Chapter 8

Chemical Bonding I: Basic Concepts

Topics

- **Lewis Dot Symbols**

- **Ionic Bonding**

- **Covalent Bonding**

- **Electronegativity and Polarity**

- **Drawing Lewis Structures**

- **Lewis Structures and Formal Charge**

- **Resonance**

- **Exceptions to the Octet Rule**

- **Bond Enthalpy**

Types of Chemical bonds

What is a bond?

- A bond is a **force** that holds atoms together and make them **function together**

- Why are compounds (atoms aggregate with each other) formed?

  - Because this situation gives the system **the lowest possible energy.**

8.1 Lewis Dot Symbols

- **Valence electrons determine an element's chemistry.**

- ***Lewis dot symbols*** **represent the valence electrons of an atom as dots arranged around the atomic symbol.**
- **Most useful for main-group elements**

Lewis Dot Symbols

→ **Place one dot per valence electron on each of the four sides of the element symbol.**

→ **Pair the dots (electrons) until all of the valence electrons are used.**

Nitrogen, N, is in Group 5A and therefore has 5 valence electrons.

$$: \overset{\displaystyle .}{N} \cdot \qquad \cdot \overset{\displaystyle ..}{\underset{\displaystyle .}{N}} \cdot \qquad \cdot \overset{\displaystyle .}{\underset{\displaystyle .}{N}} : \qquad \cdot \overset{\displaystyle .}{\underset{\displaystyle ..}{N}} \cdot$$

	1A(1)	2A(2)		3A(13)	4A(14)	5A(15)	6A(16)	7A(17)	8A(18)
	ns^1	ns^2		ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6
2	· Li	· Be ·		· B ·	· C ·	· N ·	: O ·	: F :	: Ne :
3	· Na	· Mg ·		· Al ·	· Si ·	· P ·	: S ·	: Cl :	: Ar :

(Period shown on left axis)

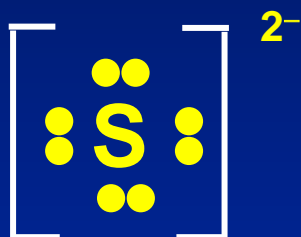# Lewis Dot Symbols of the Main Group Elements

Write Lewis dot symbols for the following

(a) N

(b) S^{2-}

(c) K^+ K^+

8.2   Ionic Bonding

- An atom with a **low ionization** energy (**metal that looses its electron easily**) reacts with an atom with **high electron affinity** (nonmetal).

- **Valence electrons move** from one atom to the other; every atom becomes an ion with a certain charge

- Opposite charges hold the ions together.

- Closely packed oppositely charged ions are held by strong electrostatic attraction forces

Ionic Bonding

- **Ionic bond: electrostatic force that holds oppositely charge particles together**

- **Formed between cations and anions**

- **Example**

Na•   +   :Cl: ⟶   Na$^+$ +   :Cl:$^-$

IE_1 + EA_1 = 496 kJ/mol − 349 kJ/mol = 147 kJ/mol

m.p. = 801°C ΔH^o_f **= − 410.9 kJ/mol**

**When atoms lose or gain electrons, they acquire a noble gas configuration, but do not *become* noble gases**

The net attractive electrostatic forces that hold the cations and anions together are ionic bonds

$$[Na \cdot] \quad + \quad [: \ddot{Cl} :] \quad \longrightarrow \quad [Na]^+ \quad [: \ddot{Cl} :]^-$$
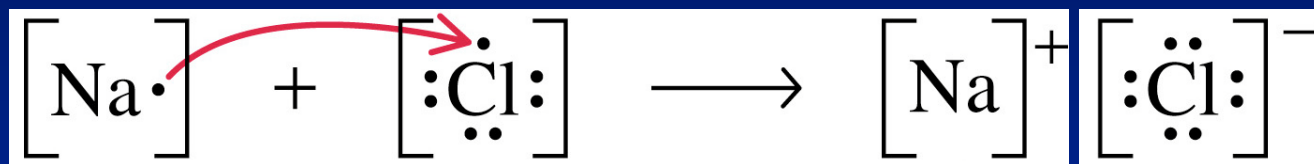
The highly ordered solid collection of ions is called an ionic compound (crystal)

- **Ionic crystals have great thermal stability and consequently acquire high melting points**

Microscopic View of NaCl Formation

$Cl_2 + 2Na \longrightarrow 2NaCl$
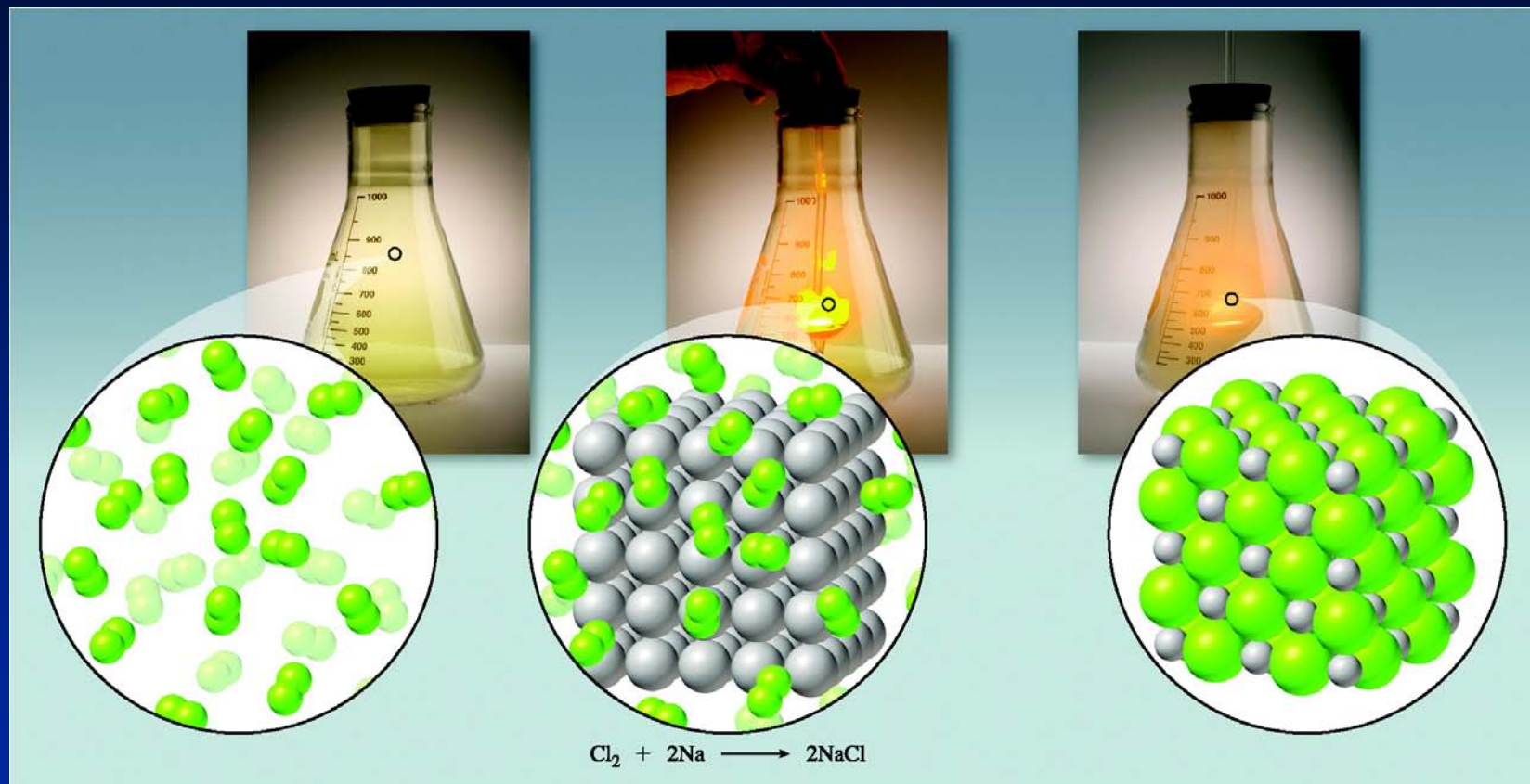
Lattice Energy

- **Ionic solid is formed because the aggregated oppositely charged ions have a lower energy than the original elements**

- **How strongly the ions attract each other in the solid state is expressed by the *lattice energy***

- ***Lattice energy:***

  The change in energy that takes place when one mole of ionic solid is separated into gaseous ions (+ve) or when one of gaseous ions are packed together to form an ionic solid (-ve)

- *Lattice energy* = the energy required to completely separate one mole of a solid ionic compound into gaseous ions
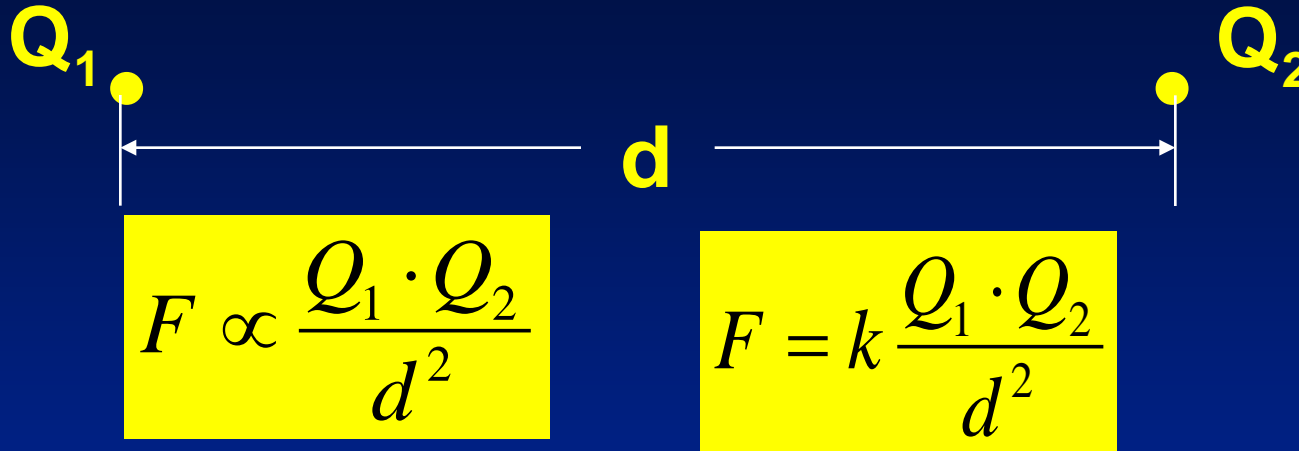
$$MX(s) \longrightarrow M^+(g) + X^-(g)$$

$NaCl(s) \rightarrow Na^+(g) + Cl^-(g)$ $\Delta H_{lattice} = +788$ kJ/mol
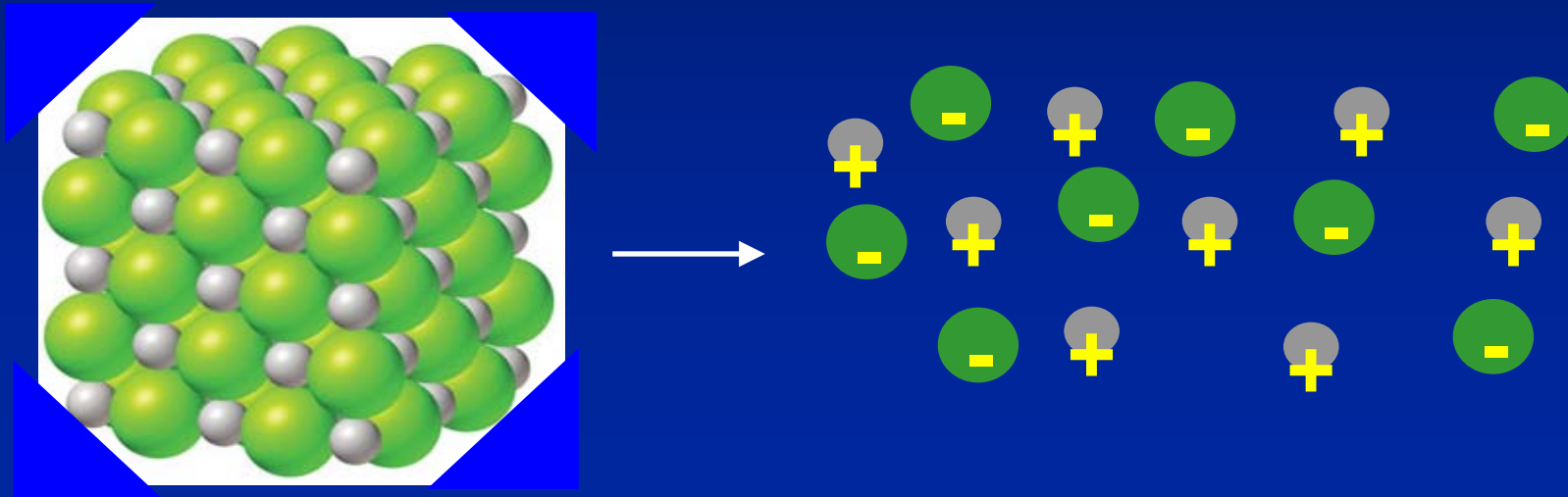
Lattice energy

- **Lattice energy is a <u>quantitative measure of the stability</u> of ionic compound**
- **The higher the lattice energy the more stable the compound**

Calculating Lattice Energy: Coulombic attraction

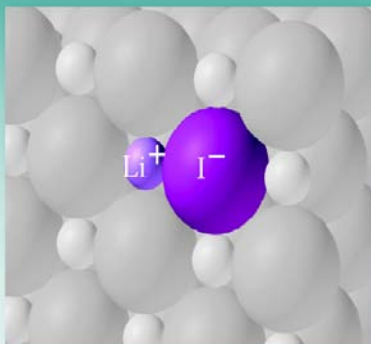**Q = amount of charge;   d = distance of separation**

Q_1 Q_2

d

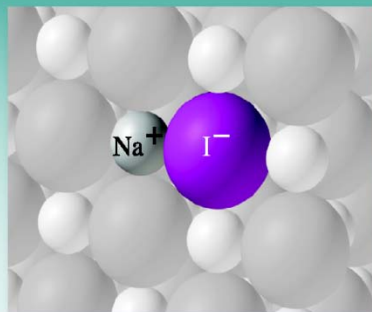$$F \propto \frac{Q_1 \cdot Q_2}{d^2}$$

$$F = k\frac{Q_1 \cdot Q_2}{d^2}$$

- **Lattice energy (like a coulombic force) depends on**
  - **Magnitude of charges**
  - **Distance between the charges**

- **Lattice energy is greater with more highly charged ions and distances between ions decrease**

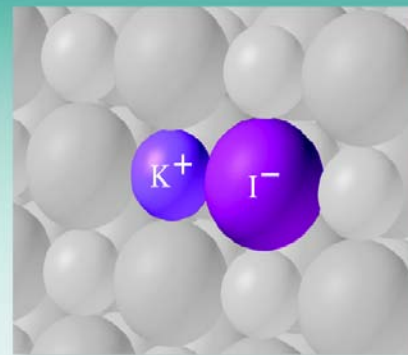# Lattice energies of alkali metal iodides

Li$^+$ I$^-$
0.76 Å   2.20 Å

$$F \propto \frac{(+1) \times (-1)}{(0.76 + 2.20)^2} \propto -0.11$$

Na$^+$ I$^-$
1.02 Å   2.20 Å

$$F \propto \frac{(+1) \times (-1)}{(1.02 + 2.20)^2} \propto -0.10$$

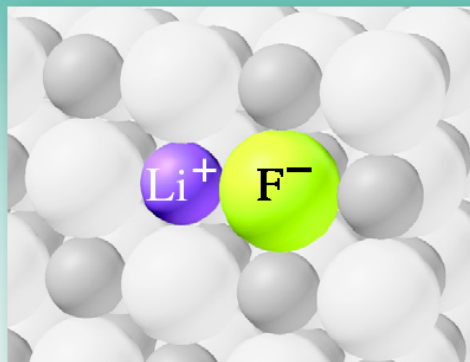K$^+$ I$^-$
1.38 Å   2.20 Å

$$F \propto \frac{(+1) \times (-1)}{(1.38 + 2.20)^2} \propto -0.08$$

Largest lattice energy
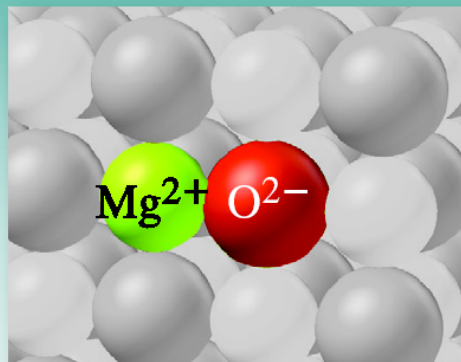(732 kJ/mol)

Intermediate lattice energy
(686 kJ/mol)

Smallest lattice energy
(632 kJ/mol)

The ionic radii sums for LiF and MgO are 2.01 and 2.06 Å, respectively, yet their lattice energies are 1030 and 3795 kJ/mol. Why is the lattice energy of MgO nearly four times that of LiF?

Li^+ F^-
0.76 Å   1.33 Å

Mg^{2+} O^{2-}
0.72 Å   1.40 Å

$$F \propto \frac{(+1) \times (-1)}{(0.76 + 1.33)^2} \propto -0.23$$

$$F \propto \frac{(+2) \times (-2)}{(0.72 + 1.40)^2} \propto -0.89$$

Smaller lattice energy
(1017 kJ/mol)

Larger lattice energy
(3890 kJ/mol)

- *Born-Haber cycle*: A method to determine lattice energies

• Born-Haber cycle for CaO

$$Ca(s) \quad + \quad (1/2)\ O_2(g) \quad \xrightarrow{\ \#6\ } \quad CaO(s)$$

#1 ↓   #3 ↓

$$Ca(g) \qquad\qquad O(g)$$

#2 ↓   #4 ↓   #5

$$Ca^{2+}(g) \quad + \quad O^{2-}(g)$$
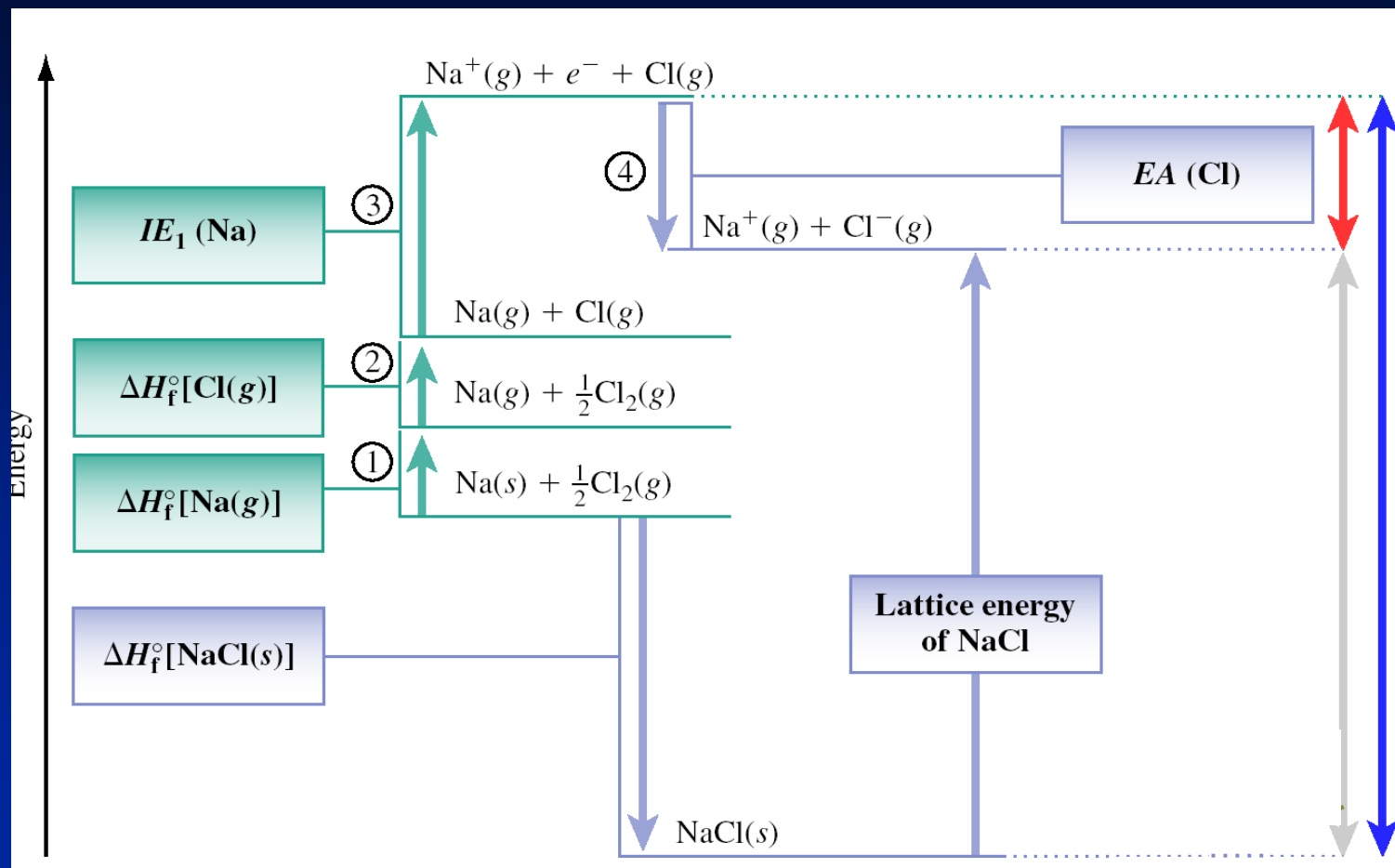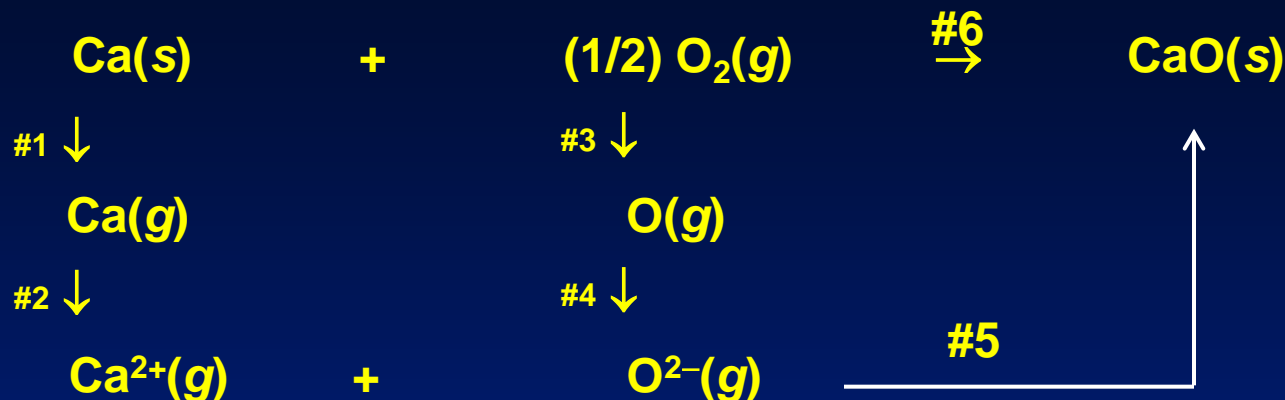
#1 Heat of sublimation $=\ \Delta H_f°[Ca(g)]\ =\ +178$ kJ/mol

#2 1st & 2nd ionization energies $=I_1(Ca) + I_2(Ca) =\ +1734.5$ kJ/mol

#3 (1/2) Bond enthalpy $=\ (1/2)\ D(O{=}O)\ =\ \Delta H_f°[O(g)]\ =\ +247.5$ kJ/mol

#4 1st & 2nd electron affinities $=\ EA_1(O) + EA_2(O)\ =\ +603$ kJ/mol

#5 $-$ (Lattice Energy) $=\ -\Delta H_{lattice}[CaO(s)]\ =\ $ (the unknown)

#6 Standard enthalpy of formation $=\ \Delta H_f°[CaO(s)]\ =\ -635$ kJ/mol

$+178 +1734.5 +247.5 +603 -\Delta H_{latt} = -635$

$$\boxed{\Delta H_{lattice}\ =\ +3398\ \text{kJ/mol}}$$

8.3 Covalent Bonding

- **Atoms share electrons to form covalent bonds.**

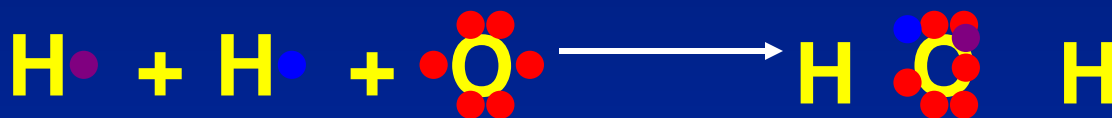$$H\bullet \ + \ \bullet H \longrightarrow H\bullet H \ \text{ or } \ H–H$$

- **In forming the bond the atoms achieve a more stable electron configuration.**

- **Octet:** Eight is a "magic" number of electrons.

- **Octet Rule:**
  Atoms will gain, lose, or share electrons to acquire eight valence electrons

Examples:

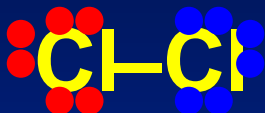Na• + •Cl• ⟶ Na⁺ + •Cl•⁻

H• + H• + •O• ⟶ H •C• H

•Lewis Structures

H• + •H ⟶ H•H   H–H

•Cl• + •Cl• ⟶ •Cl•Cl•   •Cl–Cl•

Shared electrons ⇒ Bonds
Non-bonding valence electrons ⇒ Lone pairs

Multiple Bonds

- The number of shared electron pairs is the number of bonds.

Cl—Cl Cl—Cl **Single Bond**

O=C=O O=C=O **Double Bond**
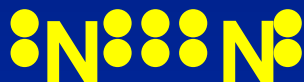
N≡N N≡N **Triple Bond**

Bond strength and bond length

bond strength   single < double < triple

bond length   single > double > triple

	N–N	N=N	N≡N
Bond Strength	163 kJ/mol	418 kJ/mol	941 kJ/mol
Bond Length	1.47 Å	1.24 Å	1.10 Å

Lengths of Covalent Bonds
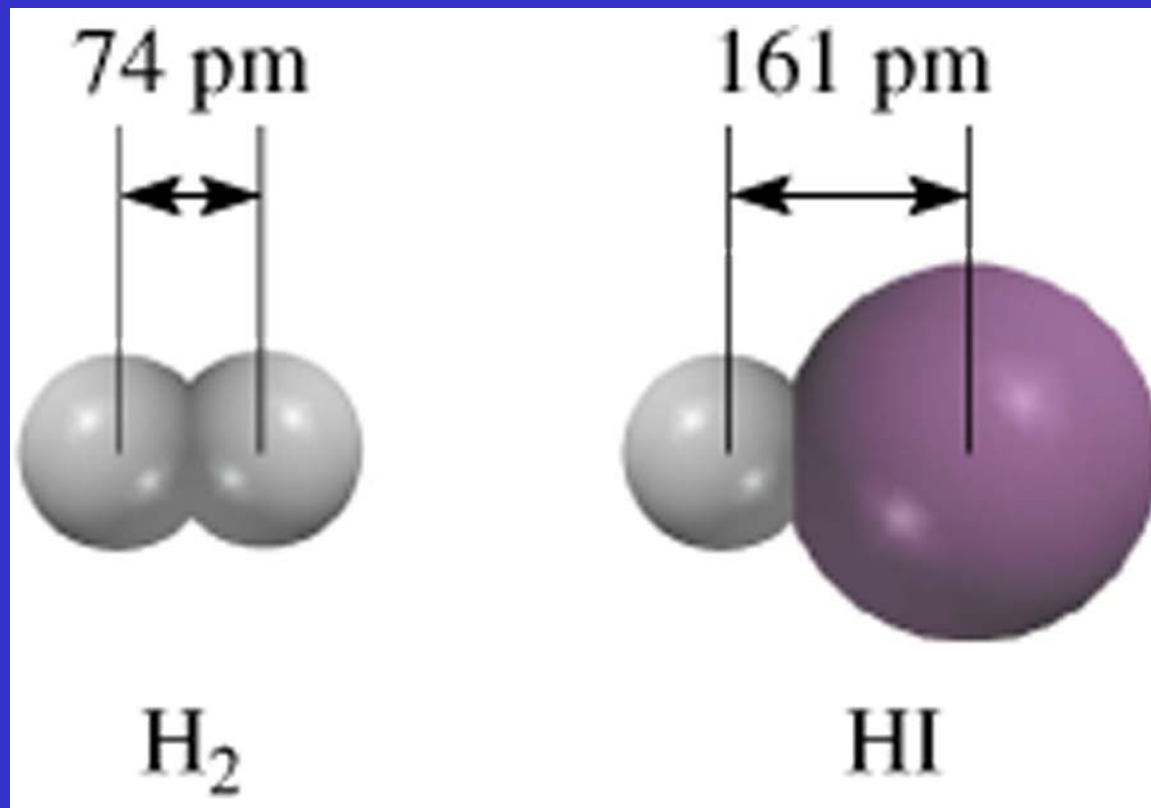
Bond Type	Bond Length (pm)
C-C	154
C=C	133
C≡C	120
C-N	143
C=N	138
C≡N	116

Bond Lengths

Triple bond < Double Bond < Single Bond

TABLE 8.5 Bond Lengths for Selected Bonds

| Bond	Bond Type	Bond Length (pm)	Bond Energy (kJ/mol)
C—C	Single	154	347
C=C	Double	134	614
C≡C	Triple	120	839
C—O	Single	143	358
C=O	Double	123	745
C—N	Single	143	305
C=N	Double	138	615
C≡N	Triple	116	891

8.4 Electronegativity and Polarity

- **bonded atoms** *Nonpolar covalent bond* = **electrons are shared *equally* by two bonded atoms**

- ***Polar covalent bond* = electrons are shared *unequally* by two**

  One end is slightly positive, the other is slightly negative. Bond polarity is indicated using small delta δ.

-

- **The density of electron cloud is shifted (some what) towards one of the two bonded atoms**

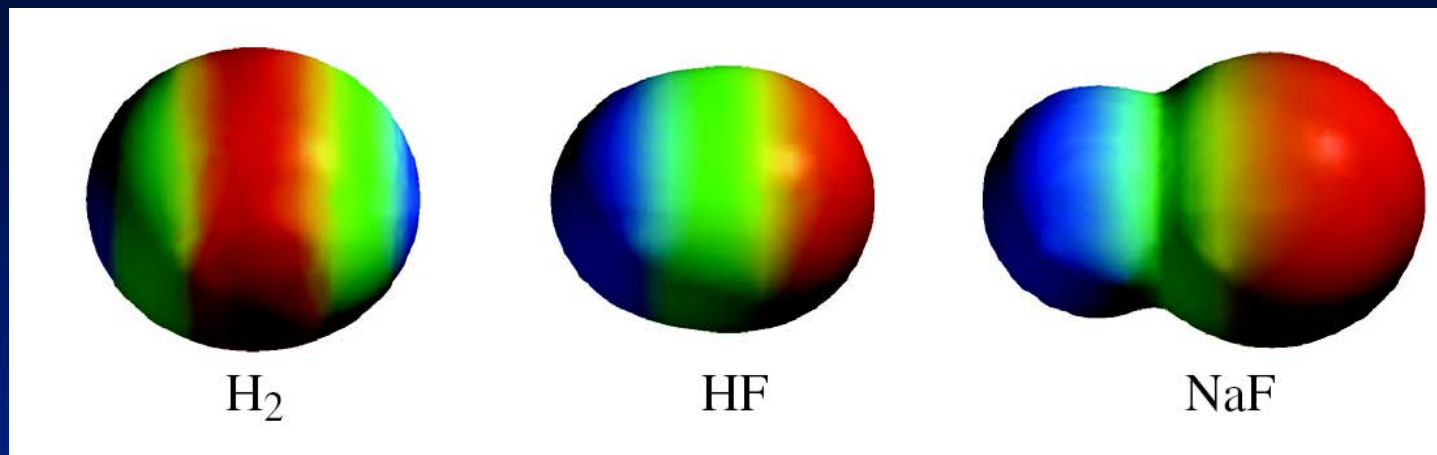| M:X	$M^{\delta+}X^{\delta-}$	$M^{+}X^{-}$
Pure covalent bond	**Polar covalent bond**	**Ionic bond**
Neutral atoms held together by *equally* shared electrons	Partially charged atoms held together by *unequally* shared electrons	Oppositely charged ions held together by electrostatic attraction

Polar Covalent Bond

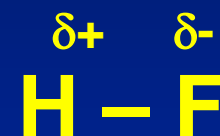**A covalent bond with greater electron density around one of the two atoms**

electron poor region

electron rich region

δ^+

δ^-

e⁻ poor e⁻ rich

H — F̈:

δ^+ δ^-

⟶

H – F
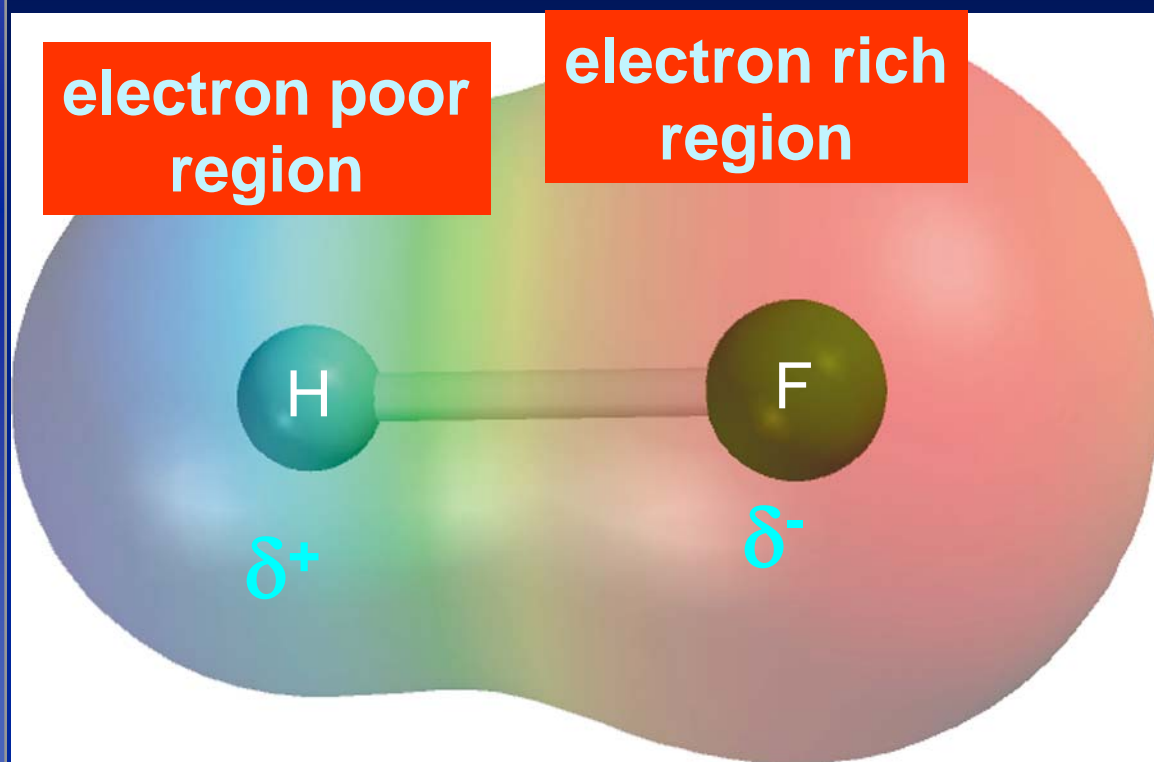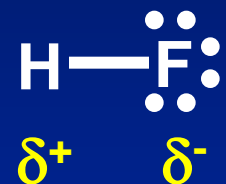
- **Electron density distributions**

H₂   HF   NaF

red $\Rightarrow$ high electron density

green $\Rightarrow$ intermediate electron density

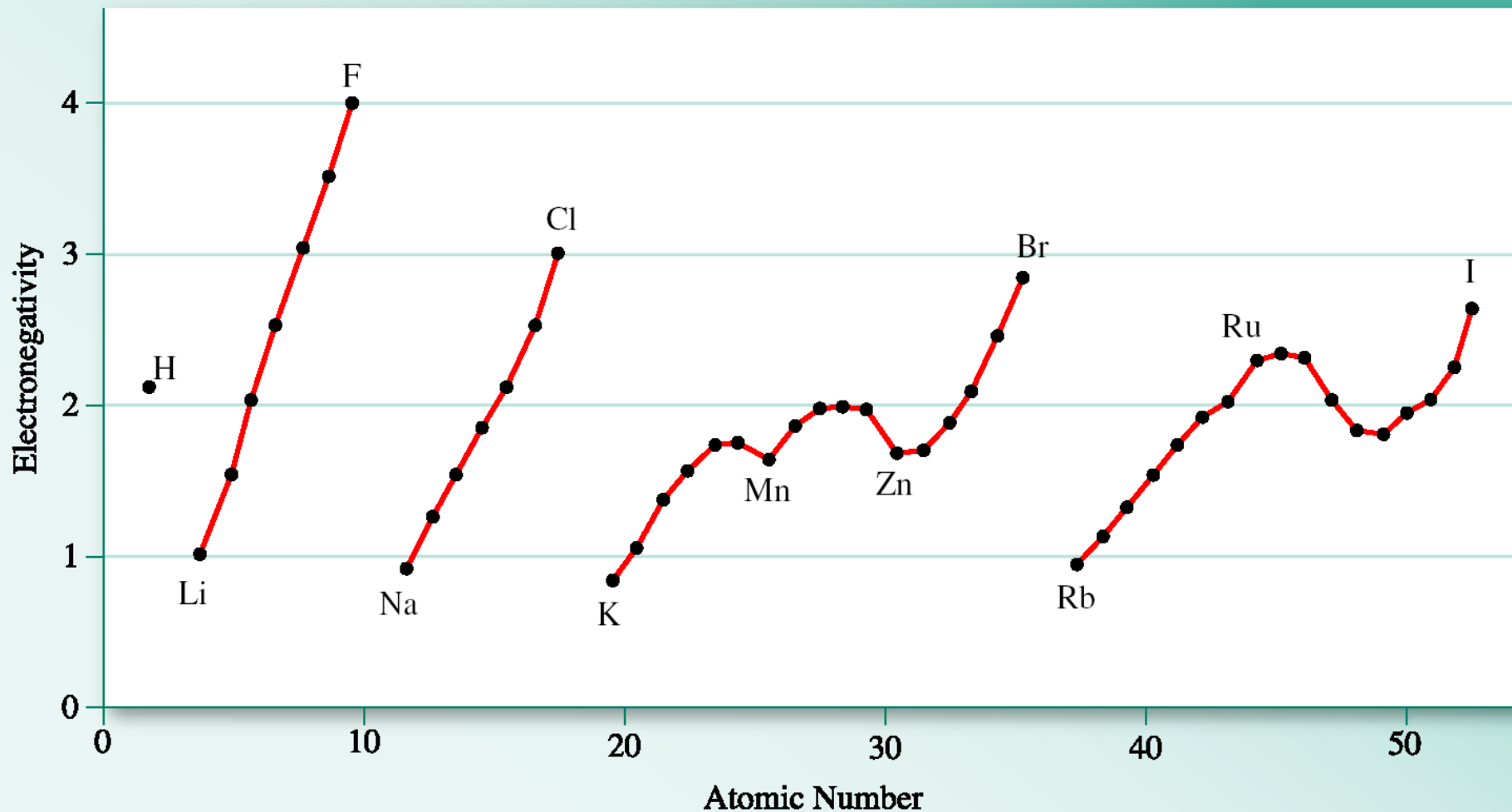blue $\Rightarrow$ low electron density

Alternate representations

$\delta+$ $\delta-$

H – F

H – F

Electronegativity

- **Ability of an atom in a molecule to draw shared electrons to itself.**
- **More electronegative elements attract electrons more strongly.**
  - **relative scale**
  - **related to *IE* and *EA***
  - **unitless**
  - **smallest electronegativity: Cs 0.7**
  - **largest electronegativity: F 4.0**

# Electronegativity

- electronegativity is known for almost every element

- electronegativity tends to **increase left to right.**

- electronegativity **decreases as we go down a group**

- Difference in electronegativity between atoms tells about the **polarity of the bond**

Electronegativity: The Pauling Scale

Increasing electronegativity →

Increasing electronegativity ↑

| 1A 1	2A 2	3B 3	4B 4	5B 5	6B 6	7B 7	8B 8	8B 9	8B 10	1B 11	2B 12	3A 13	4A 14	5A 15	6A 16	7A 17	8A 18
H 2.1																	
Li 1.0	**Be** 1.5											**B** 2.0	**C** 2.5	**N** 3.0	**O** 3.5	**F** 4.0	
Na 0.9	**Mg** 1.2											**Al** 1.5	**Si** 1.8	**P** 2.1	**S** 2.5	**Cl** 3.0	
K 0.8	**Ca** 1.0	**Sc** 1.3	**Ti** 1.5	**V** 1.6	**Cr** 1.6	**Mn** 1.5	**Fe** 1.8	**Co** 1.9	**Ni** 1.9	**Cu** 1.9	**Zn** 1.6	**Ga** 1.6	**Ge** 1.8	**As** 2.0	**Se** 2.4	**Br** 2.8	**Kr** 3.0
Rb 0.8	**Sr** 1.0	**Y** 1.2	**Zr** 1.4	**Nb** 1.6	**Mo** 1.8	**Tc** 1.9	**Ru** 2.2	**Rh** 2.2	**Pd** 2.2	**Ag** 1.9	**Cd** 1.7	**In** 1.7	**Sn** 1.8	**Sb** 1.9	**Te** 2.1	**I** 2.5	**Xe** 2.6
Cs 0.7	**Ba** 0.9	**Lu** 1.3	**Hf** 1.3	**Ta** 1.5	**W** 1.7	**Re** 1.9	**Os** 2.2	**Ir** 2.2	**Pt** 2.2	**Au** 2.4	**Hg** 1.9	**Tl** 1.8	**Pb** 1.9	**Bi** 1.9	**Po** 2.0	**At** 2.2	
Fr 0.7	**Ra** 0.9																

Variation in Electronegativity with Atomic Number
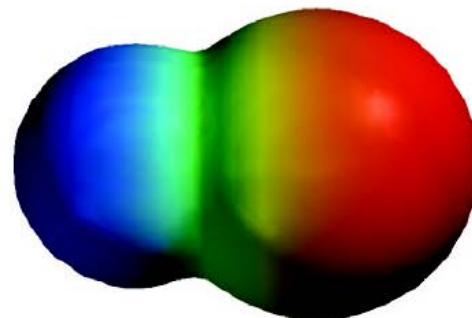
Polar and nonpolar bonds
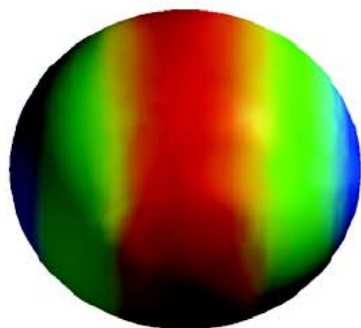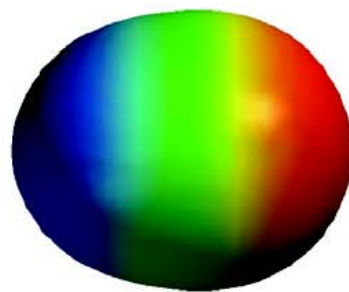
H₂   HF   NaF

$2.1 - 2.1 = 0.0$

nonpolar covalent

$4.0 - 2.1 = 1.9$

polar covalent

$4.0 - 0.9 = 3.1$

ionic

> 2.0 is ionic

Bond polarity and dipole moments

- **A molecule with a center of negative charge and a center of positive charge is dipolar (two poles), (H-F)**

- **or has a dipole moment.**

- **Dipoles will line up in the presence of an electric field.**

- **Dipole moments and partial charges**

- Polar bonds *often* result in polar molecules.

  - A **polar molecule** possesses a *dipole.*

- *dipole moment (μ)* = the quantitative measure of a dipole

$$\overset{\delta+ \quad \delta-}{\text{H} - \text{F}} \qquad \qquad \mu = Qr$$

+Q $\bullet$ $\bullet$ $- Q$

$\longleftarrow$ **r** $\longrightarrow$

SI unit: coulomb•meter (C • m)
   common unit: debye (D)

1 D = 3.34×10^{-30} C • m

HF	1.82 D
HCl	1.08 D
HBr	0.82 D
HI	0.44 D

Electronegativity difference   **Bond Type**

Zero — Covalent

Intermediate — Polar Covalent

Large — Ionic

Covalent Character decreases

Ionic Character increases
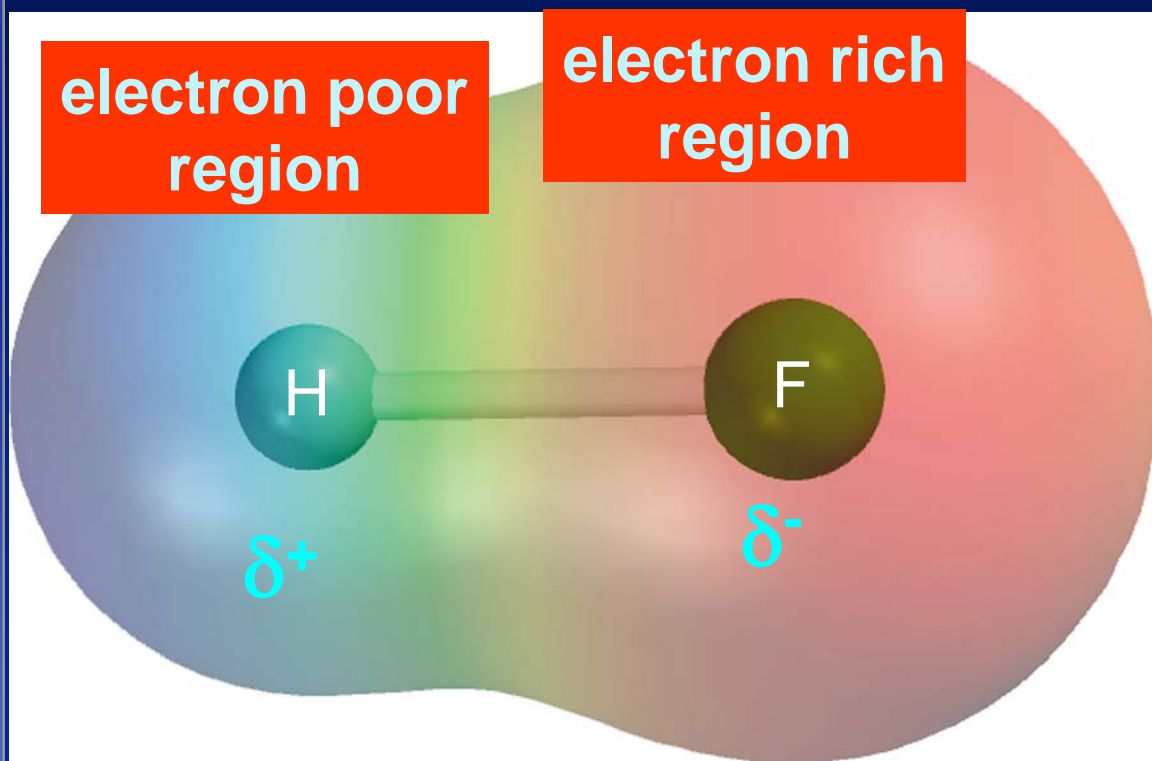
Relationship between electronegativity and bond type
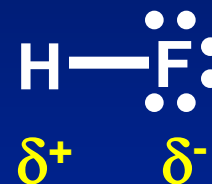
Representation of the dipolar character

$$\longmapsto$$

$\delta+$ $\delta-$

H - F
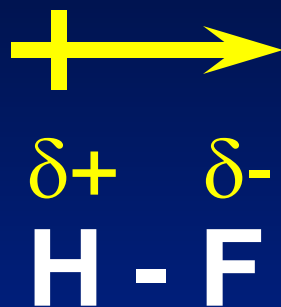
- **Any diatomic (two atoms) molecule with a polar bond will show a molecular dipole moment**

Polar Covalent Bond

A covalent bond with greater electron density around one of the two atoms

electron poor region

electron rich region

δ^+ δ^-

e⁻ poor e⁻ rich

H—F

δ^+ δ^-

Polarity of polyatomic molecules

- **The effect of polar bonds on the polarity of the entire molecule depends on the <u>molecule shape</u>**

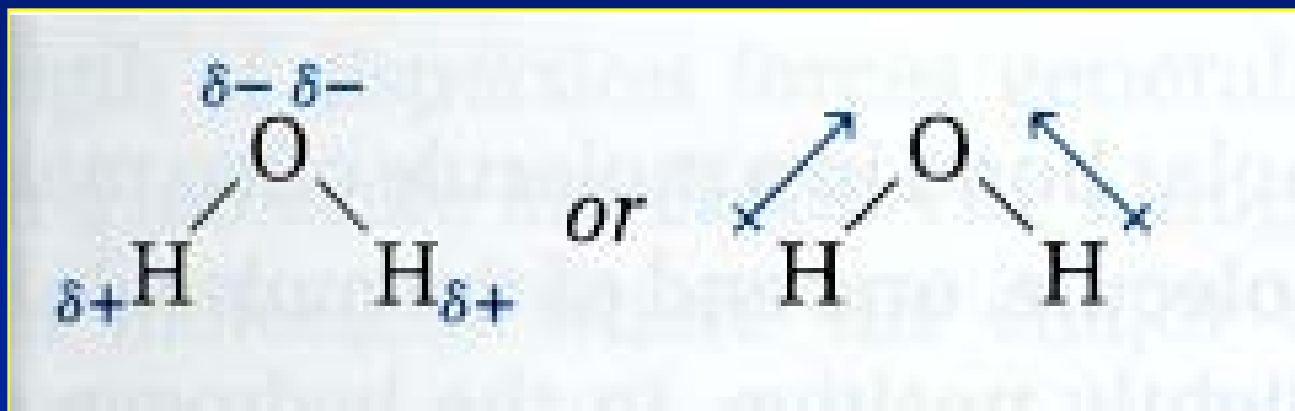 - **carbon dioxide has two polar bonds, and is linear = *nonpolar molecule***

δ^-　$2\delta^+$　δ^-

O　C　O
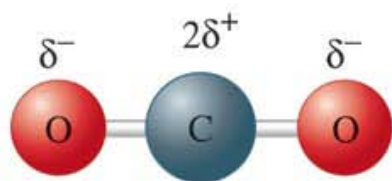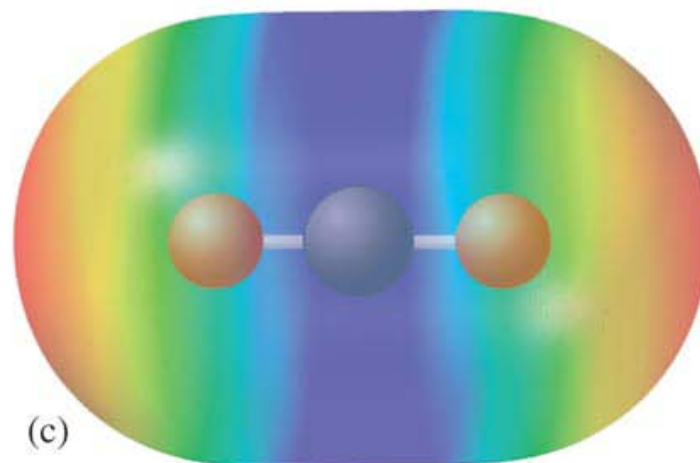
(a)　　(b)　　(c)

Polar molecules

- **The effect of polar bonds on the polarity of the molecule depends on the <u>molecular shape</u>**

  – **water has two polar bonds and a bent shape; the highly electronegative oxygen pulls the e⁻ away from H = very polar!**

Thus, H_2O molecule has a dipole moment

How to decide for molecular polarity?

- **Any diatomic molecule with a polar bond is a <u>polar molecule</u>**

- **For a three or more atoms molecule there are two considerations:**
  - **There must be a <u>polar bond</u>.**
  - **Geometry <u>can't cancel</u> it out.**

8.5 Drawing Lewis Structures

1) Draw skeletal structure with the central atom being the least electronegative element.

2) Sum the valence electrons. Add 1 electron for each negative charge and subtract 1 electron for each positive charge.

3) Subtract 2 electrons for each bond in the skeletal structure.

4) Complete electron octets for atoms bonded to the central atom except for hydrogen.

5) Place extra electrons on the central atom.

6) Add multiple bonds if atoms lack an octet.

What is the Lewis structure of NO_3^- ?

1) Draw skeletal structure with central atom being the least electronegative.

$$O$$
$$|$$
$$O - N - O$$

2) Sum valence electrons. Add 1 for each negative charge and subtract 1 for each positive charge.
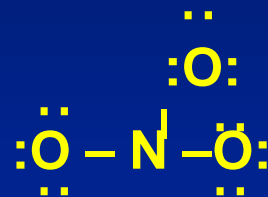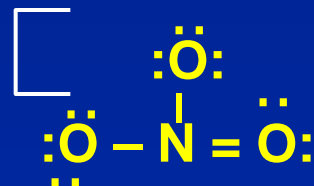
$$NO_3^- \Rightarrow (1 \times 5) + (3 \times 6) + 1 = 24 \text{ valence } e^-$$

24 e^-

3) Subtract 2 for each bond in the skeletal structure.

– 6 e^-

4) Complete electron octets for atoms bonded to the central atom except for hydrogen.

$$:\overset{..}{O}:$$
$$:\overset{..}{O} - N - \overset{..}{O}:$$

18 e^-

5) Place extra electrons on the central atom.

6) Add multiple bonds if atoms lack an octet.

$$\left[\begin{array}{c} :\overset{..}{O}: \\ | \\ :\overset{..}{O} - N = \overset{..}{O}: \end{array} \right]^-$$

24 e^-

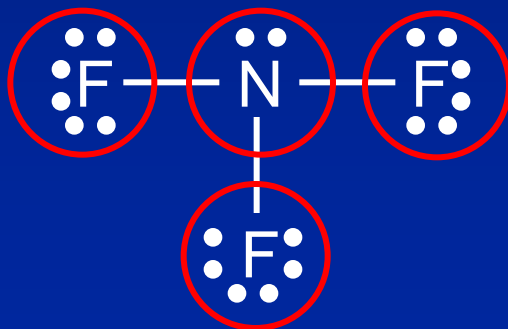# Write the Lewis structure of nitrogen trifluoride (NF_3).

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

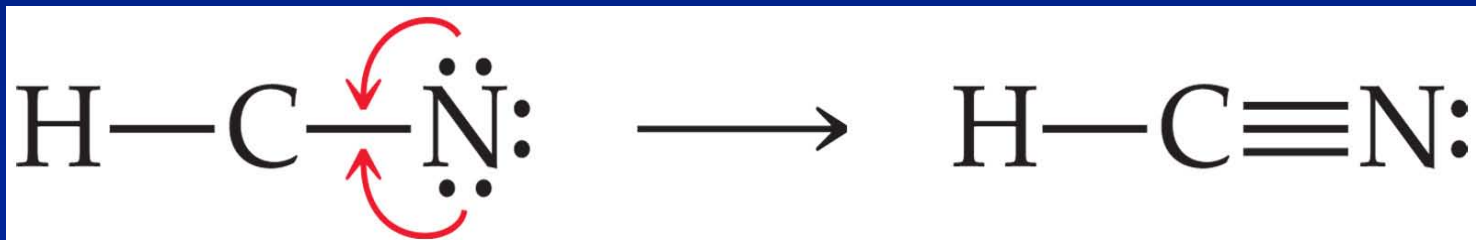**Step 2 – Count valence electrons N - 5 ($2s^2 2p^3$) and F - 7 ($2s^2 2p^5$)**

$$5 + (3 \times 7) = \textbf{26 valence electrons}$$

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

Step 4 – Arrange remaining 20 electrons to complete octets

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

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

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

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

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

Step 4 - Arrange remaining 18 electrons to complete octets

Step 5 – The central C has only 6 electrons. Form a double bond.

Write Lewis Structure for HCN

Maximum number of bonds (or atoms) surrounding the central atom

Central atom	Max # bonds	
H	1	H-
O	2	-O-
N	3	$\overset{\displaystyle \|}{-N-}$
C	4	$\overset{\displaystyle \|}{\underset{\displaystyle \|}{-C-}}$
X$^-$(F, Cl, Br, I)	1	X-

Steps for Drawing Lewis Structures

Step	CH_4	CCl_4	H_2O	O_2	CN^-
1	H–C–H (with H above and H below)	Cl–C–Cl (with Cl above and Cl below)	H–O–H	O–O	C–N
2	8	32	8	12	10
3	$8 - 8 = 0$	$32 - 8 = 24$	$8 - 4 = 4$	$12 - 2 = 10$	$10 - 2 = 8$
4	H–C̈–H (with H above and H below)	:C̈l–C–C̈l: (with :C̈l: above and :C̈l: below)	H–O–H	:Ö–Ö:	:C–N̈:
5	—	—	H–Ö̈–H	—	—
6	—	—	—	:Ö=Ö:	$[:C≡N:]^-$

8.6 Lewis Structures and Formal Charge

- The electron surplus or deficit, relative to the free atom, that is assigned to an atom in a Lewis structure.

$$\text{Formal Charge} = \begin{array}{c}\text{Total valence electrons}\end{array} - \begin{array}{c}\text{Total non-bonding electrons}\end{array} - \frac{1}{2}\begin{array}{c}\text{Total bonding electrons}\end{array}$$

Example: H_2O =   H : Ö : H
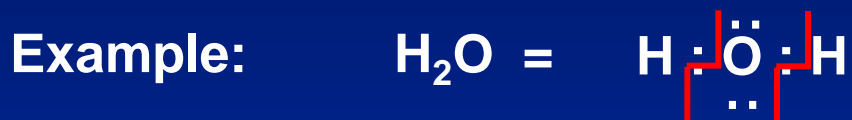
H:	orig. valence e^-	= 1
	– non-bonding e^-	= –0
	– 1/2 bonding e^-	= –1
	formal charge	= 0

O:	orig. valence e^-	= 6
	– non-bonding e^-	= –4
	– 1/2 bonding e^-	= –2
	formal charge	= 0

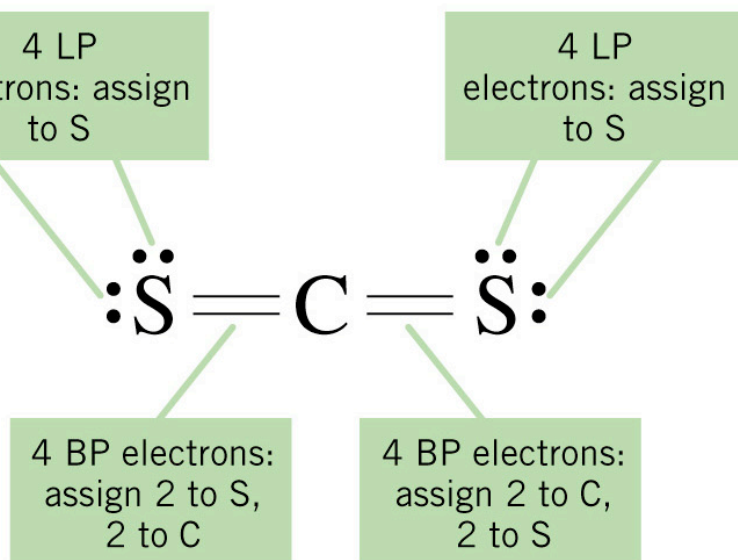**Formal charges are not "real" charges.**

Formal Charge

- **For molecules and polyatomic ions that *exceed the octet there are several different structures*.**

- **Use charges on atoms to help decide which one is the real molecule.**

- **Trying to use the oxidation numbers to put charges on atoms in molecules**

Formal charge is the difference between the number of valence electrons on the free atom and that assigned to the atom in the molecule.

- $C_f = N_v - (N_u + \frac{1}{2} N_b)$
  - C_f = formal charge
  - N_v = #valence e^- in the un-bonded atom
  - N_u = # unshared e^- owned by the atom
  - N_b = # bonding e^- shared by the atom
- In molecules C_f is close to zero
- In ions   should be equal to the charge on the ion

Calculation of Formal Charge

4 LP electrons: assign to S

4 LP electrons: assign to S

4 LP electrons: assign to C

4 LP electrons: assign to S

$$:\ddot{S}=C=\ddot{S}:$$

4 BP electrons: assign 2 to S, 2 to C

4 BP electrons: assign 2 to C, 2 to S

$$:\ddot{C}=S=\ddot{S}:$$

4 BP electrons: assign 2 to C, 2 to S

4 BP electrons: assign 2 to each S atom

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

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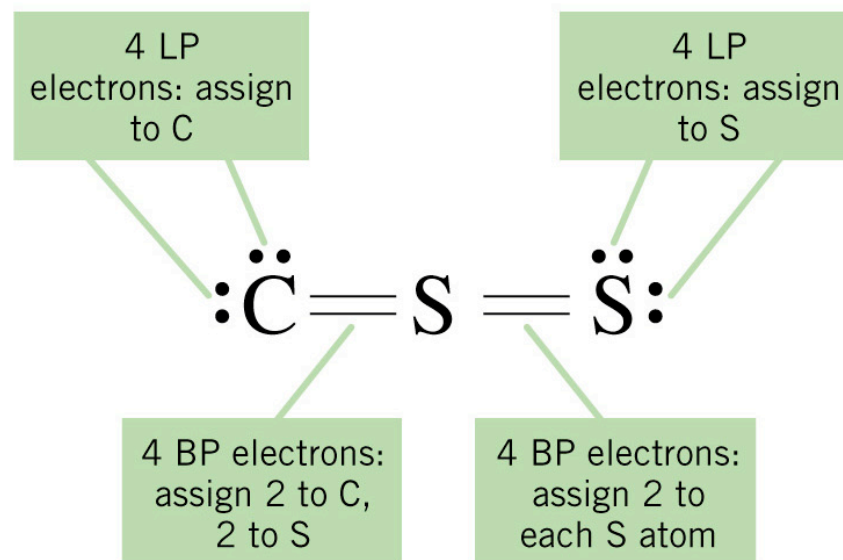
	C	S	S
Valence electrons	4	6	6
Electrons assigned	6	4	6
Formal charge	−2	+2	0

(b)

Using the assumption of formal charges to evaluate Lewis structure
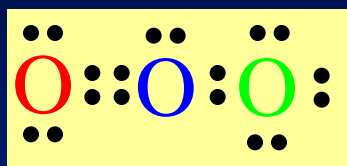
- Atoms in molecules try to achieve as low a formal charge (as close to zero) as possible

- Negative formal charges are expected to be found on the most electronegative elements.

Which is the most likely Lewis structure for CH$_2$O?

-1   +1

H—C̈=Ö—H

H—C=O (with H below), labeled 0, 0

√
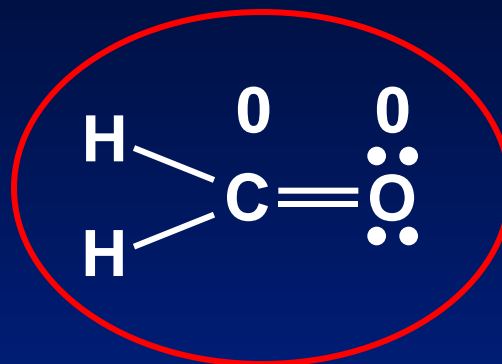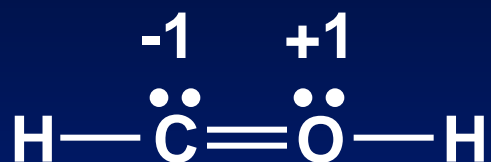
Example: Formal charges on the atoms in ozone

$\overset{\displaystyle\cdot\cdot}{\underset{\displaystyle\cdot\cdot}{O}} :: \overset{\displaystyle\cdot\cdot}{O} : \overset{\displaystyle\cdot\cdot}{\underset{\displaystyle\cdot\cdot}{O}} :$

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

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

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

Formal charge guidelines

- A Lewis structure with *no* formal charges is generally better than one with formal charges.
- Small formal charges are generally better than large formal charges.
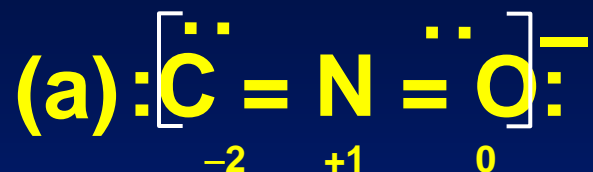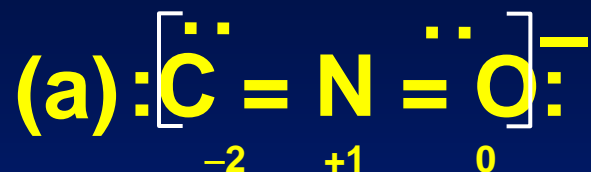- Negative formal charges should be on the more electronegative atom(s).

Example:
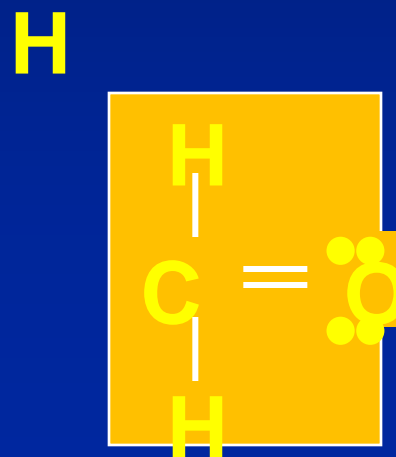
H   C   O   H   or   C   O   ?

H

H

Answer:

H —C̈⁻=Ö⁺— H

H
|
C=Ö
|
H

Identify the best structure for the isocyanate ion below

(a) $\left[:\ddot{C} = N = \ddot{O}: \right]^{-}$

       −2   +1   0

(b) $\left[:C \equiv N - \ddot{\underset{..}{O}}: \right]^{-}$

       −1   +1   −1

(c) $\left[:\ddot{\underset{..}{C}} - N \equiv O: \right]^{-}$

       −3   +1   +1

Identify the best structure for the isocyanate ion below

(a) $[:C = N = O:]^-$

-2 $+1$ 0

(b) $[:C \equiv N - O:]^-$

-1 $+1$ -1

(c) $[:C - N \equiv O:]^-$

-3 $+1$ $+1$

8.7 Resonance

• *Resonance* structures are used when two or more equally valid Lewis structures can be written.

Example: NO$_2$

$$\left[:\ddot{O} - \ddot{N} = \ddot{O}: \right]^-$$

These two bonds are known to be identical.

Solution:

$$\left[:\ddot{O} - \ddot{N} = \ddot{O}: \right]^- \longleftrightarrow \left[:\ddot{O} = \ddot{N} - \ddot{O}: \right]^-$$
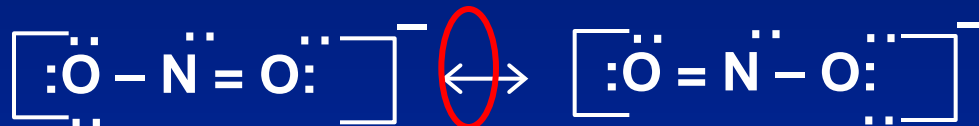
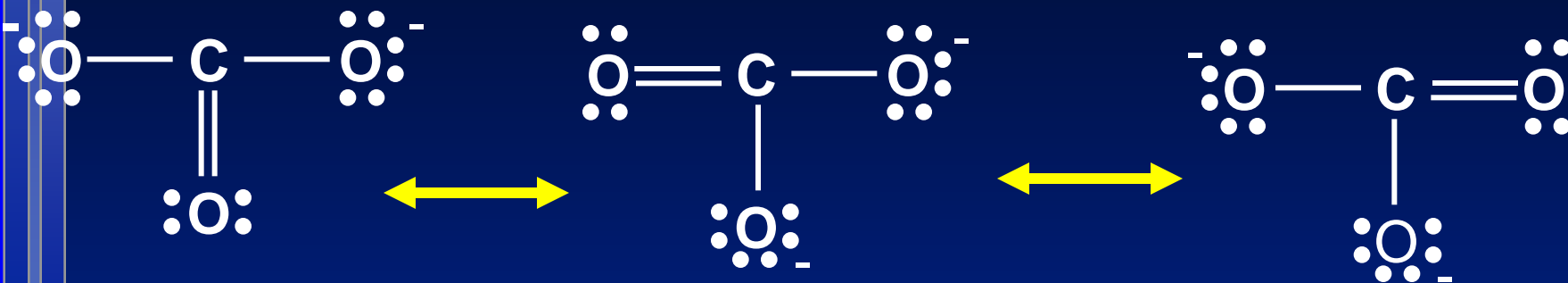Two *resonance structures*, their average or the *resonance hybrid*, best describes the nitrite ion.

The double-headed arrow indicates resonance.

A *resonance structure* is one of two or more Lewis structures for a single molecule that cannot be represented accurately by only one Lewis structure.
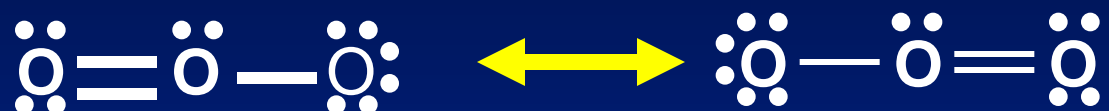
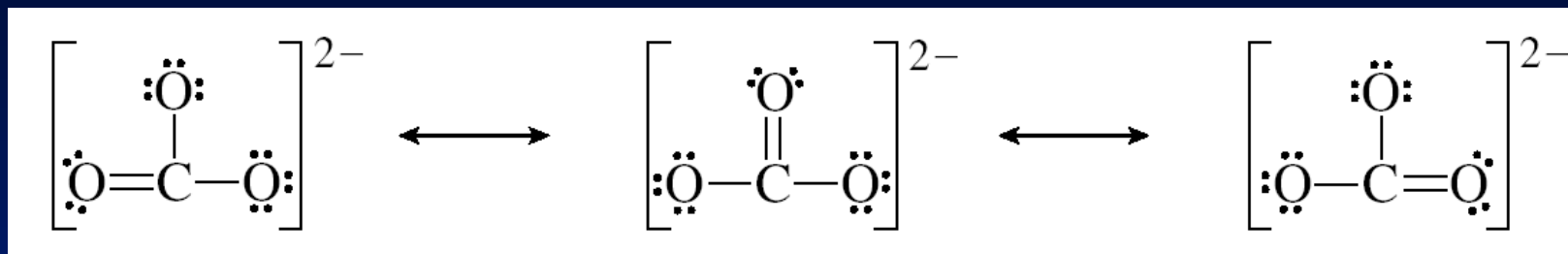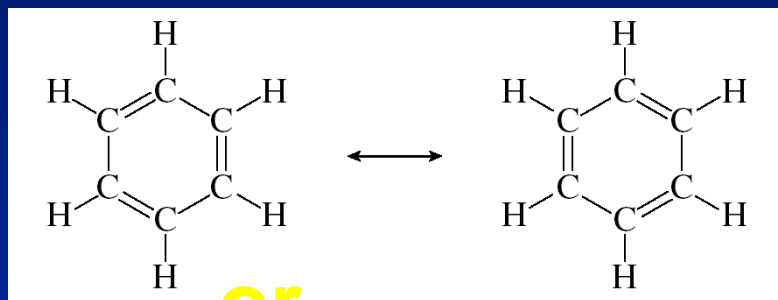**What are the resonance structures of the carbonate (CO_3^{2-}) ion?**
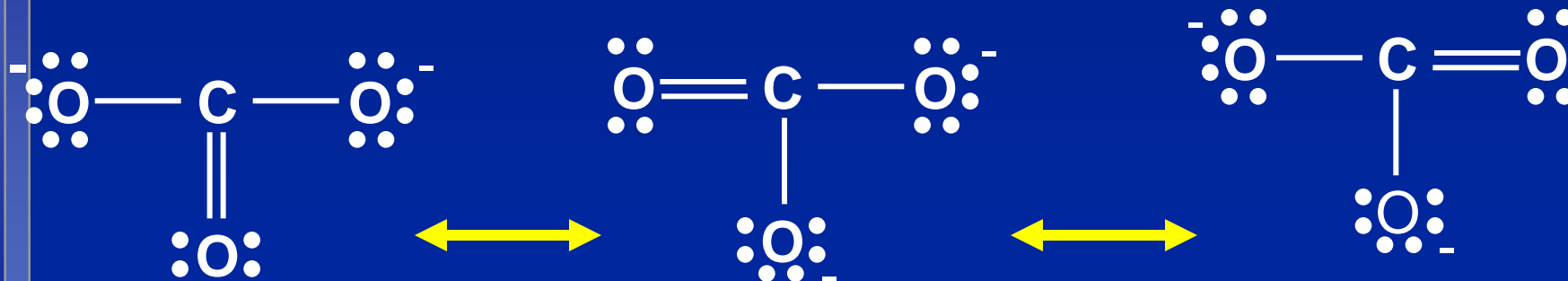
●In truth, the electrons that form the second C—O bond in the double bonds do not always sit between that C and that O, but rather can **move among the three oxygen atoms and the carbon**.

●They are not **localized**, but rather are **delocalized**.
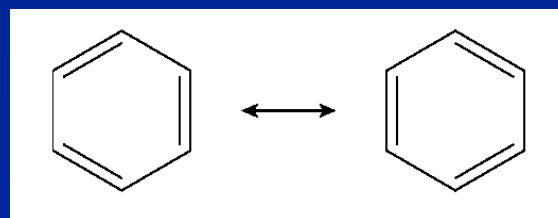
Additional Examples

Carbonate: CO_3^{2-}

Benzene: C_6H_6

or

8.8 Exceptions to the Octet Rule

• **Exceptions to the octet rule fall into three categories:**
  - **Molecules with an incomplete octet**
  - **Molecules with an odd number of electrons**
  - **Molecules with an expanded octet**
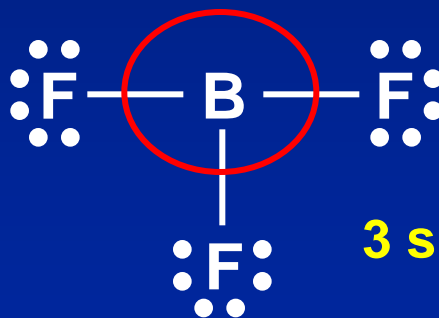
Exceptions to the Octet Rule

The Incomplete Octet

BeH_2

Be – 2e⁻

2H – 2x1e⁻

4e⁻

H——Be——H

BF_3

B – 3e⁻

3F – 3x7e⁻

24e⁻

3 single bonds (3x2) = 6

9 lone pairs (9x2) = 18

Total = 24

Incomplete Octets

Example: BF_3 (boron trifluoride)

$BF_3 \Rightarrow (1 \times 3) + (3 \times 7) = 24$ **val.** e^-

:Ḟ:
|
:Ḟ — B — Ḟ:

:Ḟ:
|
:Ḟ — B = Ḟ: **+1**

-1
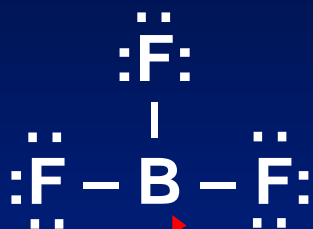
no octet
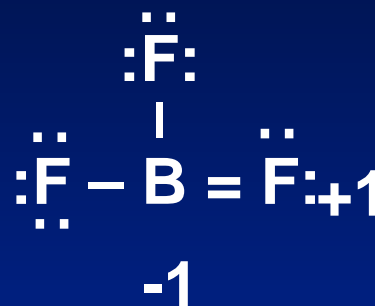
– **Common with Be, B and Al compounds, but they often dimerize or polymerize.**

Example:

Cl   Cl   Cl

Be   Be   Be   Be

Cl   Cl   Cl
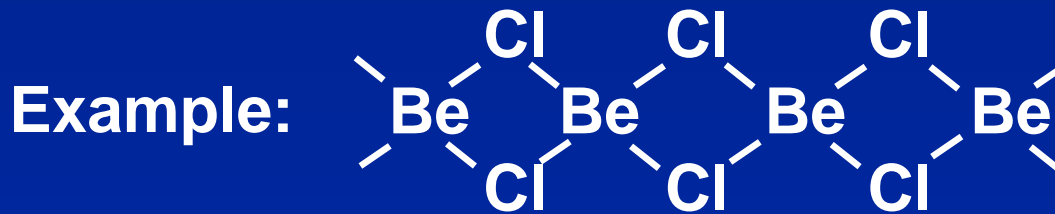
Odd Numbers of Electrons

Example: NO (nitrogen monoxide or nitric oxide)

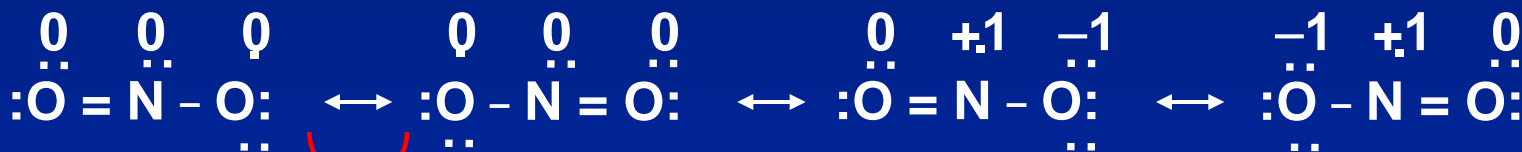$$NO \Rightarrow (1 \times 5) + (1 \times 6) = 11 \text{ valence } e^-$$

$$\overset{\displaystyle 0}{:\!N} = \overset{\displaystyle 0}{\ddot{O}:} \quad \longleftrightarrow \quad \overset{\displaystyle -1}{:\!\ddot{N}} = \overset{\displaystyle +1}{\ddot{O}:}$$

better

Are these both equally good?

Example: NO$_2$ (nitrogen dioxide)

$$NO_2 \Rightarrow (1 \times 5) + (2 \times 6) = 17 \text{ val. } e^-$$

$$\overset{0}{:\!\ddot{O}} = \overset{0}{N} - \overset{0}{\ddot{O}:} \longleftrightarrow \overset{0}{:\!\ddot{O}} - \overset{0}{N} = \overset{0}{\ddot{O}:} \longleftrightarrow \overset{0}{:\!\ddot{O}} = \overset{+1}{N} - \overset{-1}{\ddot{O}:} \longleftrightarrow \overset{-1}{:\!\ddot{O}} - \overset{+1}{N} = \overset{0}{\ddot{O}:}$$
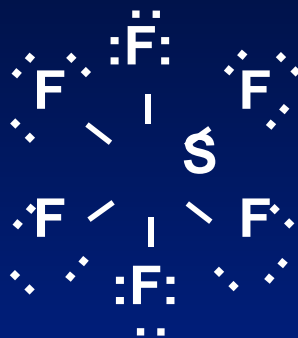
best

Are these all equally good?

Expanded Octet

− **Elements of the 3rd period and beyond have *d*-orbitals that allow more than 8 valence electrons.**

SF_6 =

48 valence *e*⁻

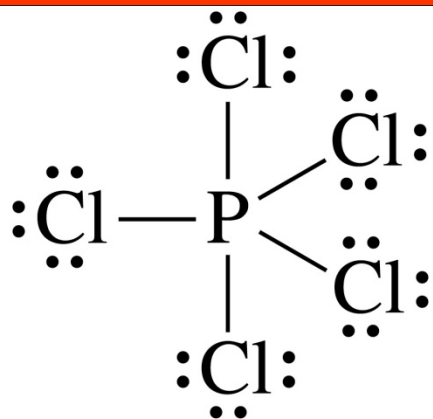**(S has 12 valence electrons)**

XeF_2 =

22 valence *e*⁻
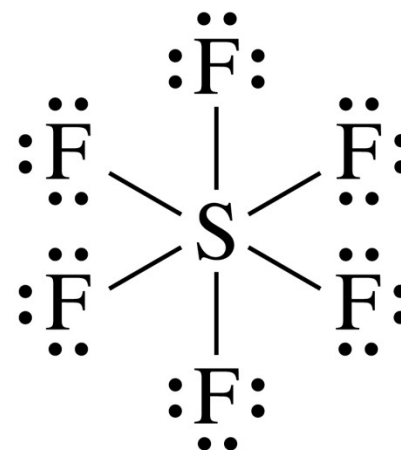
(Xe has 10 valence electrons)

The expanded octet

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

Phosphorus pentachloride

Sulfur hexafluoride
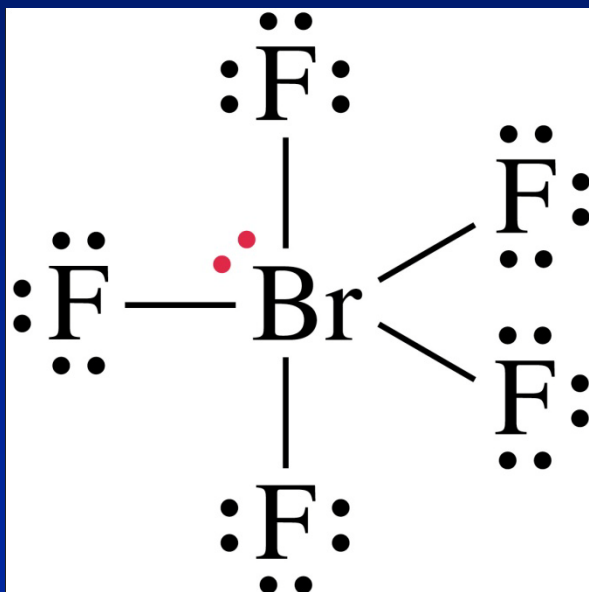
#Ve= 5 + 7(5)= 40

#Ve = 6 + 6(7)= 48

Expanded octet

An expanded valence shell may also need to accommodate lone-pair electrons as well as bonding pairs

Molecules with expanded octet

- **Terminal atoms are most often halogens. In few cases one or more O-atoms are at the end of the molecule**

- **The central atom is a nonmetal in the 3rd, 4th or 5th period of the Periodic Table**
  - 3rd P   S   Cl
  - 4th As   Se   Br   Kr
  - 5th Sb   Te   I   Xe

- **All atoms have d-orbitals available for bondig (3d, 4d, 5d) where the extra pairs of electrons are located**

- **Elements of Period 2, NEVER form compounds with expanded octet.**

8.9 Bond Enthalpy

- **Bond enthalpy** is the energy associated with breaking a particular bond in one mole of gaseous molecules.

  – Bond enthalpy is one measure of molecular stability.

  – **Symbol:** ΔH^o

  – For diatomic molecules these are accurately measured quantities.

$Cl_2(g) \rightarrow Cl(g) + Cl(g)$ $\Delta H^o = 243.4$ kJ

$HCl(g) \rightarrow H(g) + Cl(g)$ $\Delta H^o = 431.9$ kJ   } **single bonds**

$O_2(g) \rightarrow O(g) + O(g)$ $\Delta H^o = 495.0$ kJ   **double bond**

$N_2(g) \rightarrow N(g) + N(g)$ $\Delta H^o = 945.4$ kJ   **triple bond**

Bond Energies and Enthalpy changes in reactions

$\Delta H = \Sigma$ **BE (bonds broken)** $-$ Σ**BE (bonds formed)**

$$E_{required} \qquad\qquad E_{released}$$

Enthalpy change for a reaction

BE = bond energy per mole of bonds; it always has +ve sign

$$= \Sigma BE\ \text{(reactants)} - \Sigma BE\ \text{(products)}$$

Use bond energies to calculate the enthalpy change for:

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

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

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

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

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

− **Bond enthalpies for polyatomic molecules depend upon the bond's environment.**

$$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H \quad \rightarrow \quad H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} \quad + \; H \qquad \qquad \Delta H = 435 \text{ kJ}$$

$$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H \quad \rightarrow \quad H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} \quad + \; H \qquad \Delta H = 410 \text{ kJ}$$

6% less
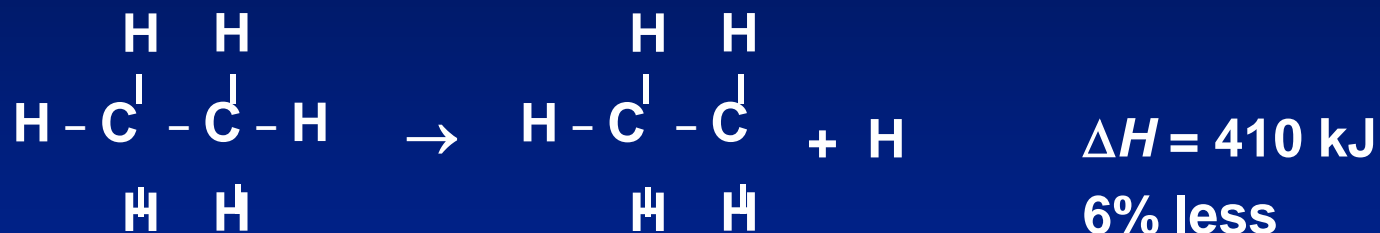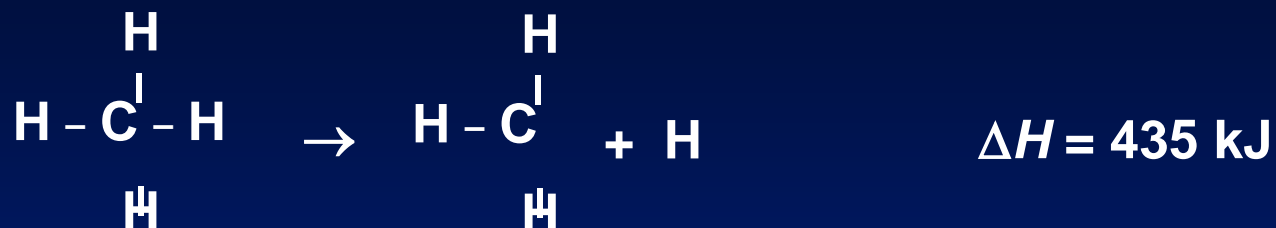
− **Average bond enthalpies are used for polyatomic molecules.**

- **Provide only estimates**

Prediction of bond enthalpy

enthalpy

atoms

reactants

BE(r)

−BE(p)
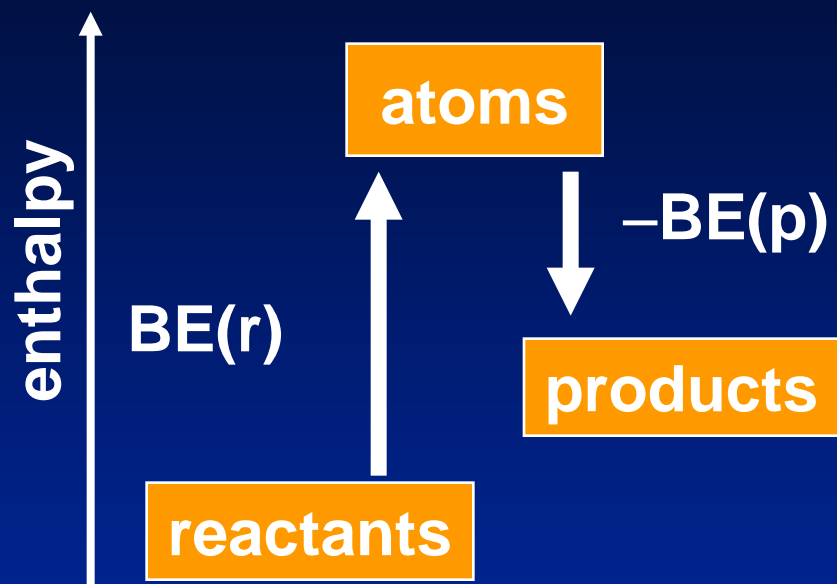
products

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

Example: Calculate the enthalpy of reaction for

$$CH_4(g) + Br_2(g) \rightarrow CH_3Br(g) + HBr(g)$$

Solution: Consider ONLY bonds broken or formed.

H
|
H – C – H   +   Br – Br   →   H – C – Br   +   H – Br
|
H   H
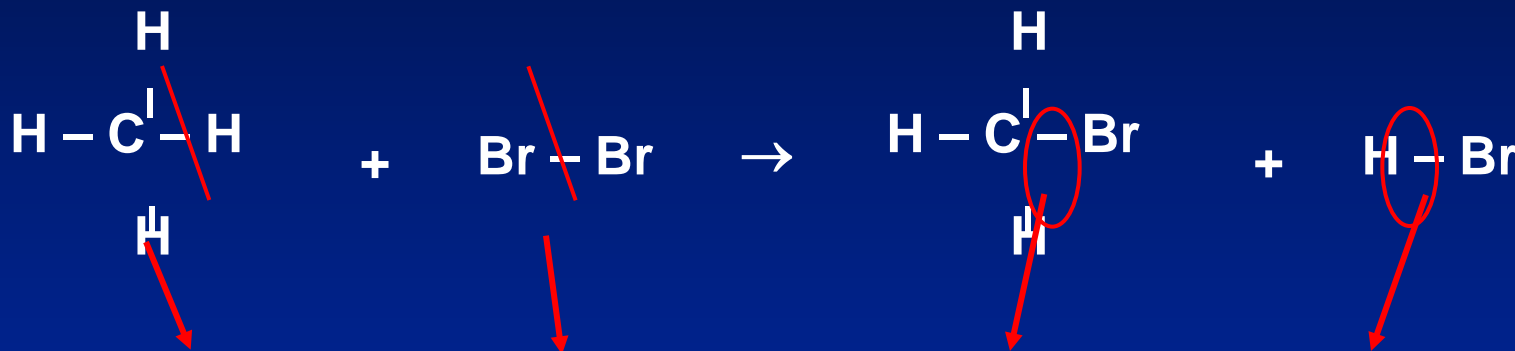
$$\Delta H_{rxn} = [\,BE(C\text{–}H) + BE(Br\text{–}Br)\,] - [\,BE(C\text{–}Br) + BE(H\text{–}Br)\,]$$

$$= [\,(413) + (193)\,] - [\,(276) + (366)\,]$$

$$= -36 \text{ kJ/mol}$$

TABLE 8.6   Bond Enthalpies

Bond	Bond Enthalpy (kJ/mol)	Bond	Bond Enthalpy (kJ/mol)
H—H*	436.4	C—S	255
H—N	393	C=S	477
H—O	460	N—N	193
H—S	368	N=N	418
H—P	326	N≡N	941.4
H—F	568.2	N—O	176
H—Cl	431.9	N=O	607
H—Br	366.1	O—O	142
H—I	298.3	O=O	498.7
C—H	414	O—P	502
C—C	347	O=S	469
C=C	620	P—P	197
C≡C	812	P=P	489
C—N	276	S—S	268
C=N	615	S=S	352
C≡N	891	F—F	156.9
C—O	351	Cl—Cl	242.7
C=O†	745	Cl—F	193
C≡O	1070	Br—Br	192.5
C—P	263	I—I	151.0

*Bond enthalpies shown in red are for diatomic molecules.

†The C=O bond enthalpy in CO_2 is 799 kJ/mol.

Key Points

- **Lewis dot symbols**
- **Ionic bonding**
- **Lattice energy**
- **Born-Haber cycle**
- **Covalent bonding**
- **Octet rule**
- **Lewis structures**
- **Bond order**
- **Bond polarity**