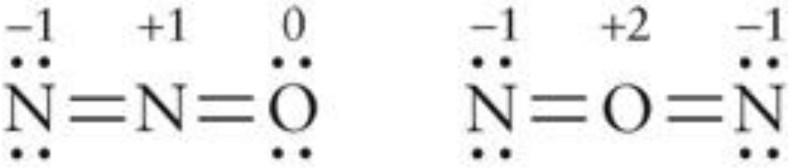
C 4 - (0 + ½ 8) = 0

The sum of formal charges is equal to the overall charge of the molecule or ion; electrically neutral molecule, have a formal charge of zero.

$$Formal\ Charge = V - \left(L + \frac{1}{2}B\right)$$

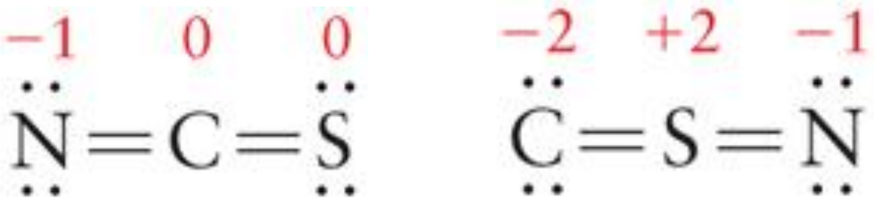
Formal charges can predict the most *favorable* Lewis structure:

NNO



$\overset{-1}{\text{N}}=\overset{+1}{\text{N}}=\overset{0}{\text{O}}$ $\quad$ $\overset{-1}{\text{N}}=\overset{+2}{\text{O}}=\overset{-1}{\text{N}}$

CNS$^-$

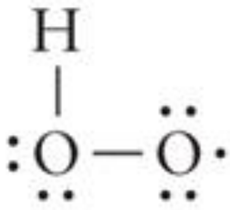


$\overset{-1}{\text{N}}=\overset{0}{\text{C}}=\overset{0}{\text{S}}$ $\quad$ $\overset{-2}{\text{C}}=\overset{+2}{\text{S}}=\overset{-1}{\text{N}}$

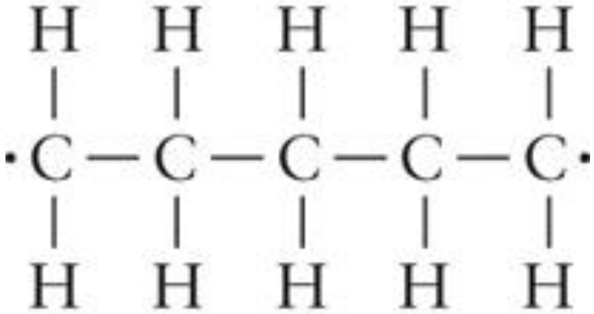
The structure with the lowest formal charges on each atom is the most plausible (lowest energy) structure.

Exceptions to the Octet Rule

Radicals are something you cannot isolate, are very unstable and are highly reactive.

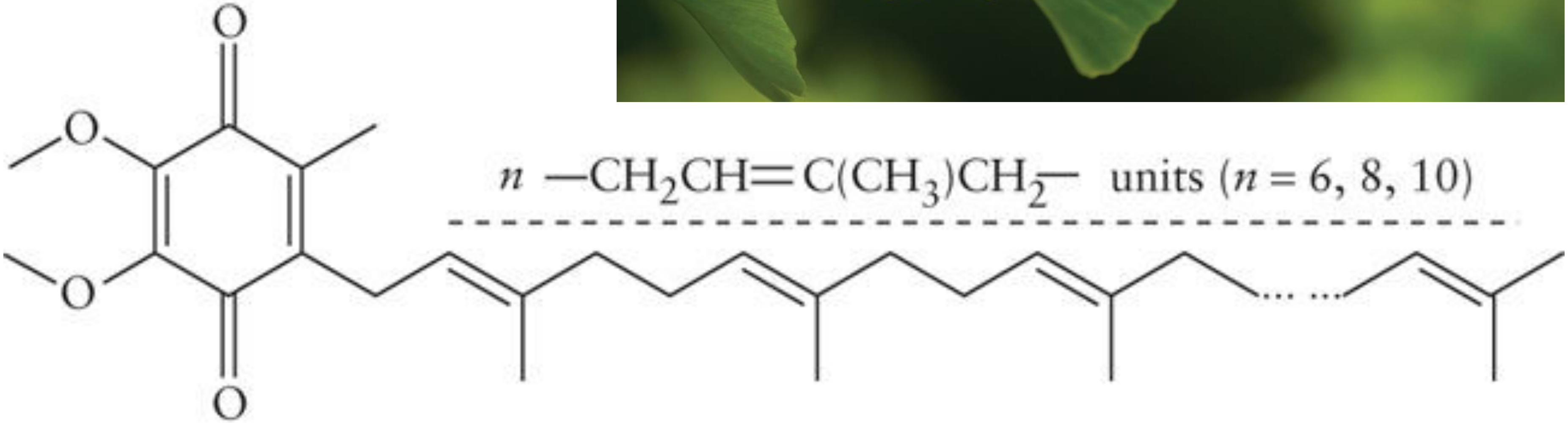


Hydrogenperoxyl, $HO_2\cdot$



A biradical

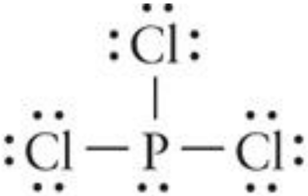
Gingko biloba like other green leafy eatable plants.



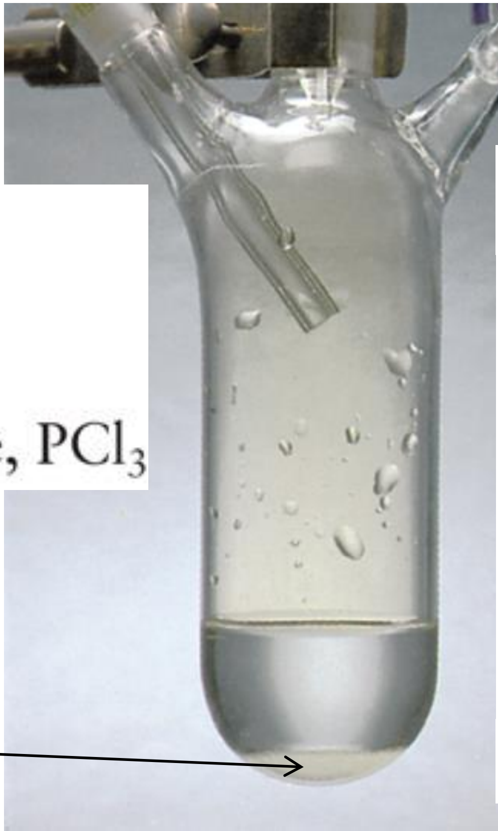
Vitamins A, C and E are antioxidant enzymes, a group of compounds called coenzyme Q. Antioxidants are **free-radical traps**.

Exceptions to the Octet Rule

Carbon, **nitrogen**, **oxygen**, and **fluorine** **obey the octet rule rigorously**. *Period 3* and subsequent periods can accommodate *more than eight electrons* in its valence shell, up to **12 electrons**.

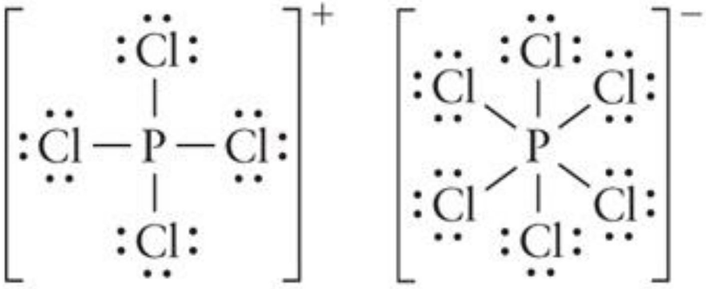


Phosphorus trichloride, PCl_3



PCl_5

$$PCl_3(l) + Cl_2(g) \rightarrow PCl_5(s)$$



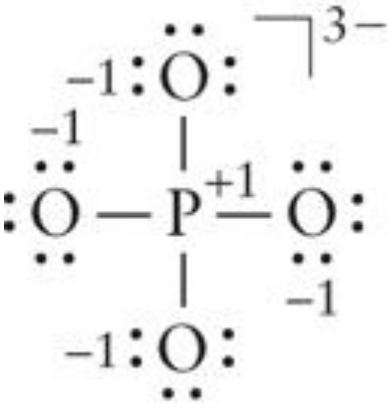
(a) PCl_4^+ (b) PCl_6^-

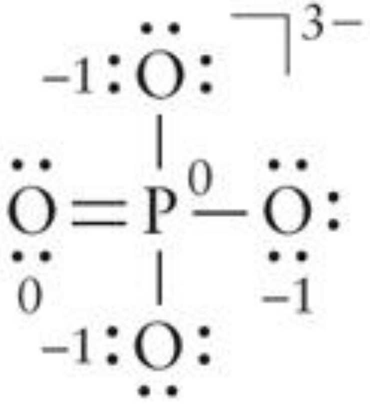
Phosphorus pentachloride, $PCl_5(s)$

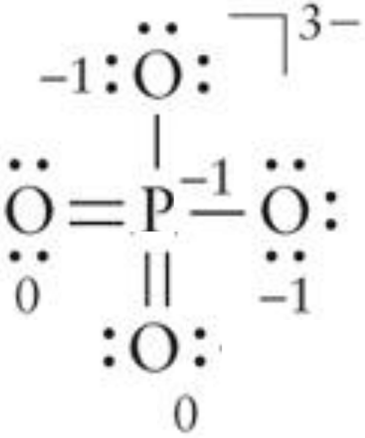
Dissociation of PCl_5

Exceptions to the Octet Rule

Determine the most stable resonance structure







P $5-(0+\frac{1}{2}10)= 0$

O $6-(4+\frac{1}{2}4)= 0$

O $6-(6+\frac{1}{2}1)= -1$

P $5-(0+\frac{1}{2}8)= +1$

O $6-(6+\frac{1}{2}1)= -1$

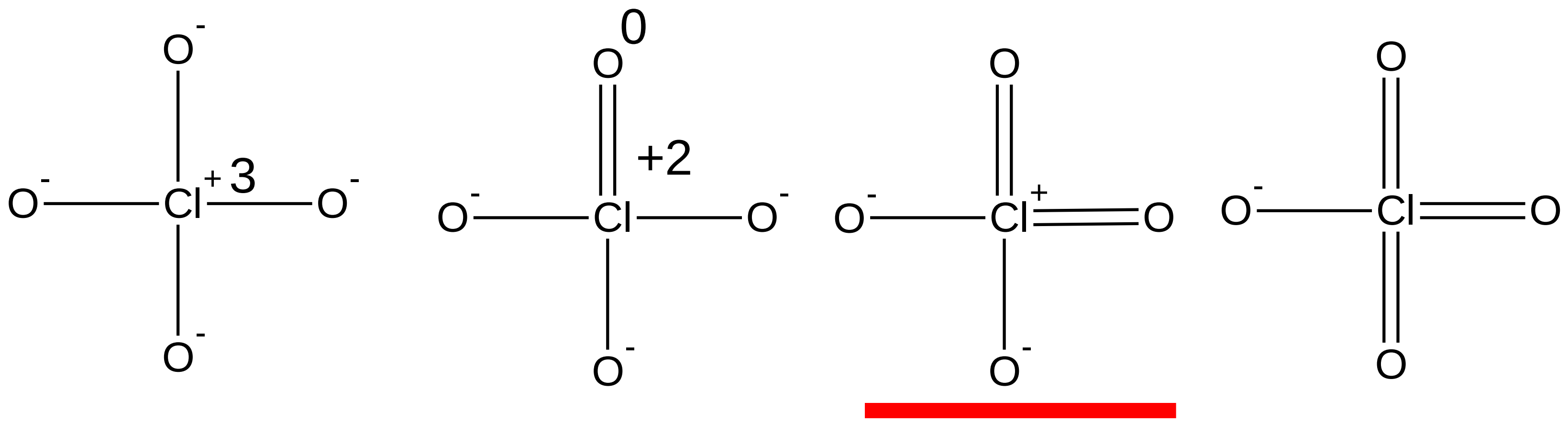
P $5-(0+\frac{1}{2}12)= -1$

O $6-(4+\frac{1}{2}4)= 0$

O $6-(6+\frac{1}{2}1)= -1$

Exceptions to the Octet Rule

ClO_4^- (VE 7+24+1=32)   12 electrons on the central atom, fewest charges



Cl: 7-4=+3	Cl: 7-5=+2	Cl: 7-6=+1	Cl: 7-7=0
O: 6-7= (-1)4	O: 6-6=0	O: 6-6=0	O:6-6=0
net -1	O: 6-7= (-1)3	O: 6-7= (-1)2	O: 6-7= -1
	net: -1	net -1	net -1

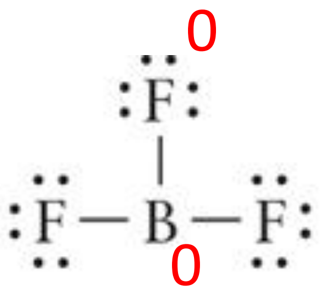
All atoms have a charge

High charge for Cl

Central atom has to many electrons

Self Test

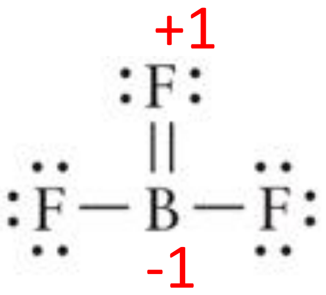
Which is the more stable?



Boron trifluoride, BF_3

F $7-(6+\frac{1}{2}2)= 0$

B $3-(0+\frac{1}{2}6)= 0$



Boron trifluoride, BF_3

F $7-(4+\frac{1}{2}4)= +1$

B $3-(0+\frac{1}{2}8)= -1$

Correcting the covalent model

$\mathrm{:\ddot{\underset{\cdot\cdot}{Cl}}{-}\ddot{\underset{\cdot\cdot}{Cl}}:} \longleftrightarrow \mathrm{:\ddot{\underset{\cdot\cdot}{Cl}}:^{-}\ \ddot{\underset{\cdot\cdot}{Cl}}:^{+}} \longleftrightarrow \mathrm{:\ddot{\underset{\cdot\cdot}{Cl}}^{+}\ :\ddot{\underset{\cdot\cdot}{Cl}}:^{-}}$

Both ionic structures **have the same** resonance hybrid energy.

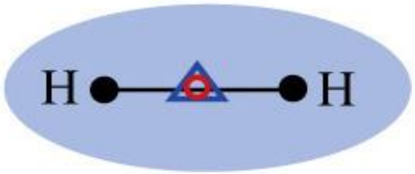
Heterodiatomic molecules **do not** have the same **resonance** hybrid energy

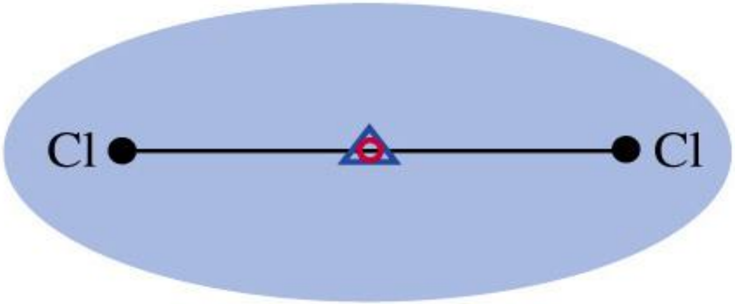
$\mathrm{H{-}\ddot{\underset{\cdot\cdot}{Cl}}:} \longleftrightarrow \mathrm{H:^{-}\ \ddot{\underset{\cdot\cdot}{Cl}}:^{+}} \longleftrightarrow \mathrm{H^{+}\ :\ddot{\underset{\cdot\cdot}{Cl}}:^{-}}$

Experiments show a small net negative charge on the Cl atom and positive on the H. This is a limitation of formal charge which estimates a net zero charge.

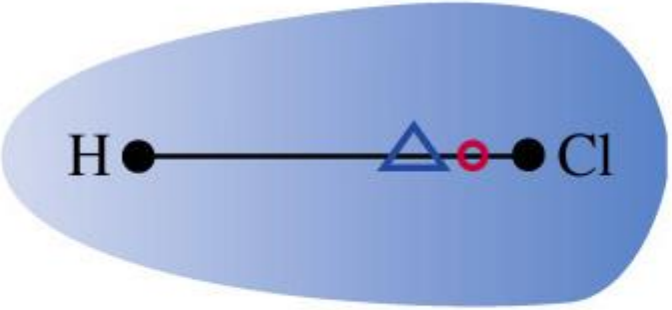
Covalent bonds

Nonpolar covalent bond: electrons are shared equally.





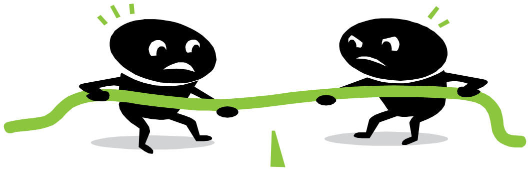
Polar covalent bond: electrons are shared unequally.



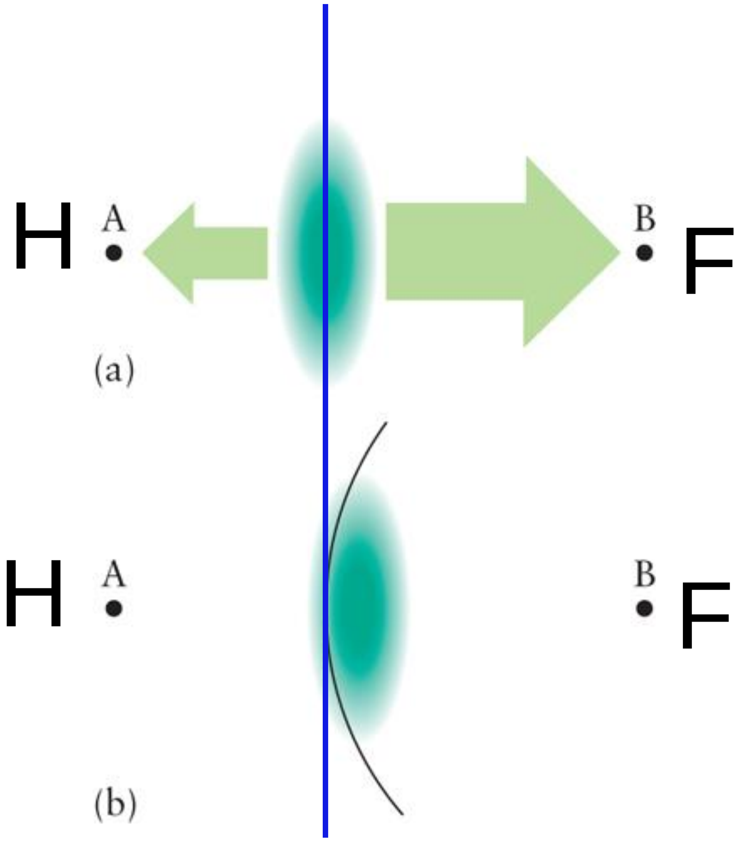
$$\overset{\delta+}{\mathrm{H}} - \overset{\delta-}{\mathrm{Cl}}$$

$$\longmapsto$$

Dipole



Arrow size indicates it’s pulling power



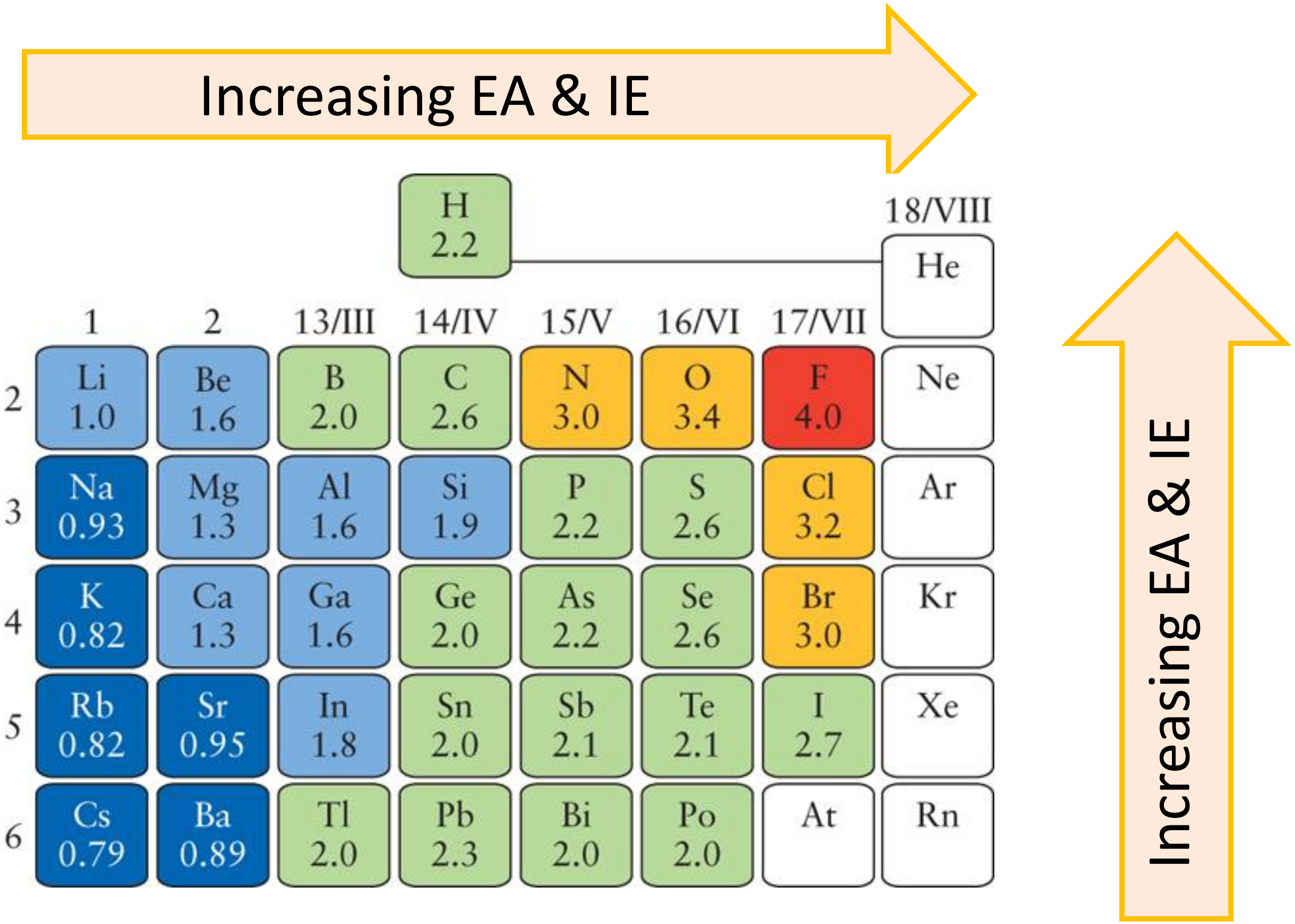
Linus Pauling proposed a quantitative **electron-pulling power ability** of an atom in a molecule called its **Electronegativity χ**.

$$\boxed{\chi = \frac{1}{2}(I - E_a)}$$

E_a: electron affinity
I: ionization energy

Blue line shows pure (top) *verses* actual (bottom) offset **electron cloud distribution** due to an atom with a greater electronegativity.

Electronegativity values by Linus Pauling.



Increasing EA & IE

Increasing EA & IE

	1	2	13/III	14/IV	15/V	16/VI	17/VII	18/VIII
				H 2.2				He
2	Li 1.0	Be 1.6	B 2.0	C 2.6	N 3.0	O 3.4	F 4.0	Ne
3	Na 0.93	Mg 1.3	Al 1.6	Si 1.9	P 2.2	S 2.6	Cl 3.2	Ar
4	K 0.82	Ca 1.3	Ga 1.6	Ge 2.0	As 2.2	Se 2.6	Br 3.0	Kr
5	Rb 0.82	Sr 0.95	In 1.8	Sn 2.0	Sb 2.1	Te 2.1	I 2.7	Xe
6	Cs 0.79	Ba 0.89	Tl 2.0	Pb 2.3	Bi 2.0	Po 2.0	At	Rn

If an atom gives up an electron reluctantly it has **high** ionization energy and if the electrons attaches favorable it has **high** electron affinity.

Electronegativity & bonds

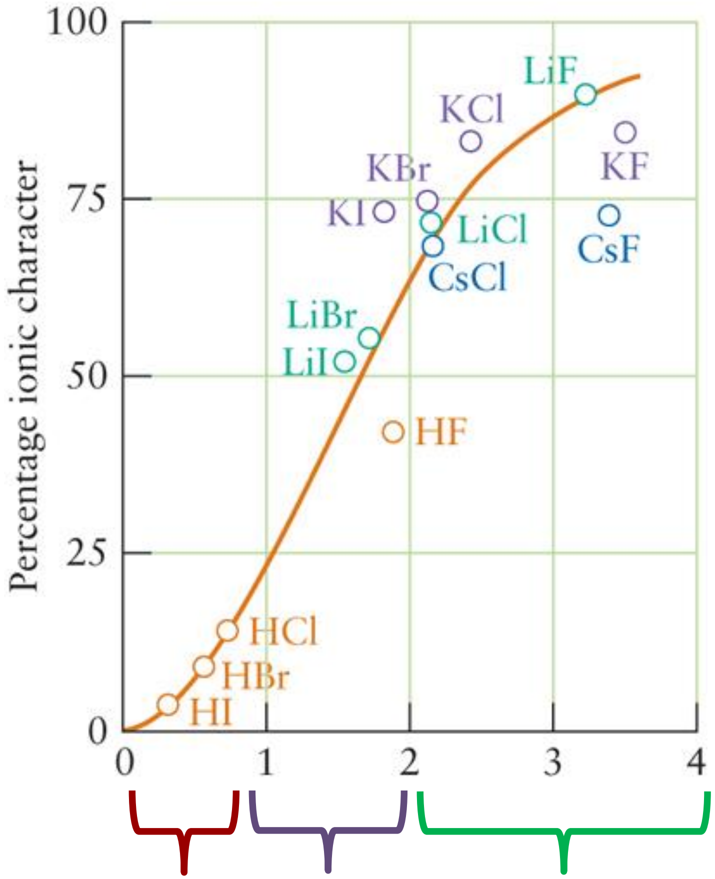
Electronegativity Difference Between Bonded Atoms	**Type of Bond**
Less than 0.5	Nonpolar Covalent
0.5 to 1.9	Polar Covalent
Greater than 1.9	Ionic

H — H 2.1 – 2.1 = 0 Nonpolar covalent

N — H 3.0 – 2.1 = 0.9 polar covalent

Na — F 4.0 – 0.9 = 3.1 Ionic

Electronegativity difference



Non-polar Covalent

Polar Covalent

Ionic

Li-F

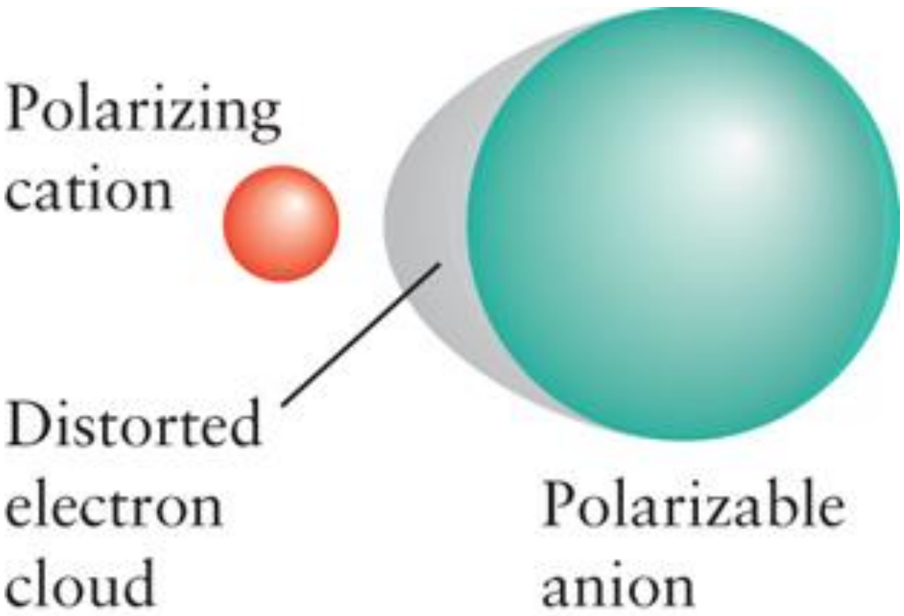
$|1.0 - 4.0| = 3.0$

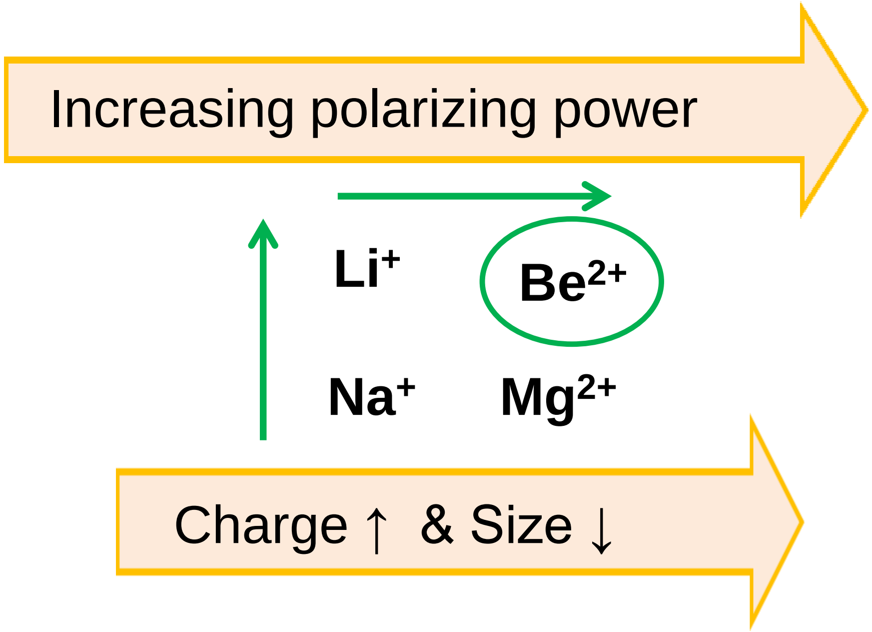
H-Cl

$|2.2 - 3.2| = 1.0$

Lattice Energy

Al^{3+} **Br^{-}**





Increasing polarizing power

Li^{+} **Be^{2+}**

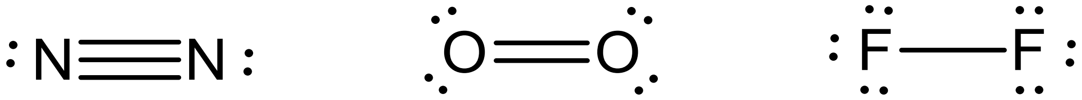
Na^{+} **Mg^{2+}**

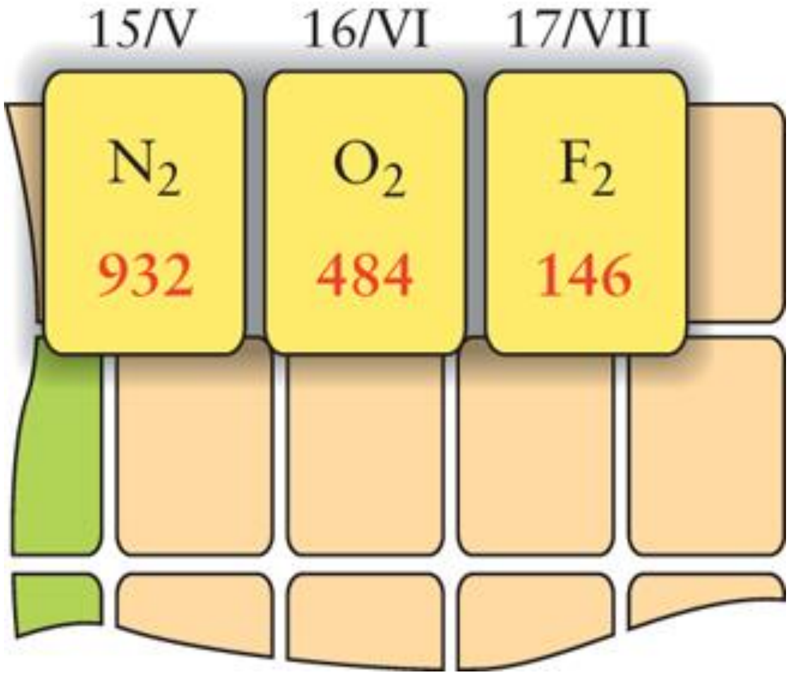
Charge ↑ & Size ↓

Polarization by small, highly charged cations of larger, nearby anions.

Higher Polarization = Higher Lattice Energy

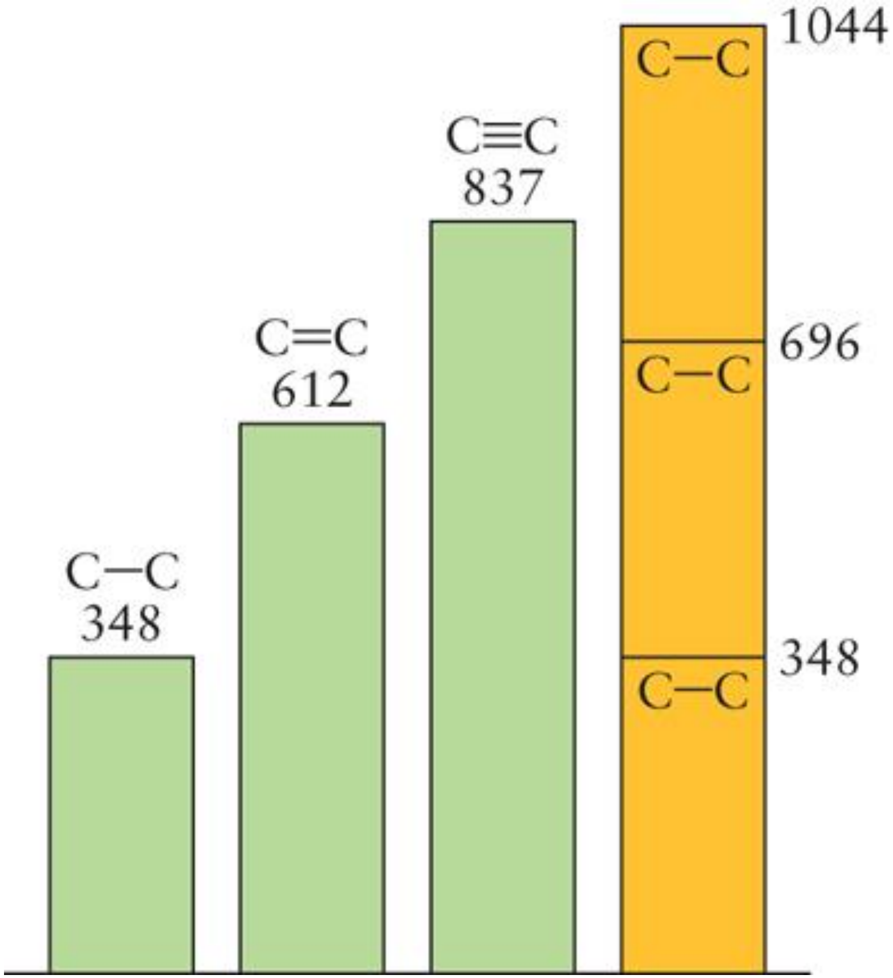
Bond Strength





Notice that a single bond is **weaker** than a triple bond.

Electrons in **double** and **triple bonds** are **not as concentrated** between two atoms as they are in a single bonds.



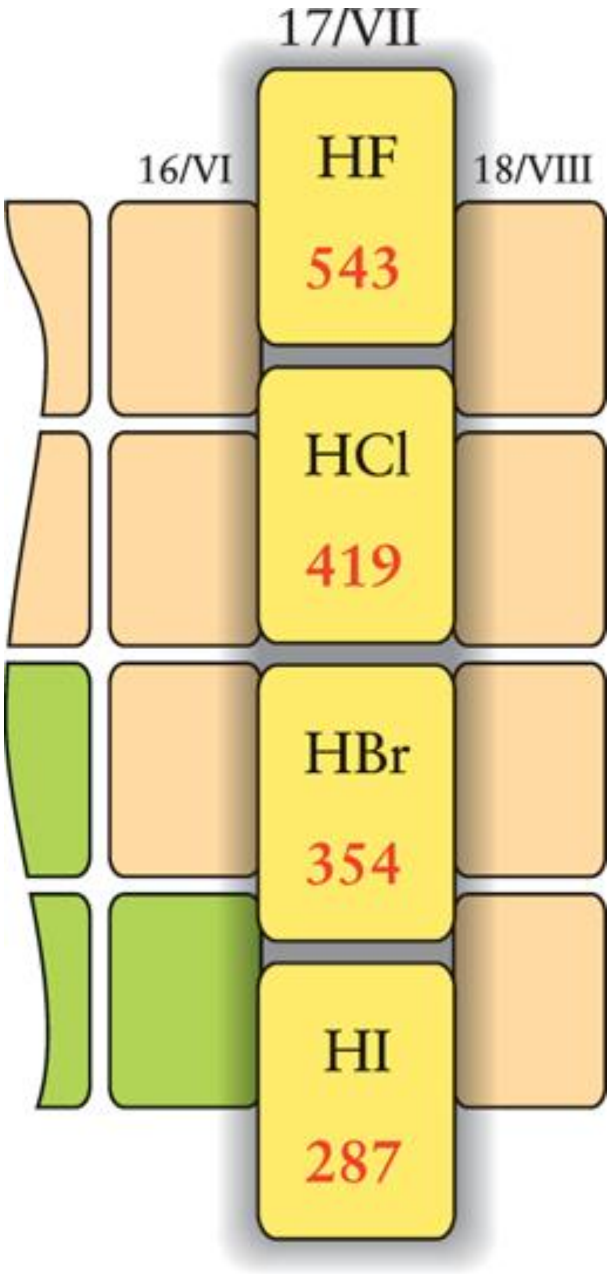
Value if each successive bond were another C-C bond

3× C-C

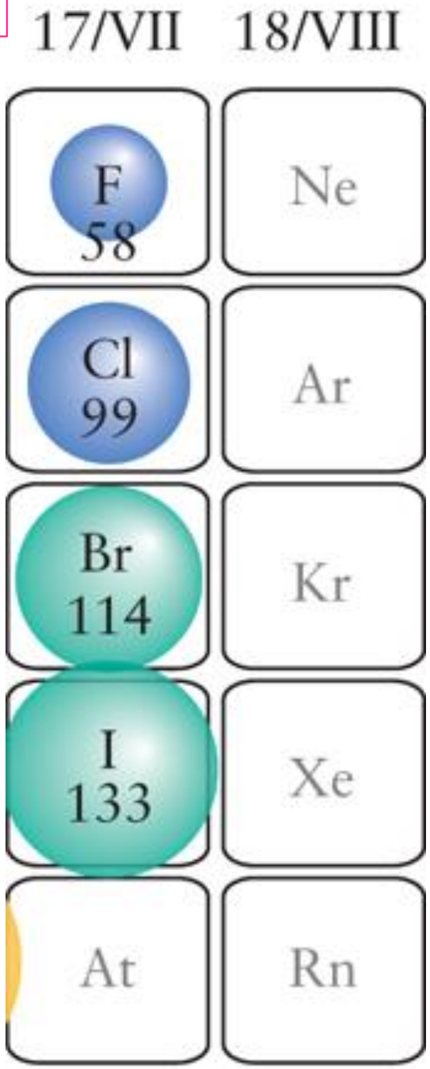
2× C-C

C-C

Strength ↓ as Size ↑

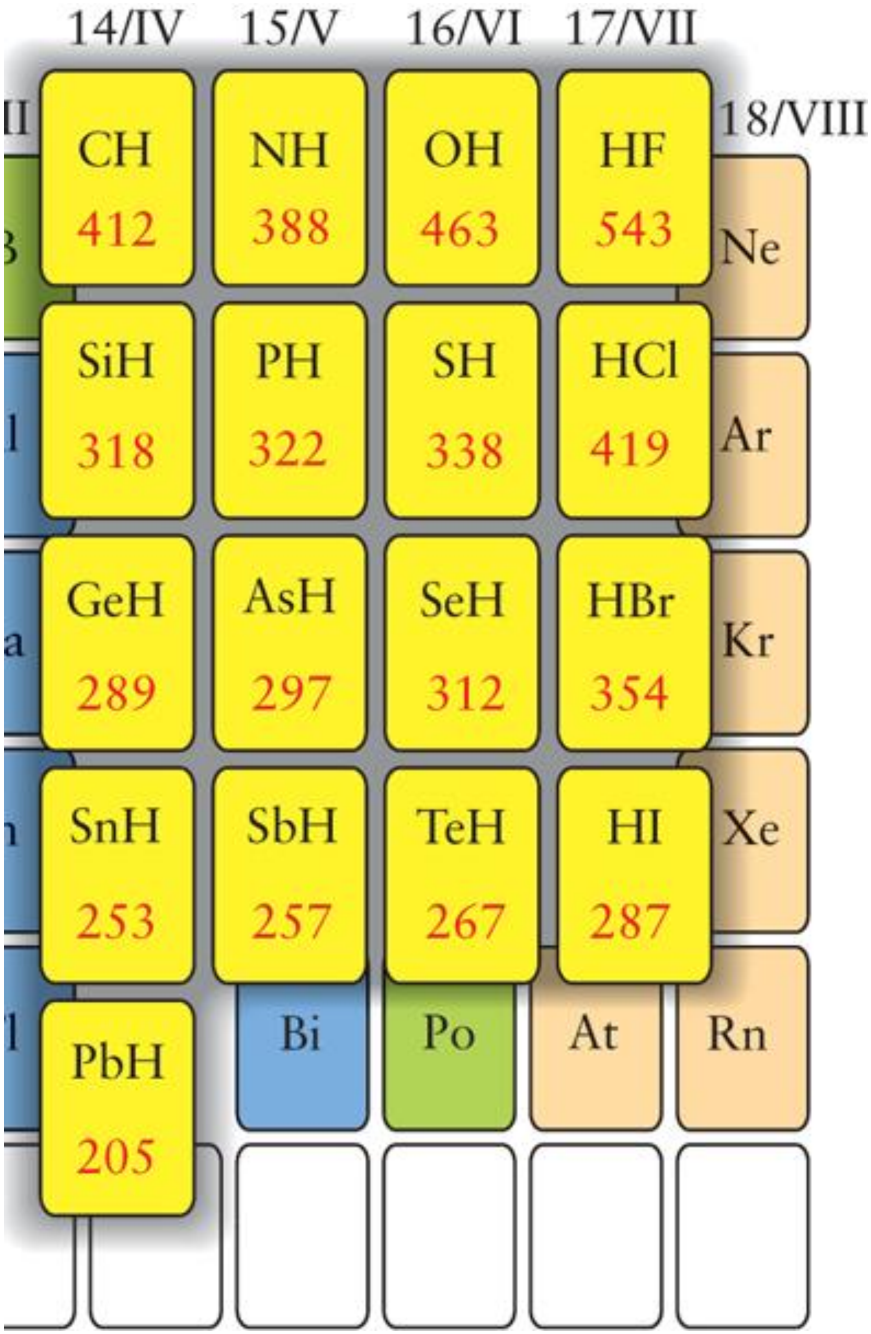


Bond Strength kJ



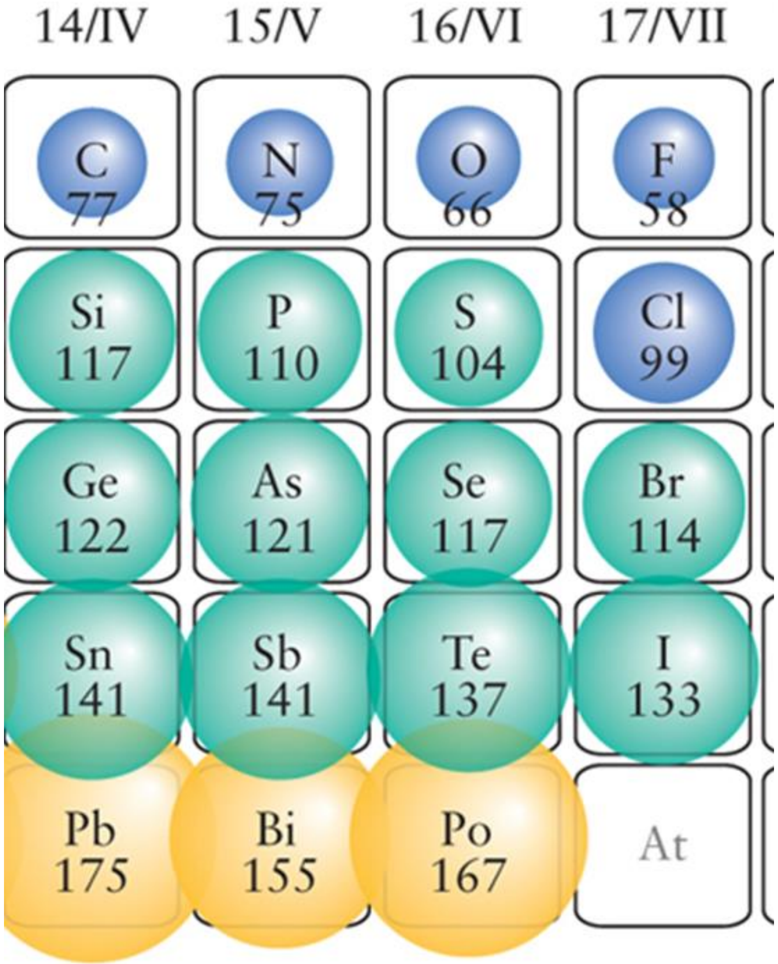
Atomic Radii

Strength↓ as Size ↑



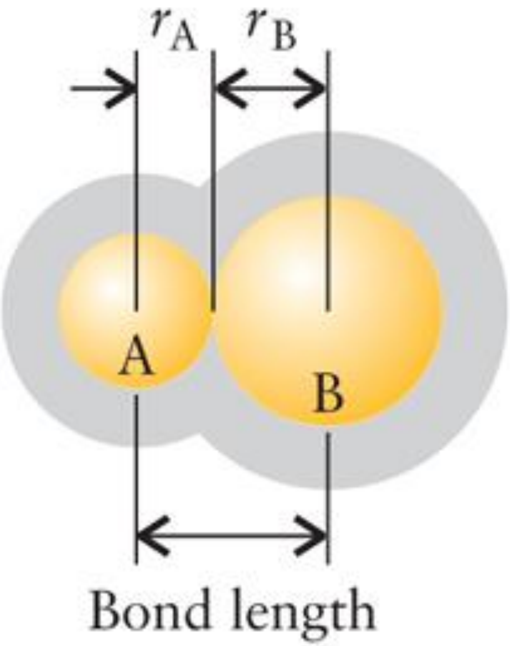
14/IV	15/V	16/VI	17/VII	18/VIII
CH 412	NH 388	OH 463	HF 543	Ne
SiH 318	PH 322	SH 338	HCl 419	Ar
GeH 289	AsH 297	SeH 312	HBr 354	Kr
SnH 253	SbH 257	TeH 267	HI 287	Xe
PbH 205	Bi	Po	At	Rn

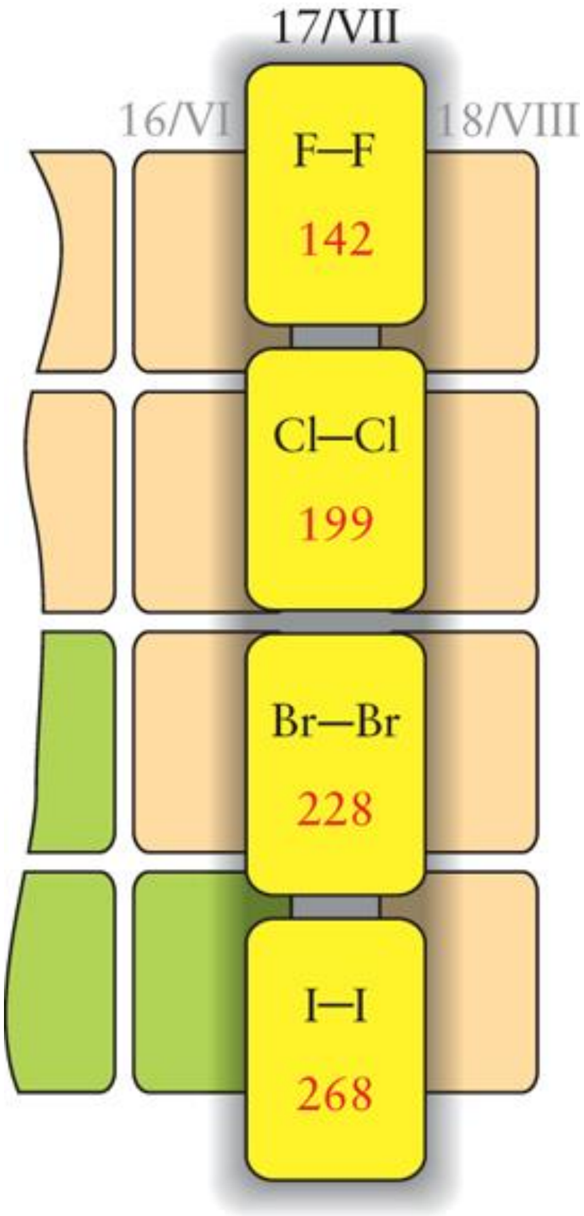
Atomic Radii

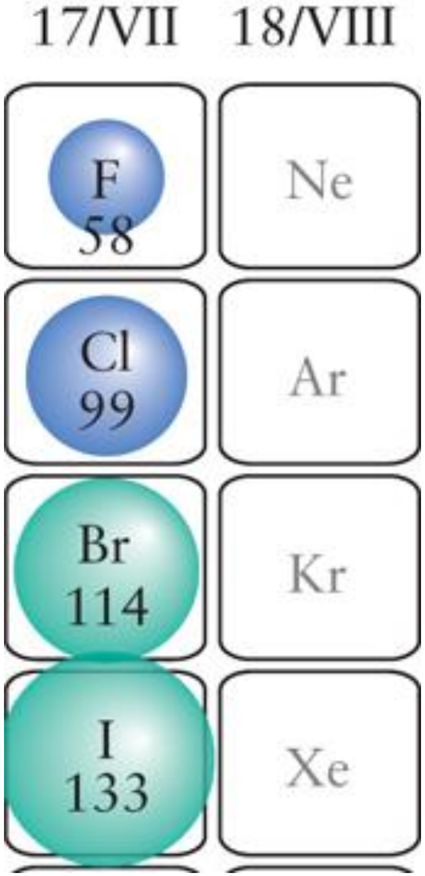


14/IV	15/V	16/VI	17/VII
C 77	N 75	O 66	F 58
Si 117	P 110	S 104	Cl 99
Ge 122	As 121	Se 117	Br 114
Sn 141	Sb 141	Te 137	I 133
Pb 175	Bi 155	Po 167	At

Bond Lengths ↑ as size ↑

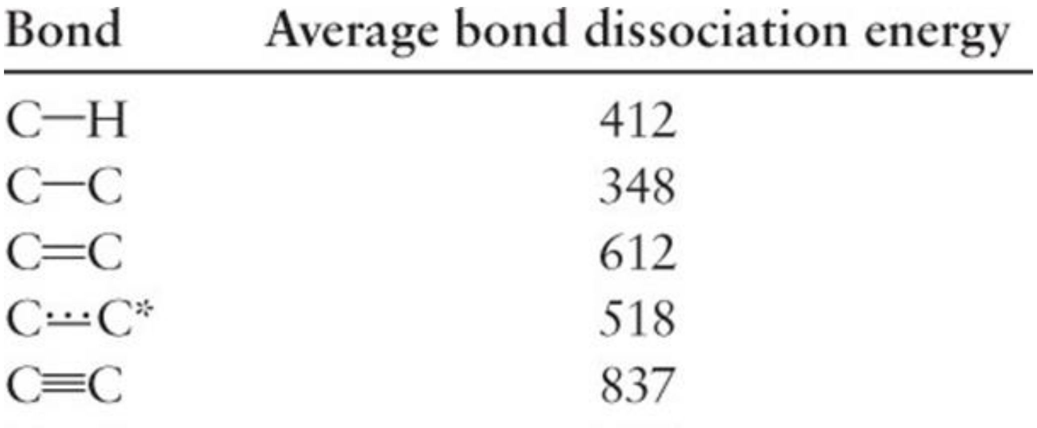






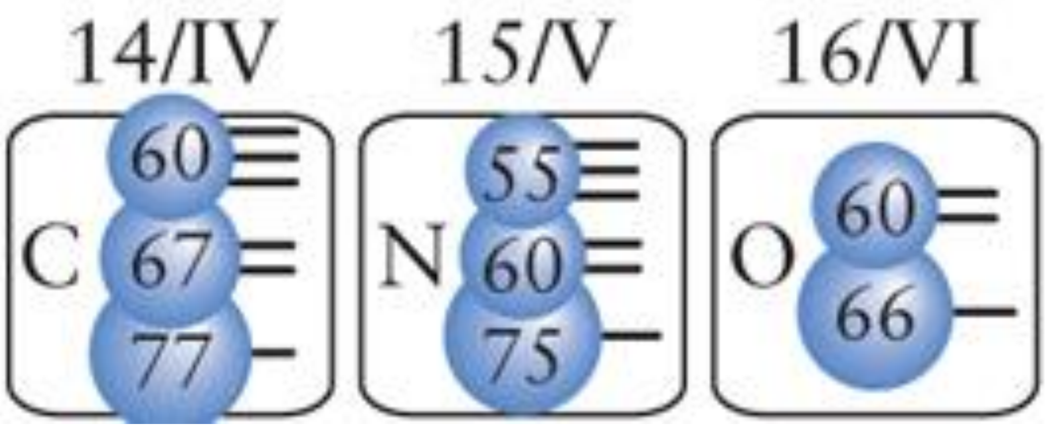
Atomic Radii

Strong bonds typically are stiffer than weak bonds.

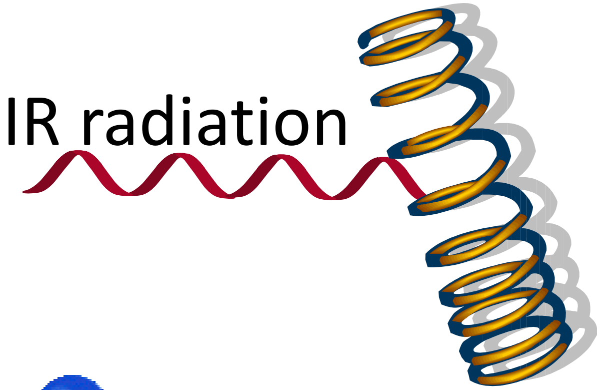


Bond	Average bond dissociation energy
C—H	412
C—C	348
C=C	612
C⋯C*	518
C≡C	837

Triple bonds are shorter and stronger.

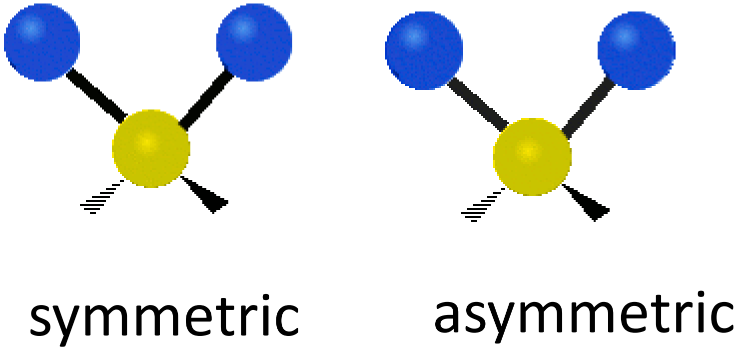


Molecules absorb infrared radiation (1000 nm or about 3×10^{14} Hz) and become vibrationally excited. We treat the bonds like springs.

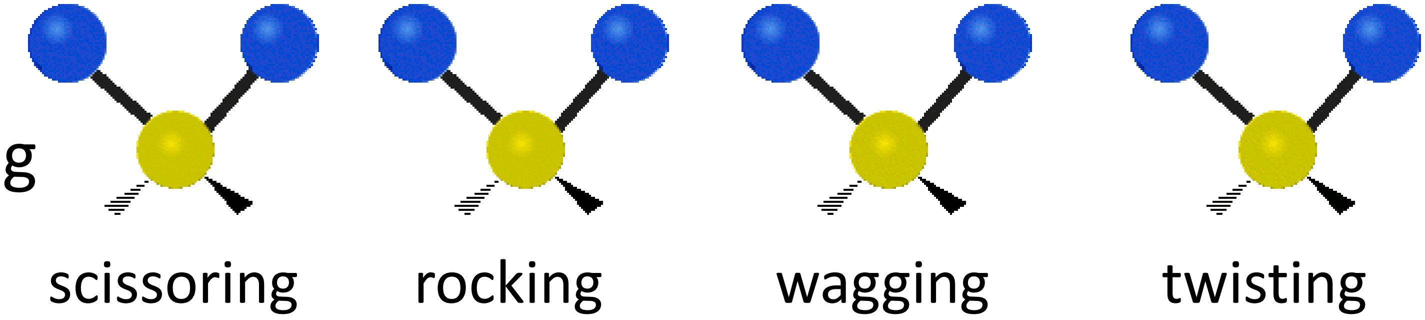


2 basic ways atoms move: stretching and bending

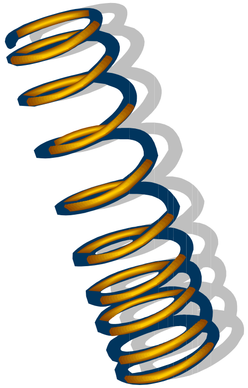
Stretching

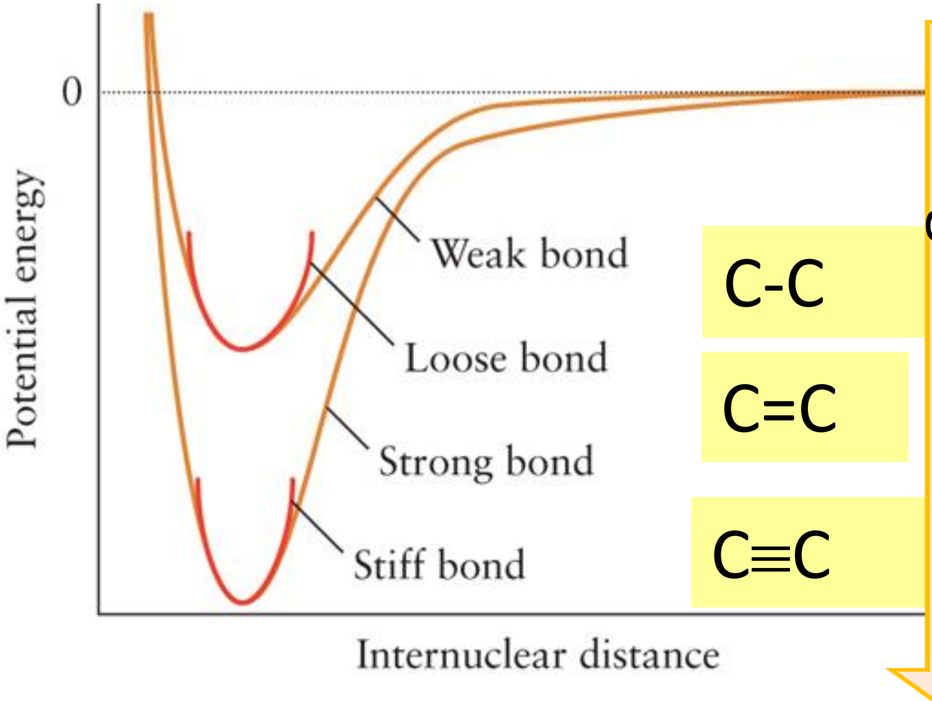


Bending



Bond strength determines the amount of IR needed to move the bonds.



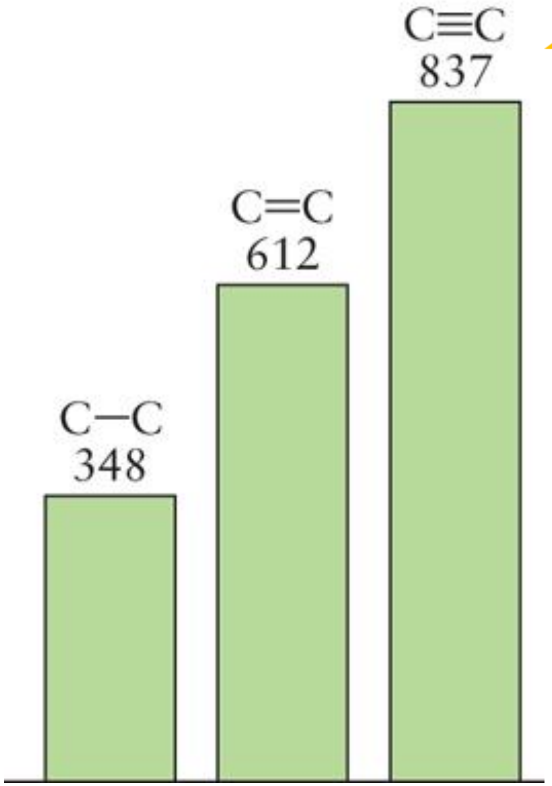


C-C

C=C

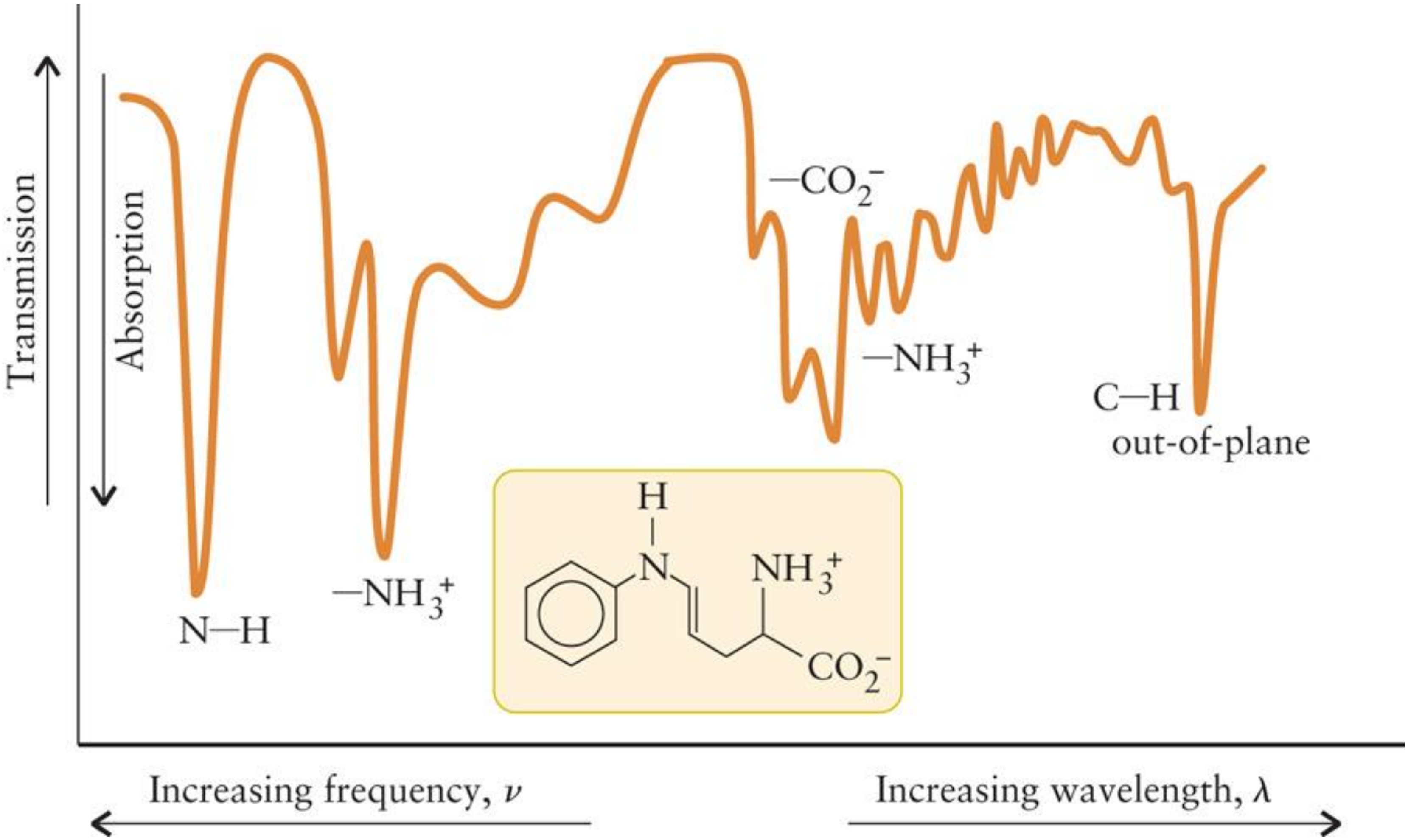
C≡C

Stronger and Shorter



Stronger and Shorter

Infrared spectroscopy of an amino acid



Stronger and Shorter