

# Chemical Principles

## **4. Chemical Bonds**

# Bond Types

- Metal Bond: metal-metal
  - Nuclei in electron sea (delocalized electrons)
- Ionic Bond: metal-nonmetal
  - Cations and anions, electrostatic,
  - Lattice energy, ion radius
- Covalent Bond: nonmetal-nonmetal
  - Sharing electron pairs
  - Polar bond and electronegativity
  - Bond energy, covalent radius

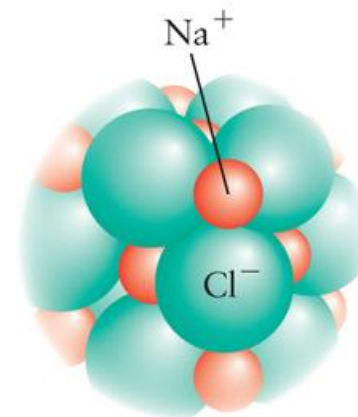
# Ionic Bond

# Ionic Bond

**Electrons transfer** from one atom to another, both become ions, the compound is held together by **electrostatic attraction**

To form ions usually requires energy (ionization and affinity), however, to form a compound the total energy is lowered.

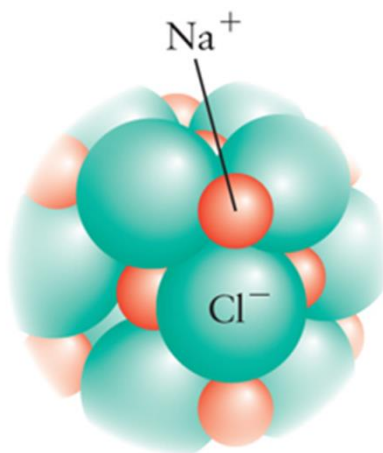
The energy is lower when  $\text{Na}^+$  and  $\text{Cl}^-$  ions bind than separated sodium and chlorine atoms.



**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**.

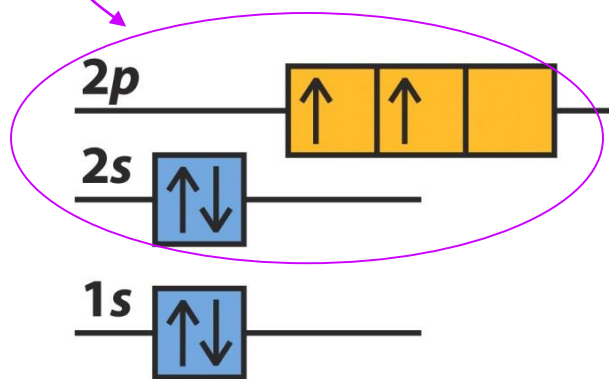


The general rule is elements gain or lose electrons, so that they have a filled valance shell:

- metals lose **valance electrons** and
- nonmetals gain electrons

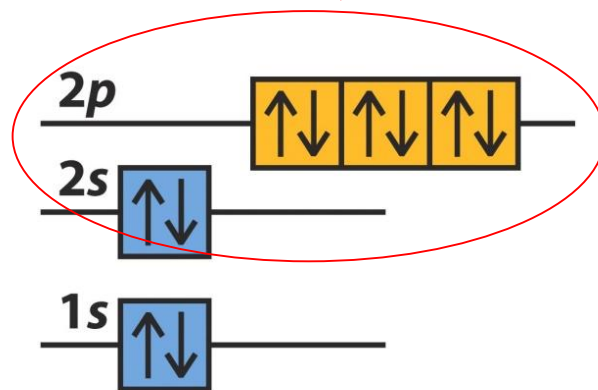
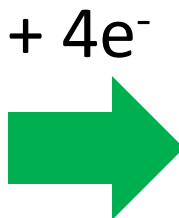
to complete/fill their noble-gas core, **octet of electrons**.

Carbon *can* gain 4 electrons



**C  $1s^2 2s^2 2p^2$ , [He]  $2s^2 2p^2$**

Elemental C



**Ne  $1s^2 2s^2 2p^6$ , [He]  $2s^2 2p^6$**

C<sup>4-</sup>

# Cations – s and p electron

	1	2	13/III	14/IV	
He	Li	Be	B		2
Ne	Na	Mg	Al		3
Ar	K	Ca	Ga		4
Kr	Rb	Sr	In	Sn	5
Xe	Cs	Ba	Tl	Pb	6
Rn	Fr	Ra			7

Metals form cations by losing electrons to their **noble-gas core** or **octet of electrons**.

S-block lose one or two s electrons

Ion	Configuration
$\text{Li}^+$	$[\text{He}] (1s^2)$
$\text{Be}^{2+}$	$[\text{He}]$
$\text{Na}^+$	$[\text{Ne}] ([\text{He}]2s^22p^6)$
$\text{Mg}^{2+}$	$[\text{Ne}]$
$\text{Al}^{3+}$	$[\text{Ne}]$

$\text{Al}^{3+}$  has p-electron involved, as on next page

# Cations – when d-block is full

	1	2	13/III	14/IV	
He	Li	Be	B		2
Ne	Na	Mg	Al		3
Ar	K	Ca	Ga		4
Kr	Rb	Sr	In	Sn	5
Xe	Cs	Ba	Tl	Pb	6
Rn	Fr	Ra			7

Period 4 and above, group 13 and 14 metallic elements may lose their **s- and p-electrons**:



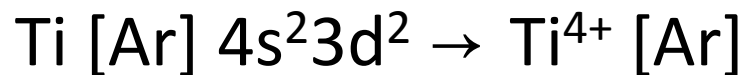
The **d electrons** of the p-block atoms are stable due to full octet and **cannot be lost**.



## Cations – when d-block is not full

A group 4 metal will

- A. lose 2 electrons.  
B. lose 4 electrons.  
C. gain 4 electrons.  
D. gain 14 electrons.



# Periodic Table of the Elements

Periodic Table of the Elements															
Group		1	2	Period 1										1	
														hydrogen	
														1.0079	
														1s <sup>1</sup>	
2		<b>Li</b> 3 lithium 6.94 2s <sup>1</sup>	<b>Be</b> 4 beryllium 9.01 2s <sup>2</sup>												
		<b>Na</b> 11 sodium 22.99 3s <sup>1</sup>	<b>Mg</b> 12 Magnesium 24.31 3s <sup>2</sup>												
3		<b>K</b> 19 potassium 39.10 4s <sup>1</sup>	<b>Ca</b> 20 calcium 40.08 4s <sup>2</sup>	<b>Sc</b> 21 scandium 44.96 3d <sup>1</sup> 4s <sup>2</sup>	<b>Ti</b> 22 titanium 47.87 3d <sup>2</sup> 4s <sup>2</sup>	<b>V</b> 23 vanadium 50.94 3d <sup>3</sup> 4s <sup>2</sup>	<b>Cr</b> 24 chromium 52.00 3d <sup>5</sup> 4s <sup>1</sup>	<b>Mn</b> 25 manganese 54.94 3d <sup>5</sup> 4s <sup>2</sup>	<b>Fe</b> 26 iron 55.84 3d <sup>6</sup> 4s <sup>2</sup>	<b>Co</b> 27 cobalt 58.93 3d <sup>7</sup> 4s <sup>2</sup>					
		<b>Rb</b> 37 rubidium 85.47 5s <sup>1</sup>	<b>Sr</b> 38 strontium 87.62 5s <sup>2</sup>	<b>Y</b> 39 yttrium 88.91 4d <sup>1</sup> 5s <sup>2</sup>	<b>Zr</b> 40 zirconium 91.22 4d <sup>2</sup> 5s <sup>2</sup>	<b>Nb</b> 41 niobium 92.91 4d <sup>4</sup> 5s <sup>1</sup>	<b>Mo</b> 42 molybdenum 95.94 4d <sup>5</sup> 5s <sup>1</sup>	<b>Tc</b> 43 technetium (98) 4d <sup>5</sup> 5s <sup>2</sup>	<b>Ru</b> 44 ruthenium 101.07 4d <sup>7</sup> 5s <sup>1</sup>	<b>Rh</b> 45 rhodium 102.90 4d <sup>8</sup> 5s <sup>1</sup>					
4		<b>Cs</b> 55 cesium 132.91 6s <sup>1</sup>	<b>Ba</b> 56 barium 137.33 6s <sup>2</sup>	<b>La</b> 57 lanthanum 138.91 5d <sup>1</sup> 6s <sup>2</sup>	<b>Hf</b> 72 hafnium 178.49 5d <sup>2</sup> 6s <sup>2</sup>	<b>Ta</b> 73 tantalum 180.95 5d <sup>3</sup> 6s <sup>2</sup>	<b>W</b> 74 tungsten 183.84 5d <sup>4</sup> 6s <sup>2</sup>	<b>Re</b> 75 rhenium 186.21 5d <sup>5</sup> 6s <sup>2</sup>	<b>Os</b> 76 osmium 190.23 5d <sup>6</sup> 6s <sup>2</sup>	<b>Ir</b> 77 iridium 192.22 5d <sup>7</sup> 6s <sup>2</sup>					
		<b>Fr</b> 87 francium (223) 7s <sup>1</sup>	<b>Ra</b> 88 radium (226) 7s <sup>2</sup>	<b>Ac</b> 89 actinium (227) 6d <sup>1</sup> 7s <sup>2</sup>	<b>Rf</b> 104 rutherfordium (261) 6d <sup>2</sup> 7s <sup>2</sup>	<b>Db</b> 105 dubnium (262) 6d <sup>3</sup> 7s <sup>2</sup>	<b>Sg</b> 106 seaborgium (266) 6d <sup>4</sup> 7s <sup>2</sup>	<b>Bh</b> 107 bohrium (264) 6d <sup>5</sup> 7s <sup>2</sup>	<b>Hs</b> 108 hassium (267) 6d <sup>6</sup> 7s <sup>2</sup>	<b>Mt</b> 109 meitnerium (268) 6d <sup>7</sup> 7s <sup>2</sup>					
5		<b>Lanthanoids</b> (lanthanides) 6			<b>Ce</b> 58 cerium 140.12 4f <sup>1</sup> 5d <sup>1</sup> 6s <sup>2</sup>	<b>Pr</b> 59 praseodymium 140.91 4f <sup>3</sup> 6s <sup>2</sup>	<b>Nd</b> 60 neodymium 144.24 4f <sup>4</sup> 6s <sup>2</sup>	<b>Pm</b> 61 promethium (145) 4f <sup>5</sup> 6s <sup>2</sup>	<b>Sm</b> 62 samarium 150.36 4f <sup>6</sup> 6s <sup>2</sup>						
		<b>Actinoids</b> (actinides) 7			<b>Th</b> 90 thorium 232.04 6d <sup>2</sup> 7s <sup>2</sup>	<b>Pa</b> 91 protactinium 231.04 5f <sup>2</sup> 6d <sup>1</sup> 7s <sup>2</sup>	<b>U</b> 92 uranium 238.03 5f <sup>3</sup> 6d <sup>1</sup> 7s <sup>2</sup>	<b>Np</b> 93 neptunium (237) 5f <sup>4</sup> 6d <sup>1</sup> 7s <sup>2</sup>	<b>Pu</b> 94 plutonium (244) 5f <sup>6</sup> 7s <sup>2</sup>						

# Anions can be formed

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

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

N  $[\text{He}]2s^22p^3$  plus  $3 e^-$  to  $\text{N}^{3-}[\text{Ne}]$

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

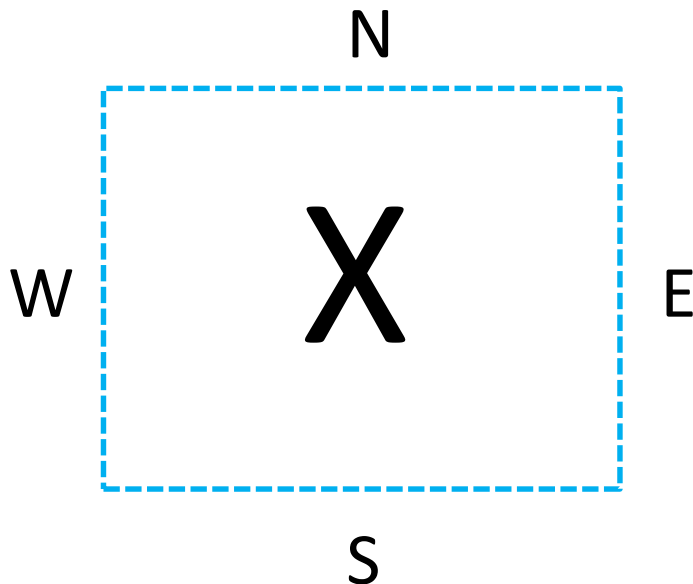
	H				18/VIII	
					He	1
	14/IV	15/V	16/VI	17/VII		
	C	N	O	F	Ne	2
	Si	P	S	Cl	Ar	3
	Ge	As	Se	Br	Kr	4
		Sb	Te	I	Xe	5
		Bi	Po	At	Rn	6

# Lewis Symbols

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



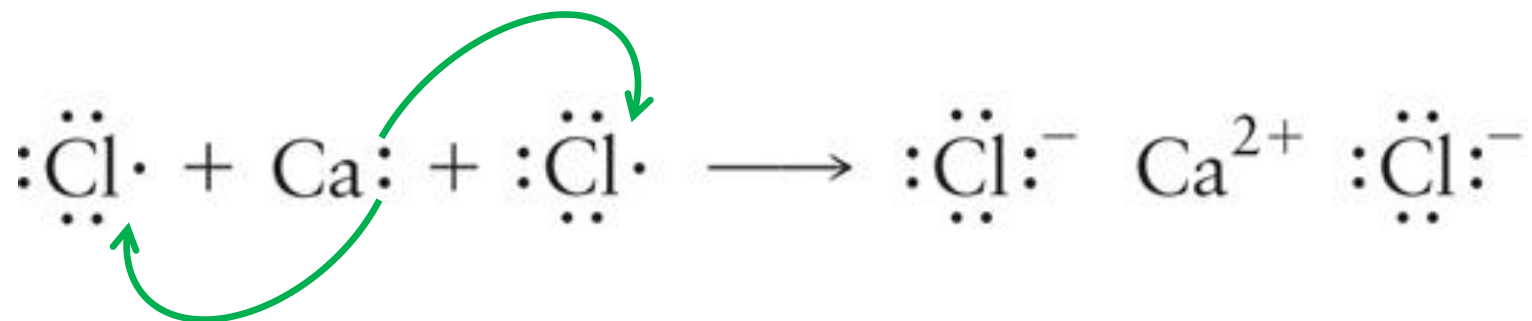
A **pair of dots** represents paired electrons (lone pair) sharing an orbital.



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

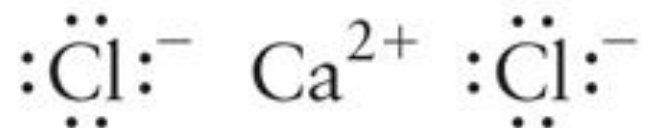
# Lewis Symbols

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



Use superscript (<sup>+</sup>, <sup>n+</sup>) or (<sup>-</sup>, <sup>m-</sup>) to indicate the net charge

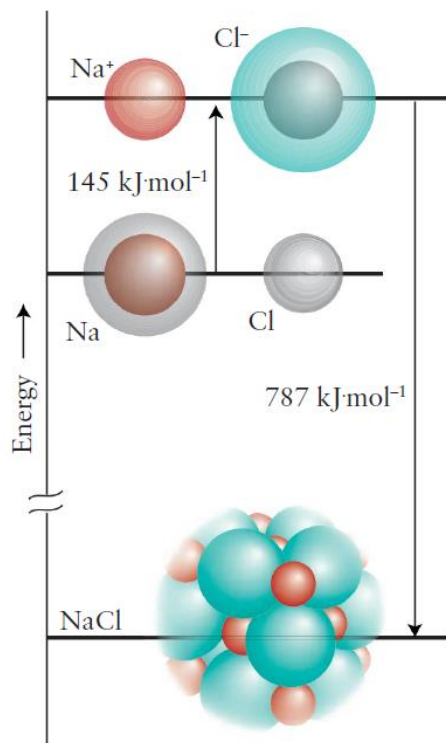
# Lewis Symbols



**Two** chloride ions ( $\text{Cl}^-$ ) ***balances the charge*** for **each** calcium ion ( $\text{Ca}^{2+}$ ) resulting in the formula  $\text{CaCl}_2$ ; the overall charges is zero.

There are **no**  $\text{CaCl}_2$  molecules, only **crystals** of three-dimensional arrays of  $\text{CaCl}_2$  ions held by the vast array of opposite charges spread throughout the crystal-hence  $\text{CaCl}_2$  is called a **formal unit**.

# How is crystal stabilized

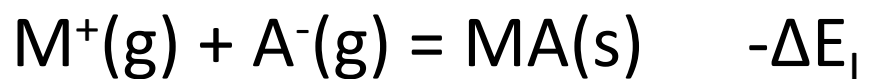


- Cation - Ionization potential, which is always positive, meaning energy is required.
- Anion - electron affinity, in most cases is positive, energy is released
- The electrostatic energy of all ions, always release energy.



# Lattice Energy

**Lattice energy** is the energy released when separated cations and anions bounded together, conventionally reported in positive value.



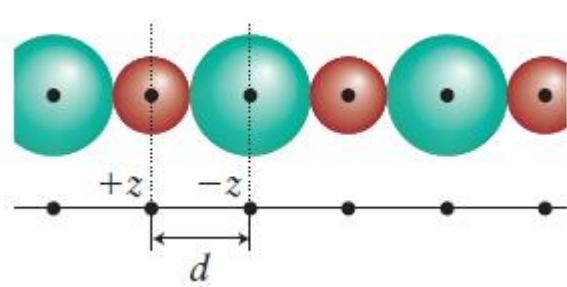
For example,  $Na^+ + Cl^- (g)$  to the ionic solid  $Na^+Cl^- (s)$  releases -787 kJ, its lattice energy is 787 kJ.

Alkali metal iodide	Lattice energy ( $\text{kJ} \cdot \text{mol}^{-1}$ )
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.

# Lattice Energy of 1-D Crystal

Start from one ion, count all interaction with others on one side:



$$\begin{aligned} E_p &= \frac{e^2}{4\pi\epsilon_0} \times \left( -\frac{z^2}{d} + \frac{z^2}{2d} - \frac{z^2}{3d} + \dots \right) \\ &= -\frac{z^2 e^2}{4\pi\epsilon_0 d} \left( 1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \dots \right) = -\frac{z^2 e^2}{4\pi\epsilon_0 d} \times \ln 2 \end{aligned}$$

Then times 2 because of another side, and  $N_A$  so that the unit is in kJ/mol

$$E_p = -2 \frac{N_A z^2 e^2}{4\pi\epsilon_0 d} \ln 2$$

Or:

$$E_p = -A \frac{N_A z^2 e^2}{4\pi\epsilon_0 d}$$

$$A = 2 \ln 2 = 1.386$$

is called **Madelung constant**.



# Lattice Energy of 1-D Crystal

The equation

$$E_P = -A \frac{N_A z^2 e^2}{4\pi\epsilon_0 d}$$

Tells us:

- The lattice energy is negative – which means the crystal is more stable than isolated ions (don't be confused that lattice energy is reported in positive value)
- The large charge ( $z$ ) and smaller radii of ions, the stronger interaction and larger lattice value.

# Madelung Constant is Applicable for 3-D Crystals

- In general, the equation works for 3-D crystals with different Madelung constants;
- The Madelung constant depends on how the ions are arranged.
- Qualitatively, stronger interactions with high charged, small radii packed crystals.

$E_P = -A \frac{z^2 N_A e^2}{4\pi\epsilon_0 d}$	<i><b>MX</b></i>	<i><b>Name</b></i>	<i><b>A</b></i>
	CsCl	cesium chloride	1.763
	CaF <sub>2</sub>	fluorite	2.519
	NaCl	rock salt	1.748
	TiO <sub>2</sub>	rutile	2.408

Which of the following compounds would be expected to have the strongest ionic bonds?

- A. KI
- B. NaI
- C. CsF
- D. LiF

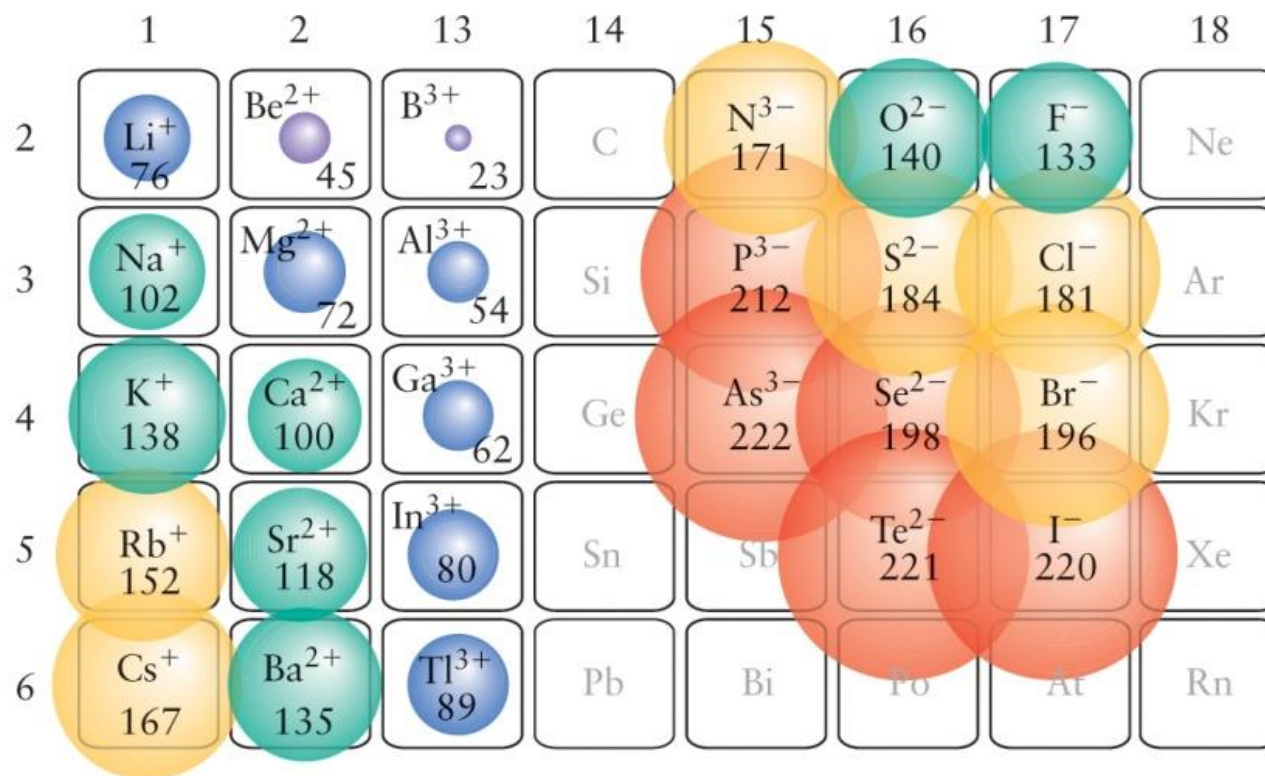
Which of the following compounds would be expected to have the strongest ionic bonds?

- A. KI
- B. NaI
- C. CsF
- D. LiF

**Smaller ions** have higher effective nuclear charges and are therefore bound together more tightly, which produces **higher lattice energies**.

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

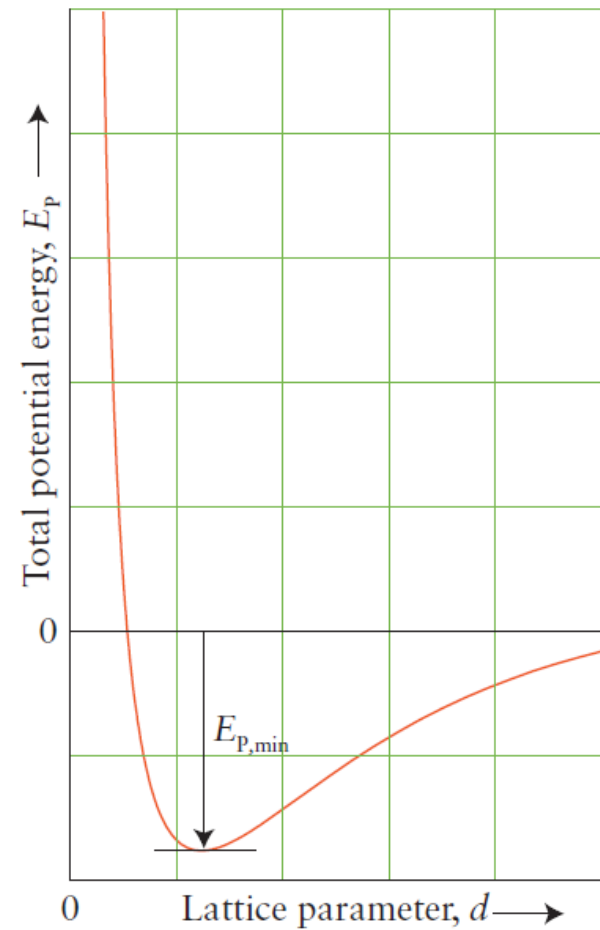
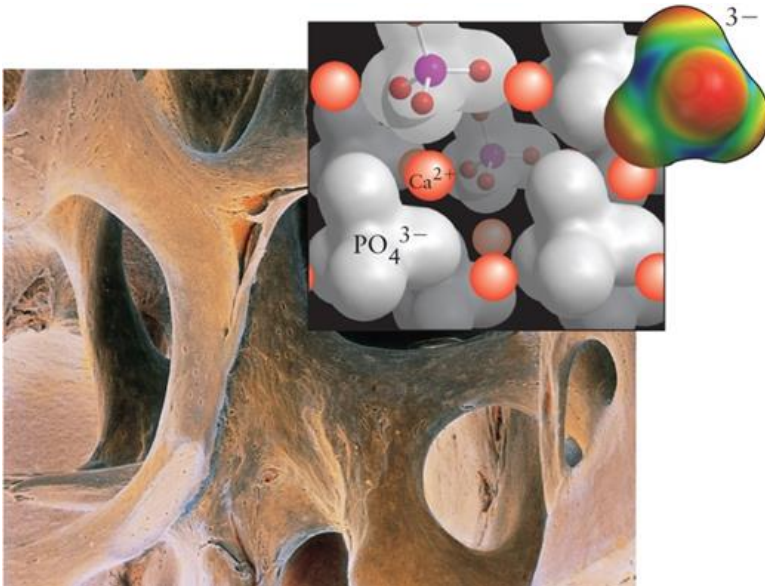
# Ion Sizes



**FIGURE 2.22** The ionic radii (in picometers) of the ions of the main-group elements. Note that cations are typically smaller than their parent atoms, whereas anions are larger—in some cases, very much larger.

# More Realistic Crystal Model

A micrograph of bone, which owes its rigidity to calcium phosphate.

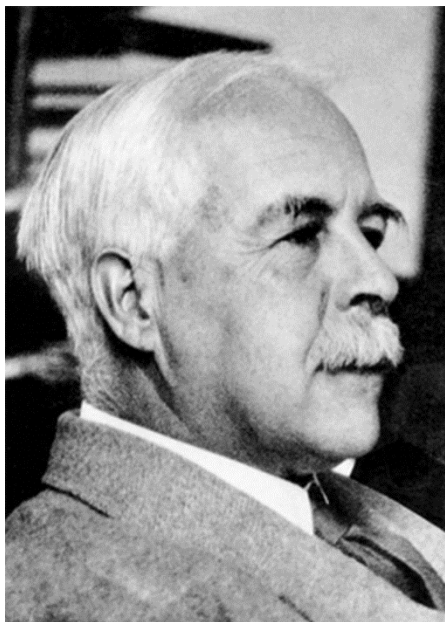


Potential of ionic interactions

- Attraction – mostly electrostatic
- Repulsion – atom-atom

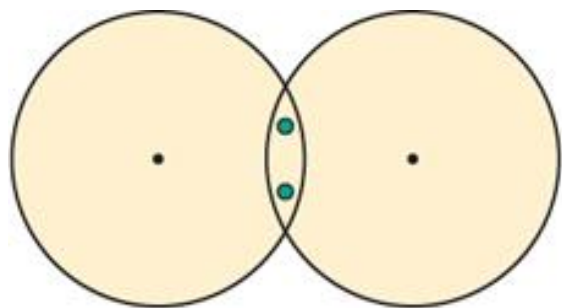
# Valence Bond

# Covalent bond : Nonmetal and Nonmetal



Bonds between two nonmetals cannot be explained by the ionic bond model.

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

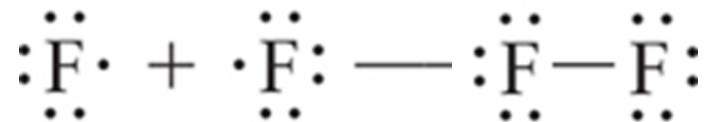


**Shared Electron Pair**

A shared electron pair stabilizes the compound - A brilliant insight before quantum mechanics.



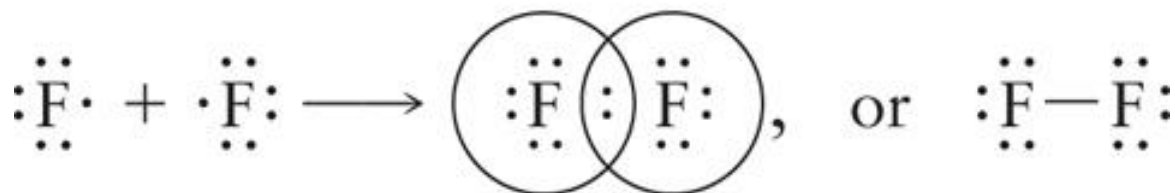
# Covalent Bond



- **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*
- It is true for Ionic bond - one atom **loses** electrons and the other atom **gains** electrons, until both atoms reach a *noble-gas configuration*.

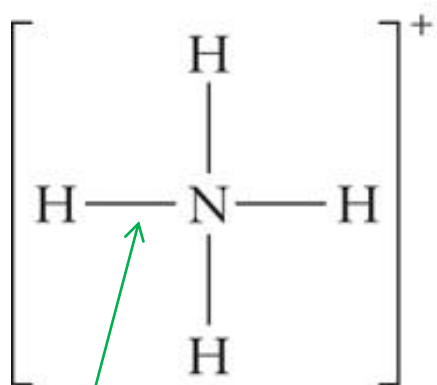
# Lewis symbols and Octet

- A dot represents an electron, double dots represent a lone pair of electrons
- One line represents a bond (pair electrons)
- The **octet** (or duplet) include all **lines** and **dots**



# Lewis notation for bonds

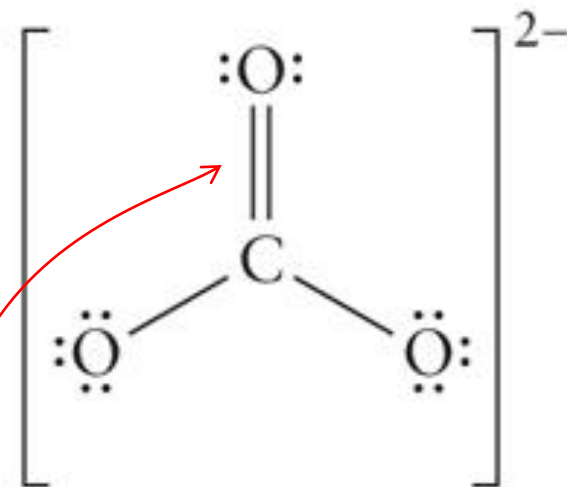
Each bond represents a shared pair (2) of electrons



Single bonds (2 electrons)

Double bonds (4 electrons)

Triple Bonds (6 electrons)

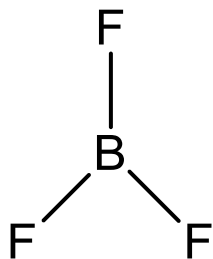


represents six electrons

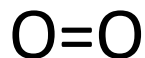


# Bond Order (B.O.)

$$\text{B.O.} = \frac{\text{number of bonds}}{\text{number of bonding pairs}}$$



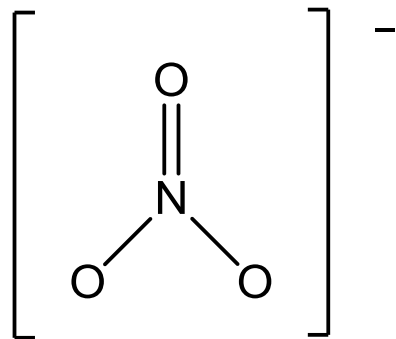
$$\text{B.O.} = \frac{3}{3} = 1$$



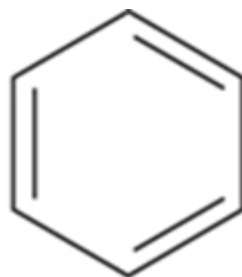
$$\text{B.O.} = \frac{2}{1} = 2$$



$$\text{B.O.} = \frac{3}{1} = 3$$



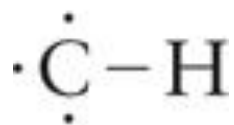
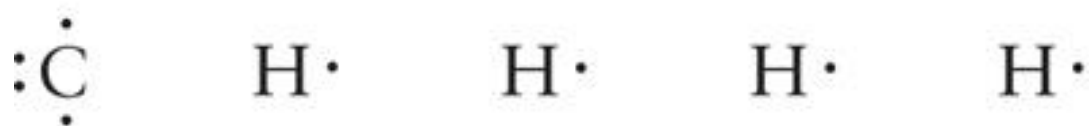
$$\text{B.O.} = \frac{4}{3} = 1.33$$



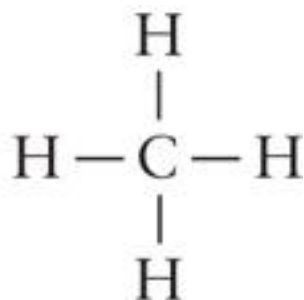
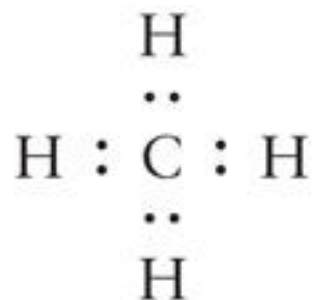
$$\text{B.O.} = \frac{9}{6} = 1.5$$

# Methane, CH<sub>4</sub>

The Lewis dot symbols for carbon and hydrogen:



The first element is the central atom.  
Arrange other atoms in a North, South,  
West and East position.

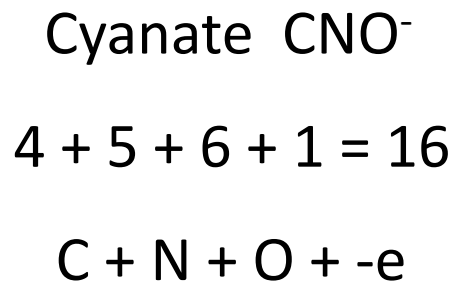
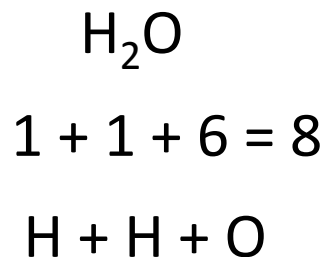


Because the carbon atom is linked  
by four bonds, the carbon is  
*tetravalent*: it has a valence of 4.

# How to Draw Linkage for Polyatomic Molecules

1. Center atom is the element with the lowest ionization potential – easy to share with others.
2. Try to be symmetric – except  $\text{N}_2\text{O}$  (NNO)
3. Usually the center atom is given first in formula

Step 1 count valence electrons, adjust for charge of ions



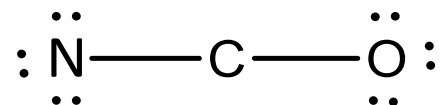
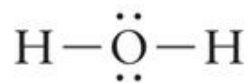
Step 2 arrange atoms (the first atom is the center ex. H)



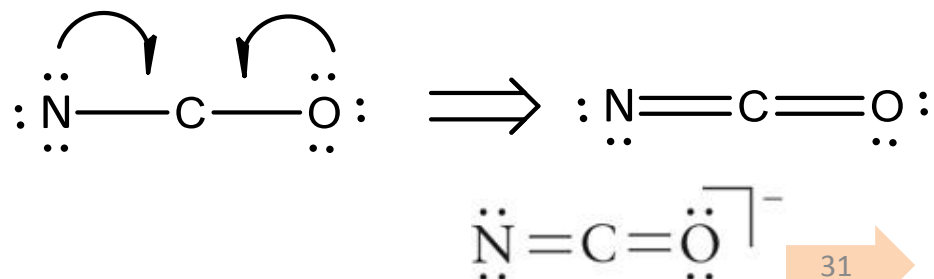
Step 3 connect atoms with bonds



Step 4 place electrons on the outside atoms first



Step 5 moving atoms to bonds to complete the octet, write charge if needed

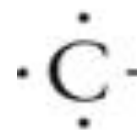


## Helpful tricks – count to the octet

How many bonds are required to be octet?



1 bond,



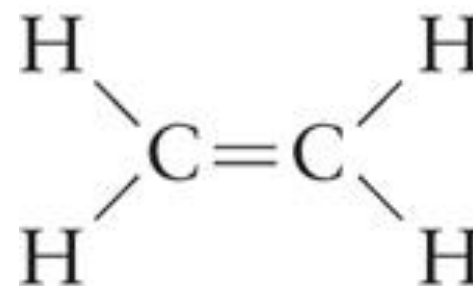
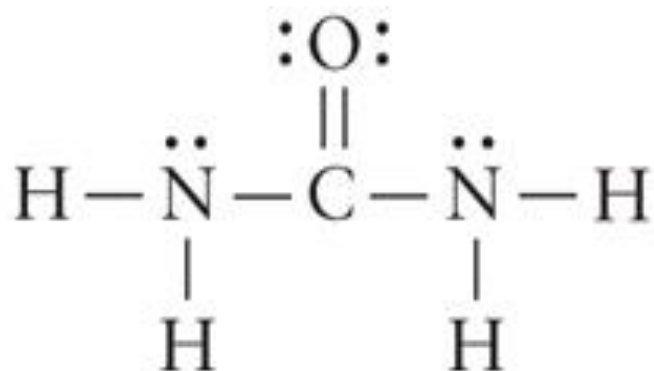
4 bonds,



2 bonds

to complete their octet

Nitrogen has 5 valence electron, 3 bonds can complete octet

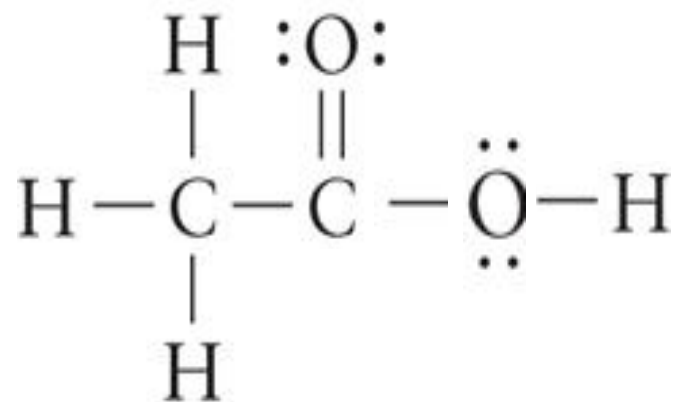




Read the formula for the order of atom attachment



acetic acid

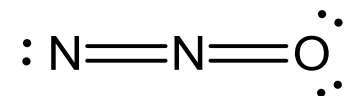


Which of the following is the correct Lewis structure for  $\text{N}_2\text{O}$ ?

N:  $5 \text{ VE} \times 2 = 10$

O:  $6 \text{ VE} \times 1 = 6$

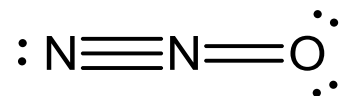
Total 16 VE



A.



B.



C.



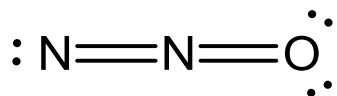
D.

Which of the following is the correct Lewis structure for N<sub>2</sub>O?

$$\text{N: } 5 \text{ VE} \times 2 = 10$$

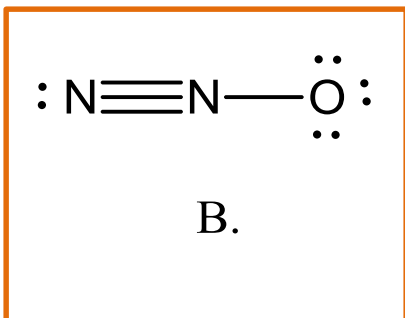
$$\text{O: } 6 \text{ VE} \times 2 = 6$$

$$\text{Total } 16 \text{ VE}$$

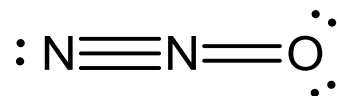


A.

Only 14 VE



B.



C.

Exceeds  
the octet



D.

Exceeds  
the octet

# More: Lewis Dot Structures

$$\text{NO}_3^- \quad 5 + 3(6) + 1 = 24 \quad \text{1 Count}$$

$$\text{N} + 3(\text{O}) + e^-$$

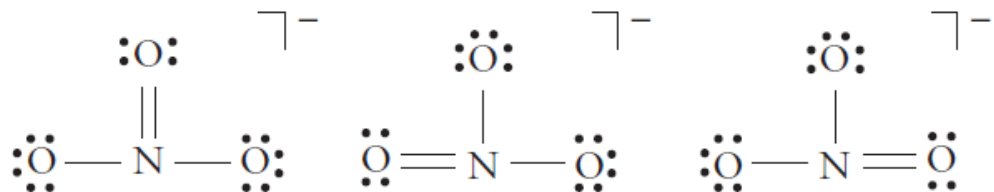
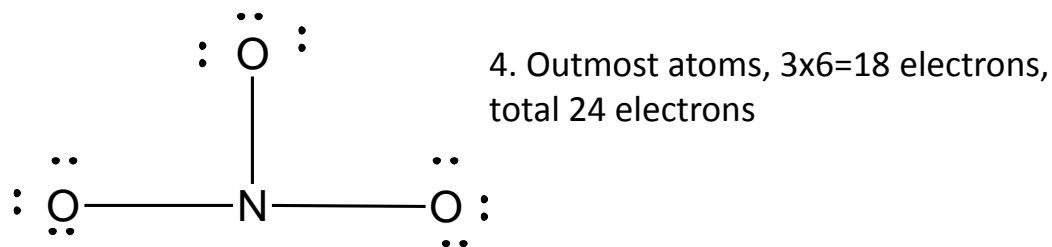
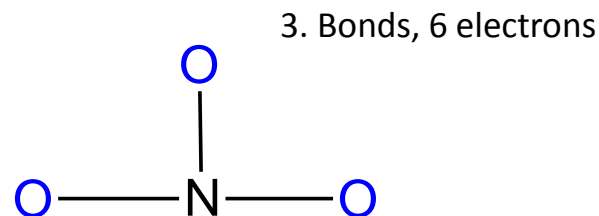
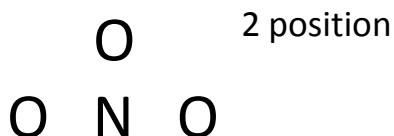
Step 1 count valence electrons, adjust for charge of ions

Step 2 arrange atoms , the first atom is typically the central atom, except hydrogen

Step 3 connect atoms with bonds

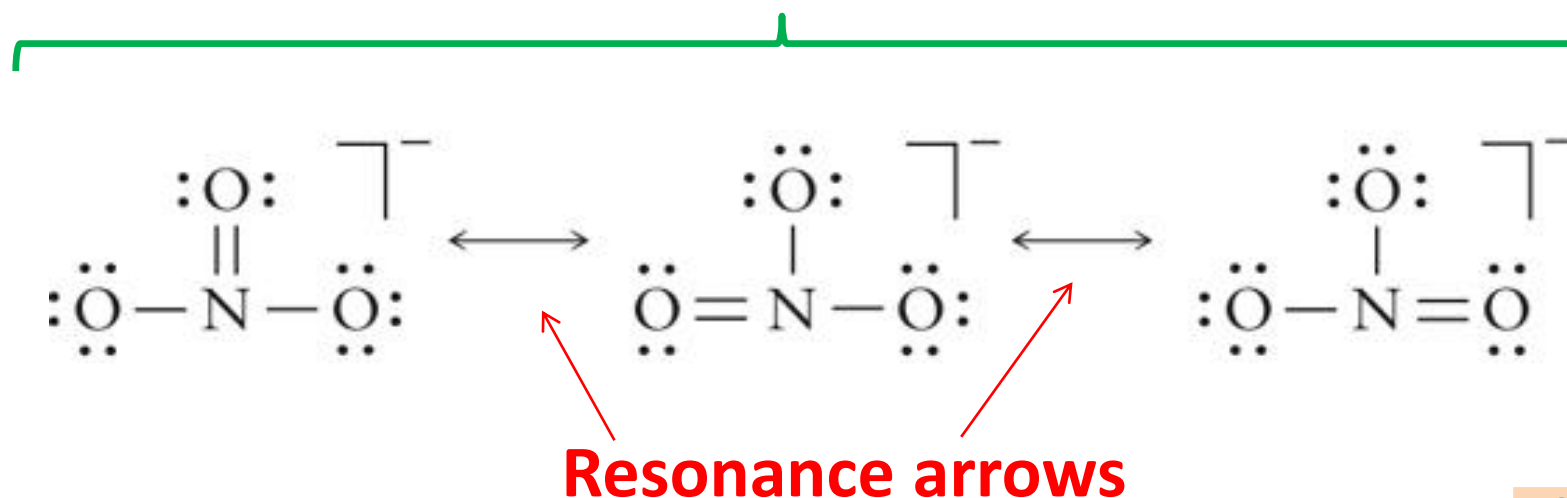
Step 4 electrons on the outside first

Step 5 complete octet

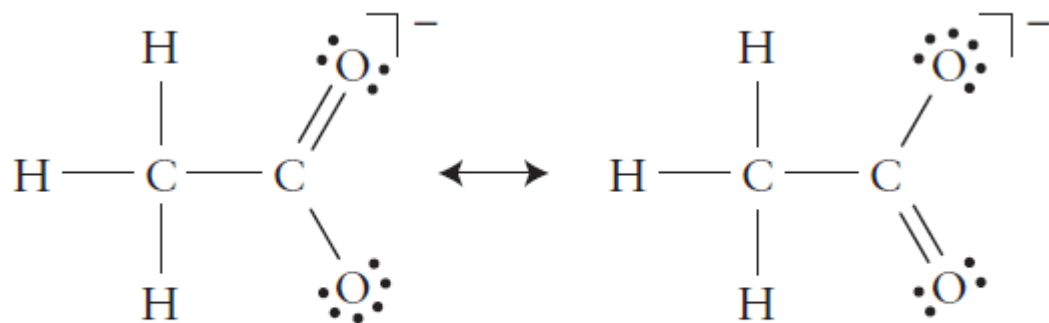


# Resonance Structures

- There is no difference among the three possible arrangements, called **resonance structure**.
- In reality, electrons are delocalized, they **hop** from one atom to another.
- The net effect is three identical bonds on average.
- If the resonance structures are different, the low energy ones contribute more.



# Resonance aromatic structures



8 Acetate ion,  $\text{CH}_3\text{CO}_2^-$



Benzene resonance structure

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

# Formal Charge

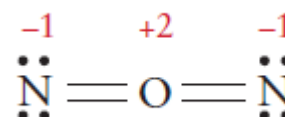
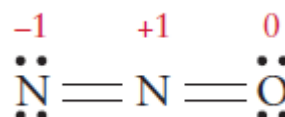
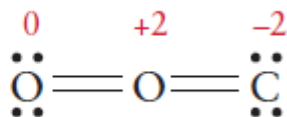
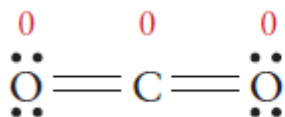
Formal charge is the charge an atom would have if the bonding is perfect covalence – electrons are shared by bonded atoms equally.

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

V – number of valence electrons

L – number of lone-pair electrons

B – number of bonds



# Formal Charge verses Oxidation numbers

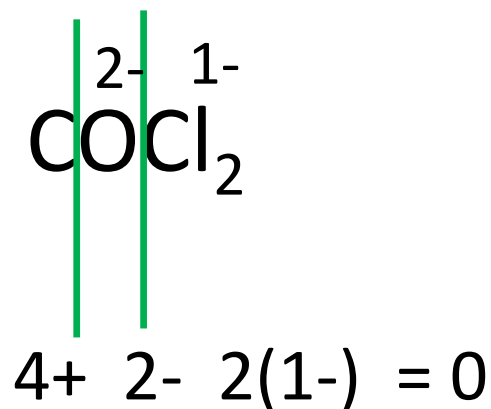
An oxidation number is the “charge” assigned to each atom by assuming the compounds is in purely ionic form (which it might not be).

## Oxidation numbers

$$\text{O} = 2-$$

$$\text{Cl} = 1-$$

$$\text{C} = 4+$$





# Formal Charge verses Oxidation numbers

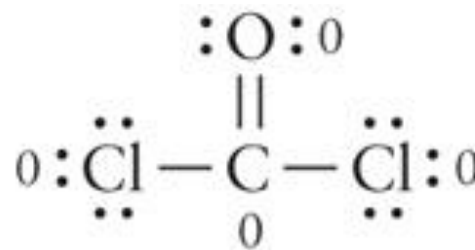


$$\text{Formal Charge} = V - \left( L + \frac{1}{2} B \right)$$

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

$$\text{Cl} \quad 7 - (6 + \frac{1}{2} 2) = 0$$

$$\text{C} \quad 4 - (0 + \frac{1}{2} 8) = 0$$

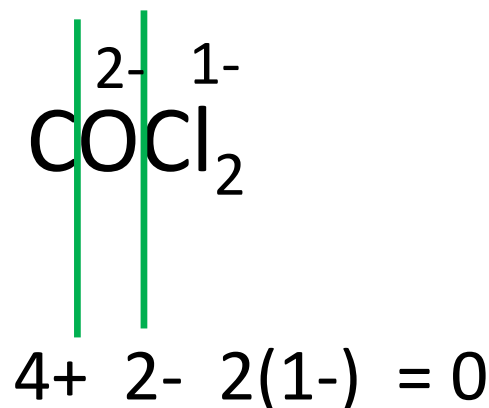


## Oxidation numbers

$$\text{O} = 2-$$

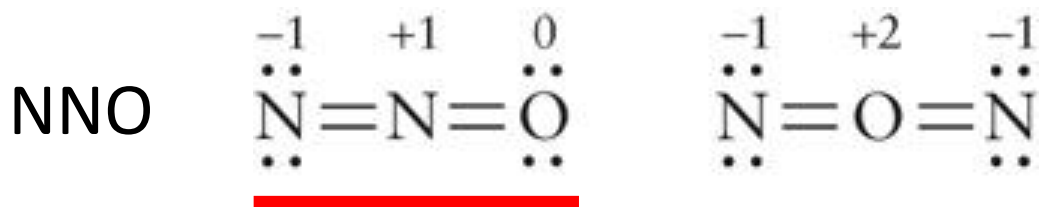
$$\text{Cl} = 1-$$

$$\text{C} = 4+$$



# Formal Charge

- Formal charges is useful for predicting the most *favorable* Lewis structure
- A Lewis structure in which the formal charges are closest to zero typically represents the lowest energy arrangement of the atoms.

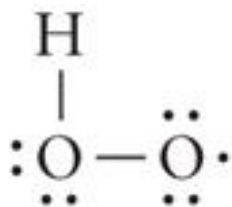


# Beyond the Octet Rule

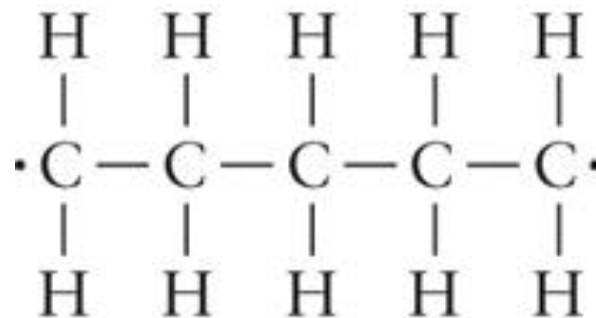
# Exceptions to the Octet Rule

- The octet rule works approximately.
- There are **many** exceptions.
- Can be determined by experiment or computation.

A **radical** is a species with an unpaired electron; a **biradical** has two unpaired electrons on either the same or different atoms. They cannot be isolated, are very unstable and highly reactive.



Hydrogenperoxyl,  $\text{HO}_2\cdot$

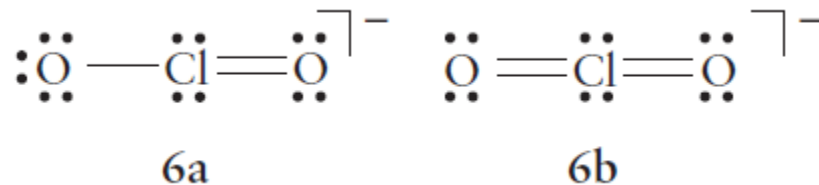
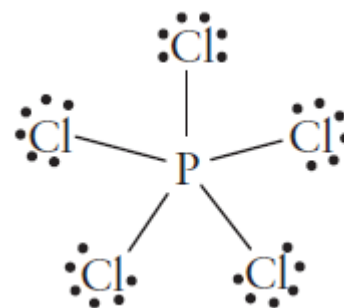


A biradical

# Exceptions to the Octet Rule

**Expanded valence shell:** Period 3 and above can accommodate more than eight electrons to 10, 12, or even more by using d-orbitals.

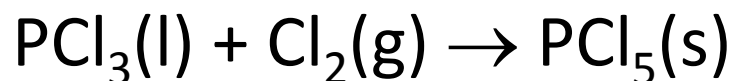
- More atoms might attach to a central atom than is allowed by the octet rule.
- The number of atoms is the same as that allowed by the octet rule, but some single bonds are replaced by double bonds.



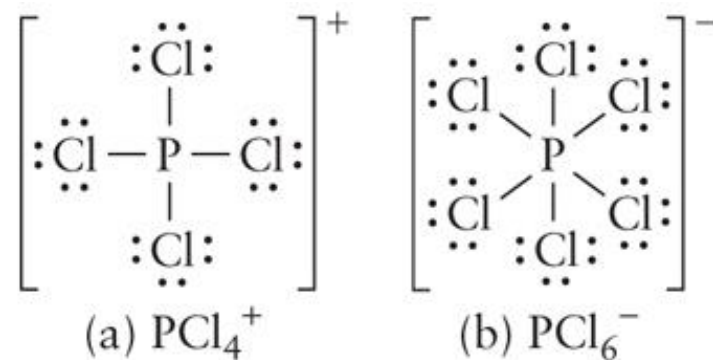
The central atom must be big enough to accommodate more bonds (no NCl<sub>5</sub>)

# Exceptions to the Octet Rule

A special case about  $\text{PCl}_5$



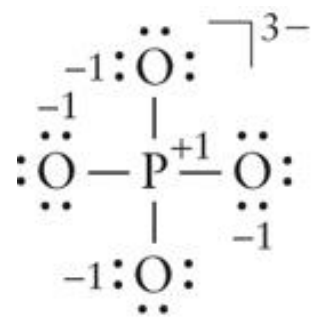
The solid is actually a complex of cation and anion



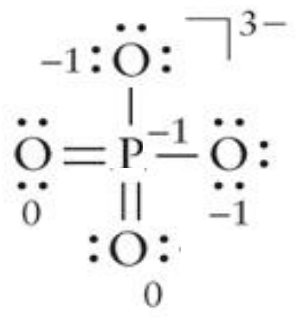
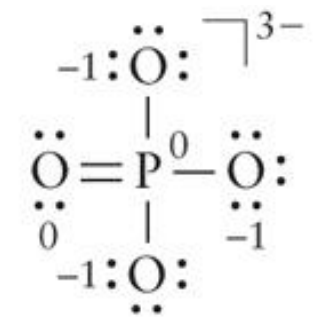
Phosphorus pentachloride,  $\text{PCl}_5(\text{s})$

# Exceptions to the Octet Rule

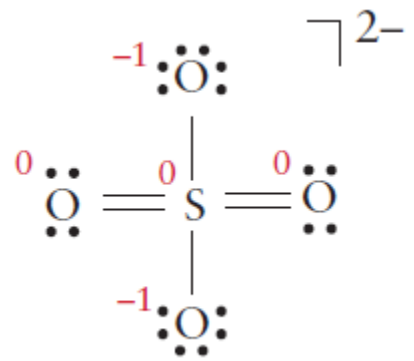
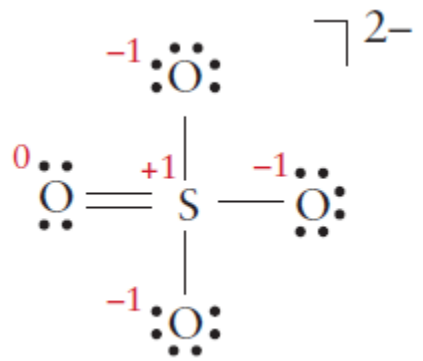
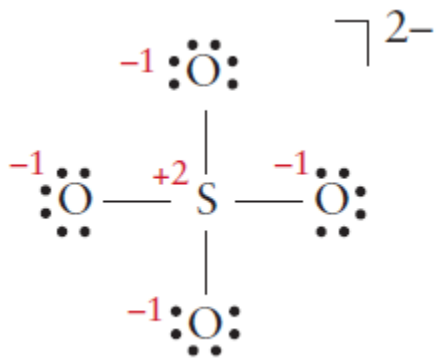
The formal charge can be used to *guess* the most stable structure.



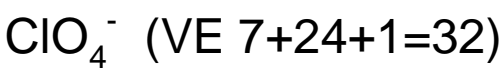
Too many FCs



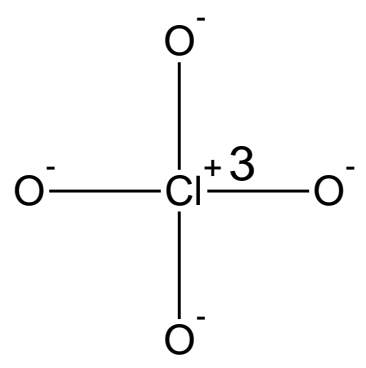
P has low EA, P<sup>-</sup> is rare.



# Exceptions to the Octet Rule

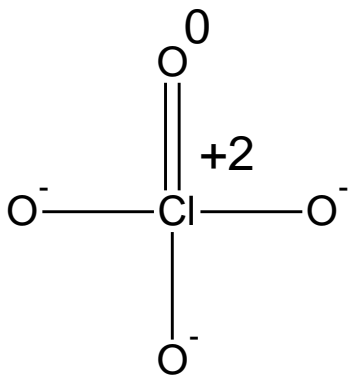


12 electrons on the central atom, fewest charges, preferred structure



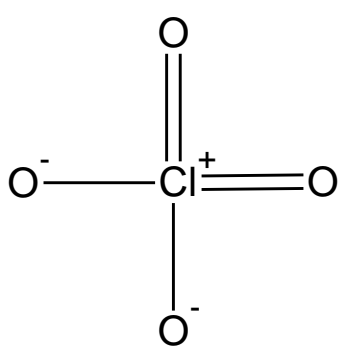
Cl:  $7-4=+3$   
O:  $6-7= (-1)4$   
net -1

High FCs



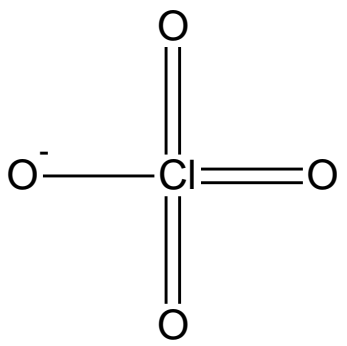
Cl:  $7-5=+2$   
O:  $6-6=0$   
O:  $6-7= (-1)3$   
net: -1

High FC



Cl:  $7-6=+1$   
O:  $6-6=0$   
O:  $6-7= (-1)2$   
net -1

12 electron on Cl



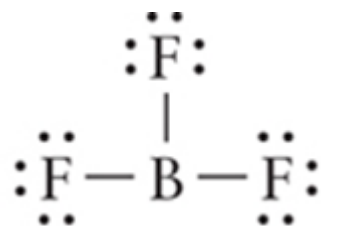
Cl:  $7-7=0$   
O:  $6-6=0$   
O:  $6-7= -1$   
net -1

14 electron on Cl

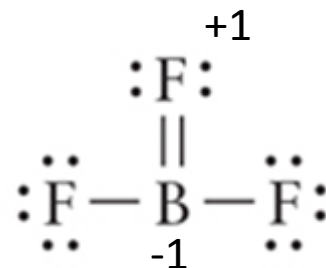


## Exceptions to the Octet Rule: Incomplete Octets

Boron has only three valence electrons, BF<sub>3</sub> has two possible structures



A



B

A – does not obey octet rule

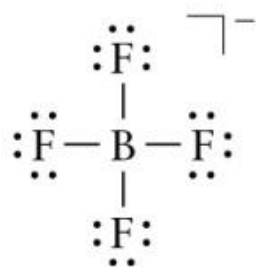
B – does obey but has formal charges

Experimental data indicates structure A contributes more.

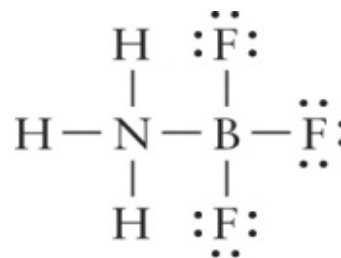
# Electron can be provided by ligand

Short on valence electron can be compensated by near-by electron-rich atom

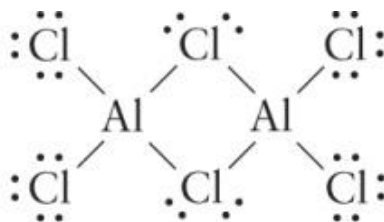
**Coordination covalence bond** – electrons donated from another atom



31 Tetrafluoroborate,  $\text{BF}_4^-$



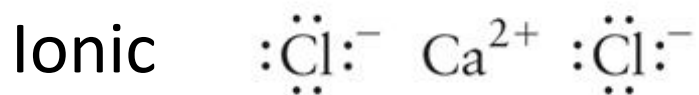
32  $\text{NH}_3\text{BF}_3$



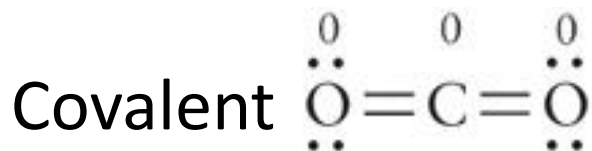
33 Aluminum chloride,  $\text{Al}_2\text{Cl}_6$

# The Properties of Bonds

Ionic and covalent bonding are **two extreme bonding models**. Most bonds lie somewhere between purely ionic and purely covalent.



Bonds between a metal and nonmetal are present in a ionic compounds.

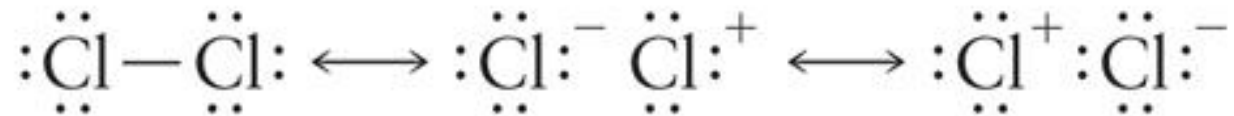


In bonds between nonmetals, covalent bonding is a good model.

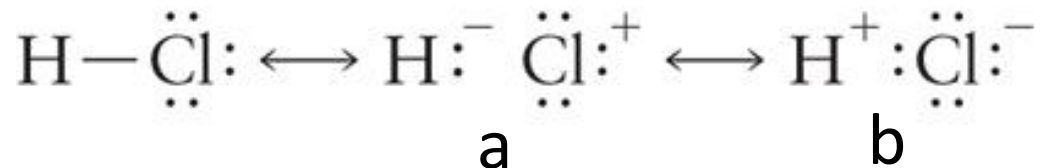
Can we describe these bonds more accurately by improving the two basic models?

## Using resonance concept

- $\text{Cl}_2$  - Both structures **have the same** resonance hybrid energy.

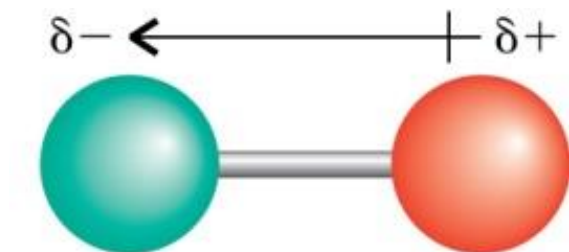


- HCl - Hetero-diatomic molecules **do not** have the same **resonance** hybrid energy

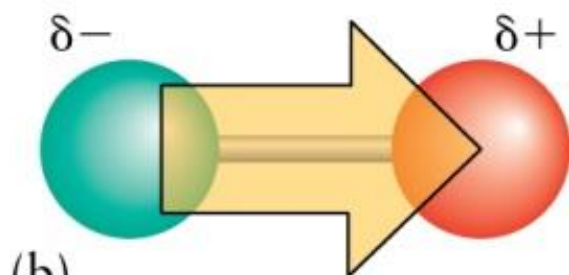


- Structure b would be more stable than a
- Experiments show a small net negative charge on the Cl atom and positive on the H, called **partial charge**.

# Electric Dipole Moment



(a)



(b)

34

The positive end (or pole) in a polar bond is represented  $+\delta$  and the negative pole  $-\delta$ , the bond length is  $r$ , then

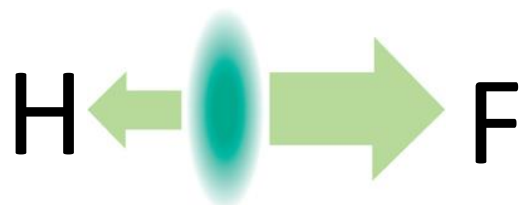
Electric dipole moment is defined as a vector:

$$\mu = \delta r$$

The direction is from negative to positive

Non-SI unit: **debye (D)**: single charge ( $\delta=e$ ) separated by 100 pm.

# Electronegativity



The **electronegativity  $\chi$**  accounts for the ability of pulling electron.

Pauling's **Electronegativity  $\chi$**  using the dissociation energy (bond strength)

$$|\chi_A - \chi_B| = \{D(A-B) - \frac{1}{2}[D(A-A) + D(B-B)]\}^{1/2}$$

If bond A-B is stronger than average of A-A and B-B, then A has higher electronegativity

**Mulliken's** definition uses ionization energy and electron affinity

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

The higher  $I$  (harder to lose) and  $E_a$  (easier to gain), the higher electronegativity

Both definitions are broadly consistence.

# Pauling's Electronegativity Values

Increasing EA & IE

H  
2.2

18/VIII  
He

1

2

13/III

14/IV

15/V

16/VI

17/VII

2

3

4

5

6

Li  
1.0

Be  
1.6

B  
2.0

C  
2.6

N  
3.0

O  
3.4

F  
4.0

Ne

Na  
0.93

Mg  
1.3

Al  
1.6

Si  
1.9

P  
2.2

S  
2.6

Cl  
3.2

Ar

K  
0.82

Ca  
1.3

Ga  
1.6

Ge  
2.0

As  
2.2

Se  
2.6

Br  
3.0

Kr

Rb  
0.82

Sr  
0.95

In  
1.8

Sn  
2.0

Sb  
2.1

Te  
2.1

I  
2.7

Xe

Cs  
0.79

Ba  
0.89

Tl  
2.0

Pb  
2.3

Bi  
2.0

Po  
2.0

At

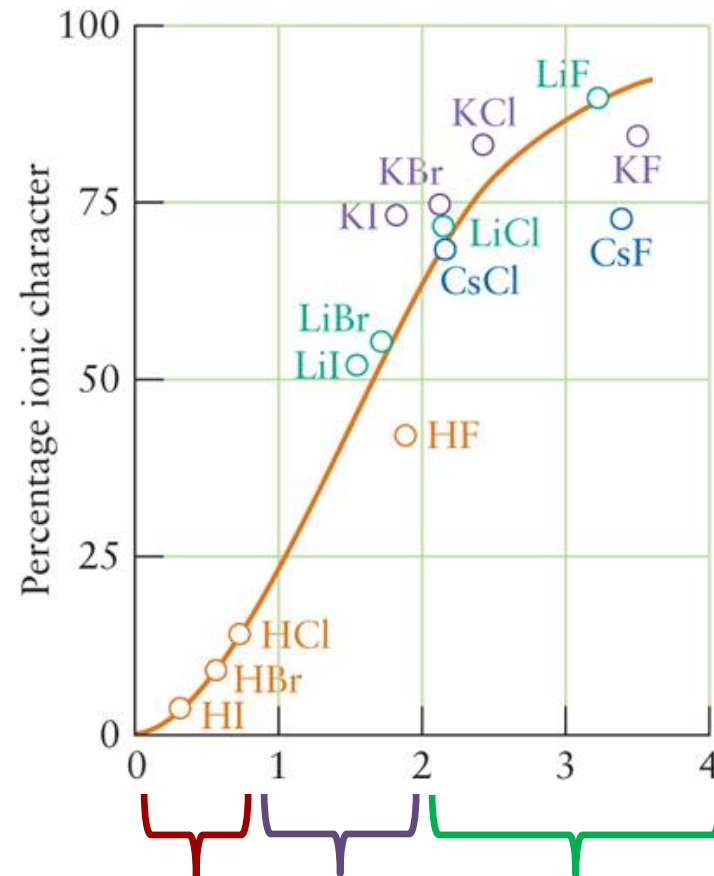
Rn

Increasing EA & IE

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



# Using electronegativity difference, $\Delta\chi$ , to distinguish bond types



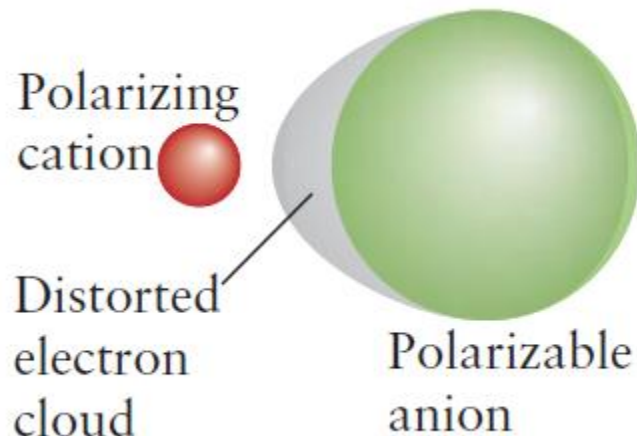
**Non-polar** **Polar** **Ionic**  
**Covalent** **Covalent**

$$\text{Li-F} \\ |1.0 - 4.0| = 3.0$$

$$\text{H-Cl} \\ |2.2 - 3.2| = 1.0$$

# The Ionic bond and polarizability

- Ionic bond has covalence bond characters
- This can be seen as the distorted electron cloud partially shared between the two nuclei

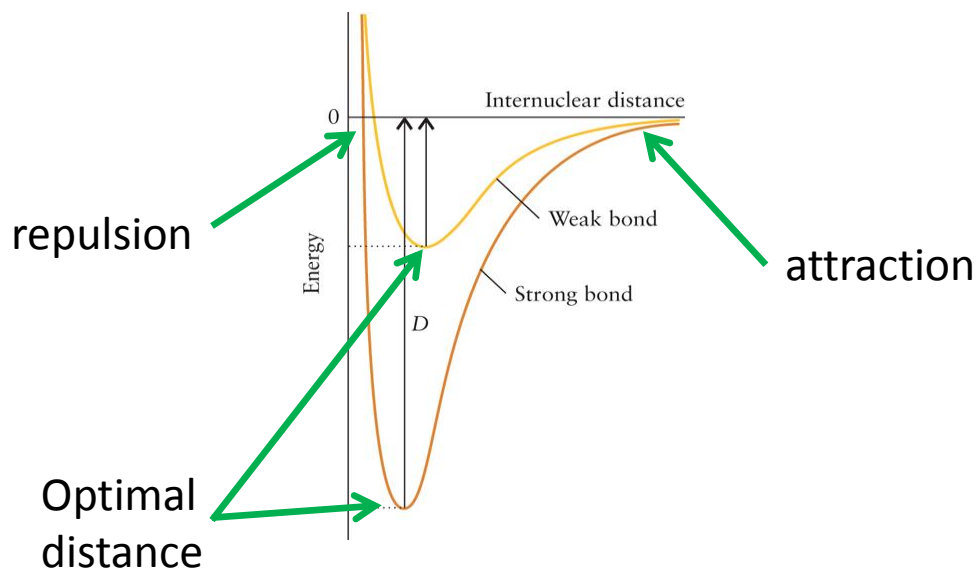


- Cation has high charge density, not easy to be distorted, has **polarizing power**.
- Ionic has low charge density, it has high value in **polarizability** – easy to be polarized.

# Bond Strength

Measured by **Dissociation Energy (D)** – the energy required to break a bond between two atoms

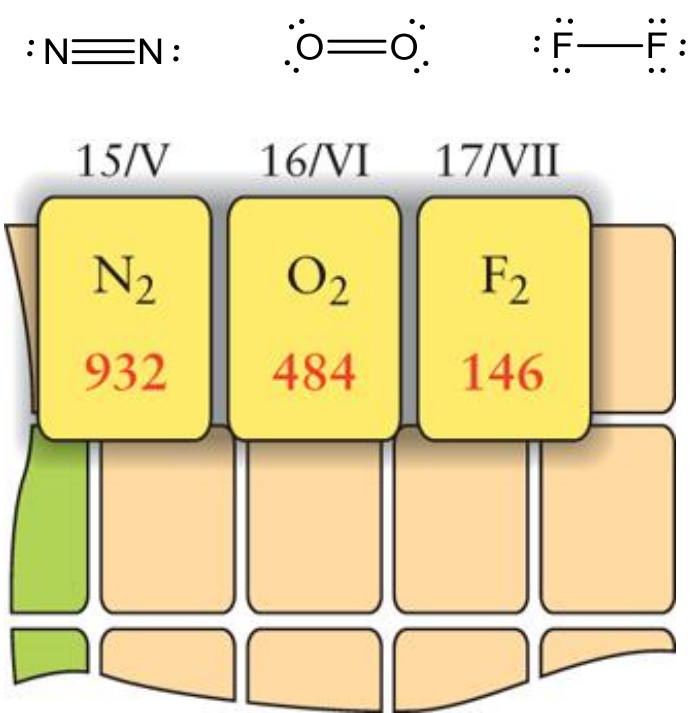
The potential of bond can be represented by



**TABLE 3.3** Bond Dissociation Energies of Diatomic Molecules ( $\text{kJ}\cdot\text{mol}^{-1}$ )

Molecule	Bond dissociation energy
$\text{H}_2$	424
$\text{N}_2$	932
$\text{O}_2$	484
$\text{CO}$	1062
$\text{F}_2$	146
$\text{Cl}_2$	230
$\text{Br}_2$	181
$\text{I}_2$	139
$\text{HF}$	543
$\text{HCl}$	419
$\text{HBr}$	354
$\text{HI}$	287

# Bond Strength and Bond Order

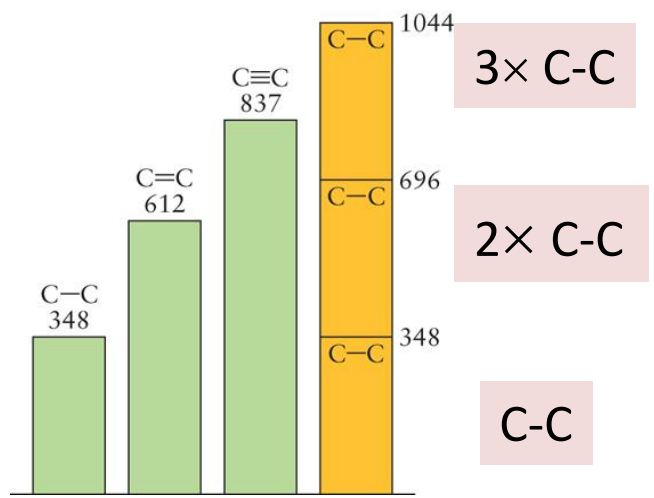


Electrons in **double** and **triple bonds** are **not as concentrated** between two atoms as they are in a single bonds.

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

← BO = 1.5

Not simply Add-up



Rank the following molecules from weakest to strongest C-O bonds.

A.  $1 < 2 < 3 < 4$

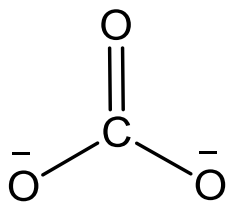
B.  $3 < 1 < 2 < 4$

C.  $4 < 2 < 1 < 3$

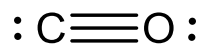
D.  $4 < 3 < 2 < 1$



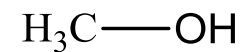
1.



2.



3.



4.

Rank the following molecules from weakest to strongest C-O bonds.

A.  $1 < 2 < 3 < 4$

B.  $3 < 1 < 2 < 4$

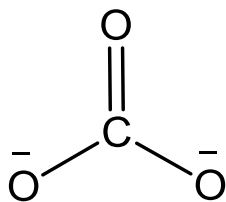
C.  $4 < 2 < 1 < 3$

D.  $4 < 3 < 2 < 1$



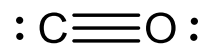
1.

BO=2



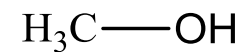
2.

BO=1.33



3.

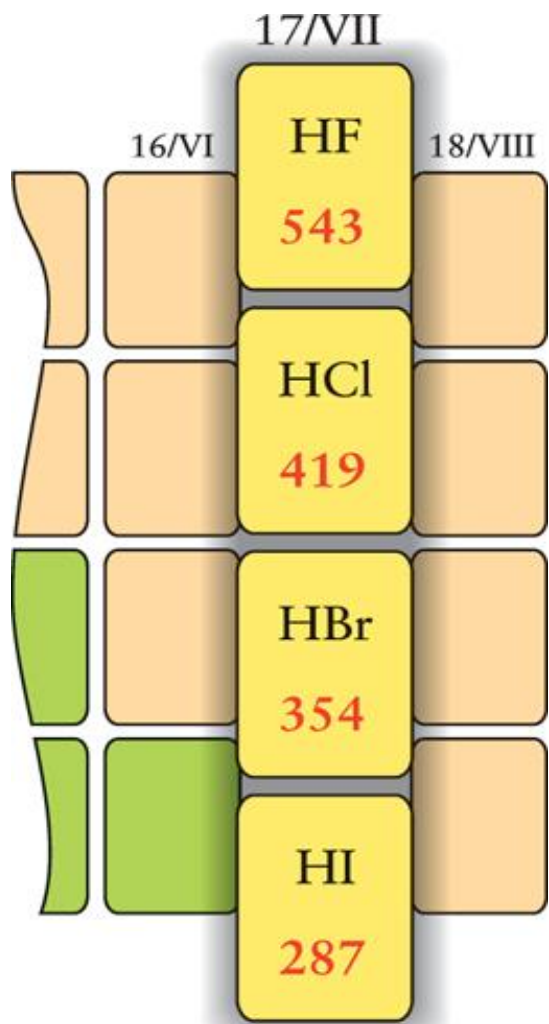
BO=3



4.

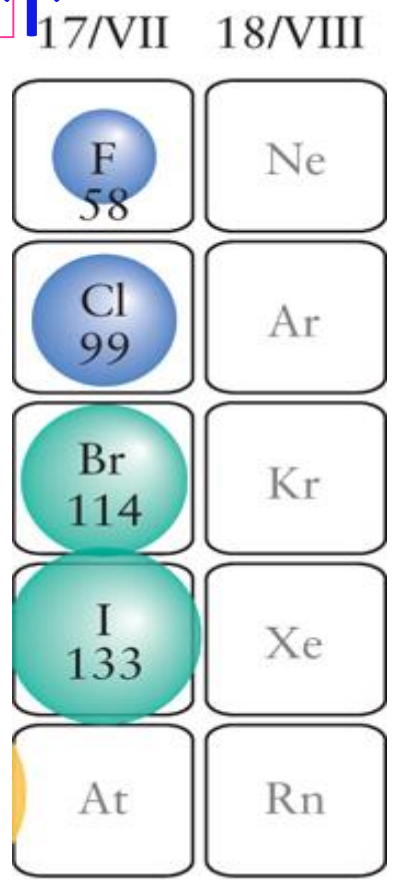
BO=1

# Bond Strength and Atomic Size



Bond Strength kJ

Strength ↓ as Size ↑









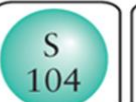
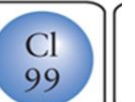












Atomic Radii

# Bond Strength and Atomic Size

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

Strength  as Size 

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



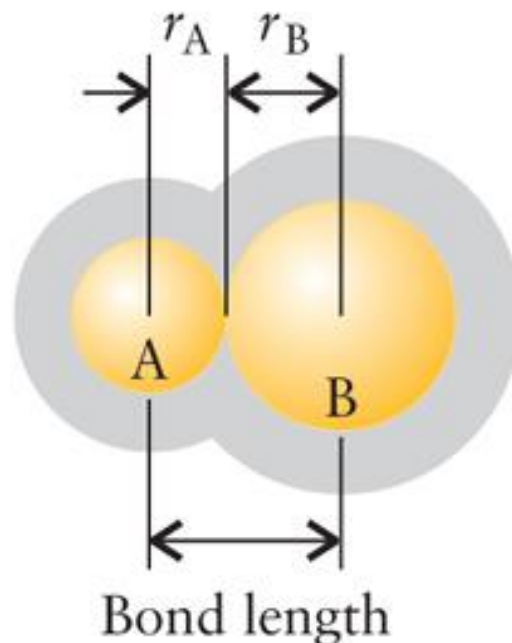
# Bond Length – Covalent Radii

- The covalent radius of an atom is the contribution it makes to the covalent bond length;
- Covalent radii can be used to estimate the bond lengths
- Covalent radius is correlated to atomic radius.

Bond Length

16/VI	17/VII	18/VIII
	F—F 142	
	Cl—Cl 199	
	Br—Br 228	
	I—I 268	

Covalent Radii



Atomic Radii

17/VII	18/VIII
F 58	Ne
Cl 99	Ar
Br 114	Kr
I 133	Xe

# Average and Actual Bond Lengths

**TABLE 2D.3** Average and Actual Bond Lengths

Bond	Average bond length/pm	Molecule	Actual bond length/pm
C—H	109	H <sub>2</sub>	74
C—C	154	N <sub>2</sub>	110
C=C	134	O <sub>2</sub>	121
C⋯C*	139	F <sub>2</sub>	142
C≡C	120	Cl <sub>2</sub>	199
C—O	143	Br <sub>2</sub>	228
C=O	112	I <sub>2</sub>	268
O—H	96		
N—H	101		
N—O	140		
N=O	120		

\*In benzene.

Bond lengths are **transferrable** properties, like bond energies