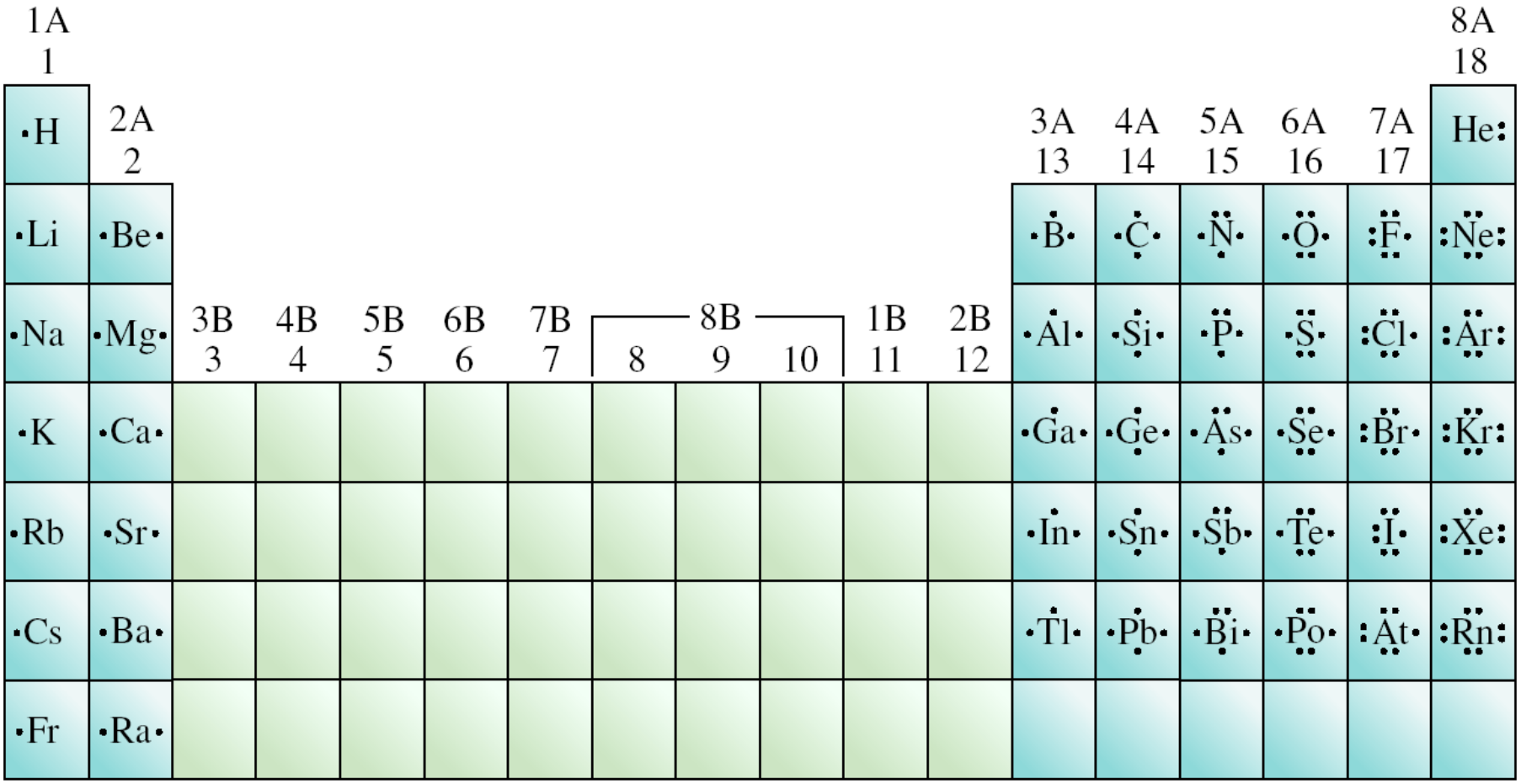
Chapter 8
Chemical Bonding I:
Basic Concepts

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 of the Main Group Elements



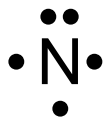
Write Lewis dot symbols for the following:

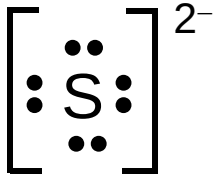
(a) N

(b) S^{2-}

(c) K^{+}

Write Lewis dot symbols for the following:

(a) N 

(b) S^{2-} 

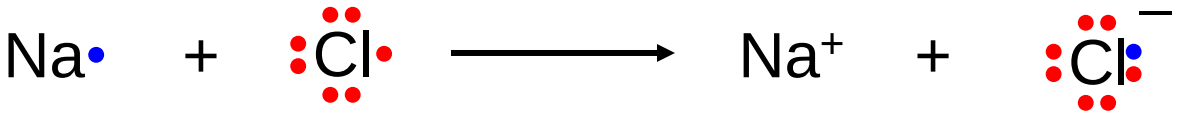
(c) K^+ K^+

8.2 Ionic Bonding

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

- Formed between cations and anions

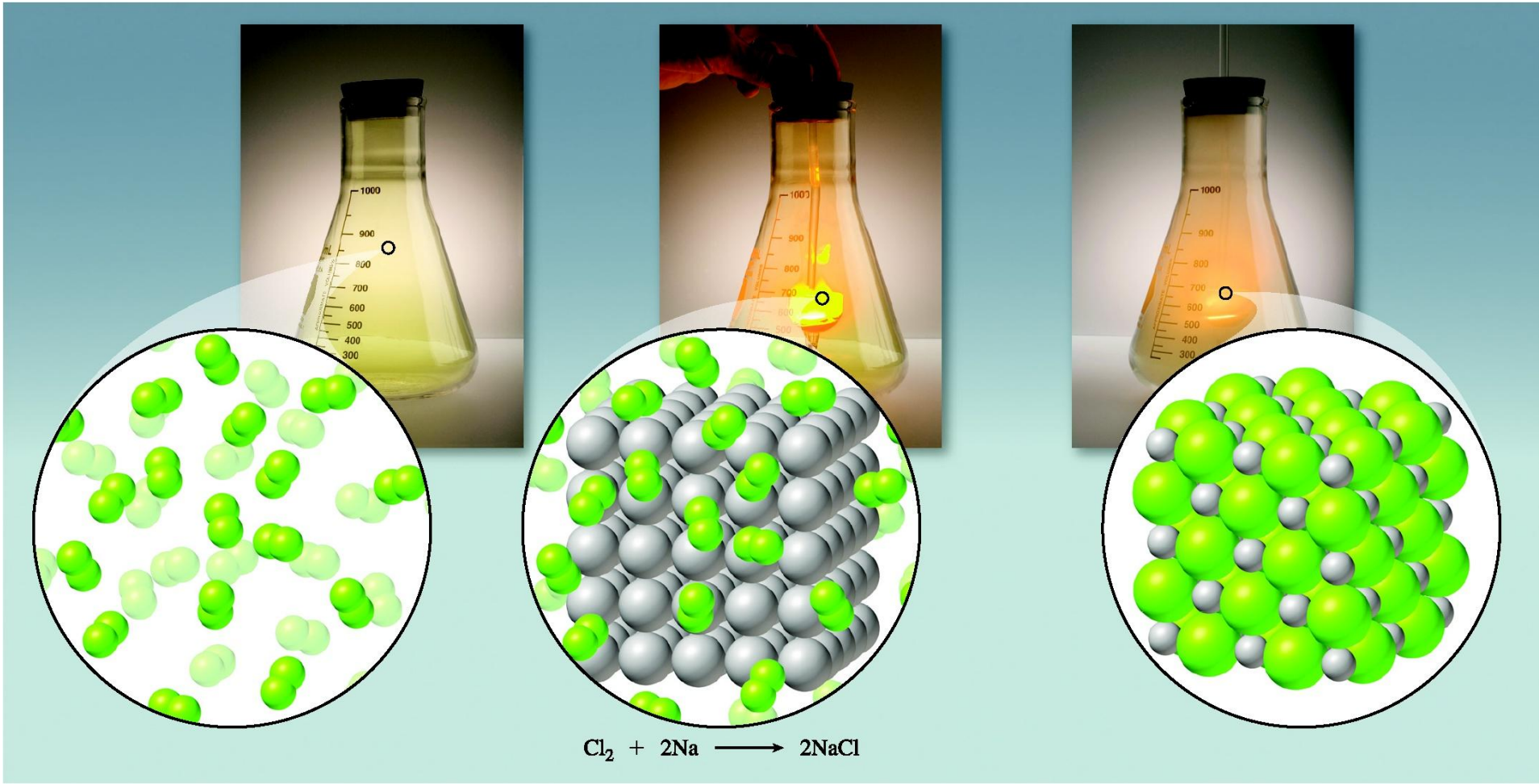
- Example



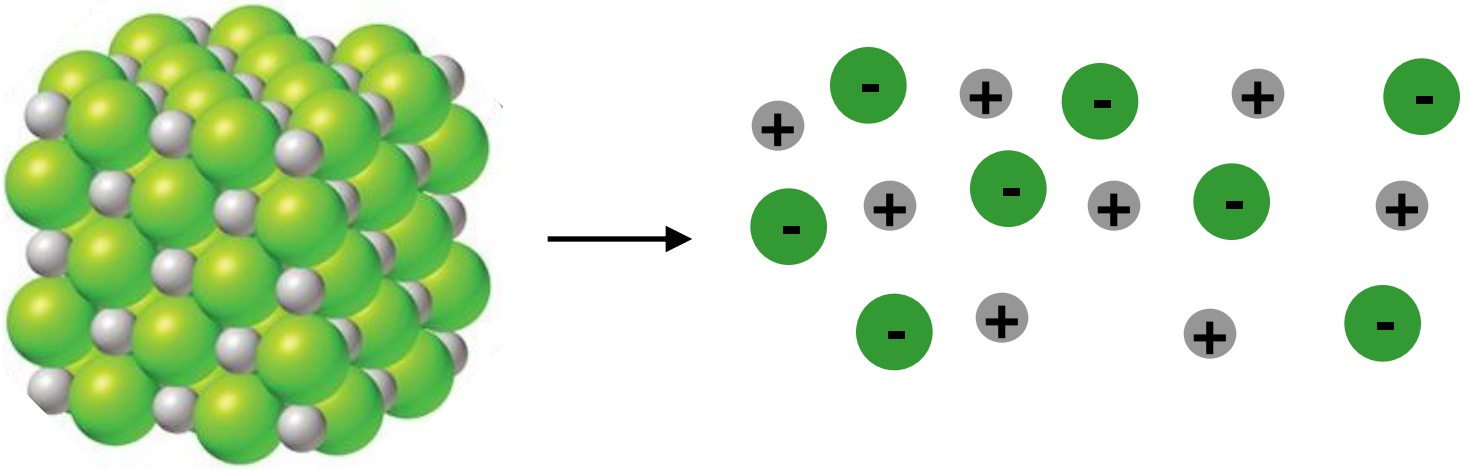
$IE_1 + EA_1 = 496 \text{ kJ/mol} - 349 \text{ kJ/mol} = 147 \text{ kJ/mol}$

m.p. = 801°C $\qquad\qquad$ $\Delta H_f^\circ = -410.9 \text{ kJ/mol}$

Microscopic View of NaCl Formation



• ***Lattice energy*** = the energy required to completely separate one mole of a solid ionic compound into gaseous ions



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

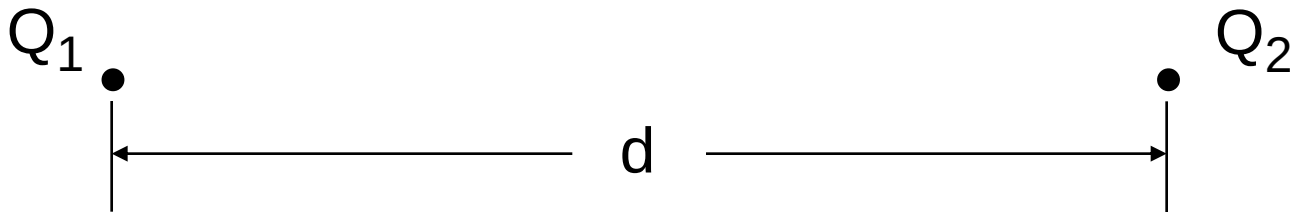
Because they are defined as an *amount* of energy, lattice energies are always positive.

- **Coulombic attraction:**

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

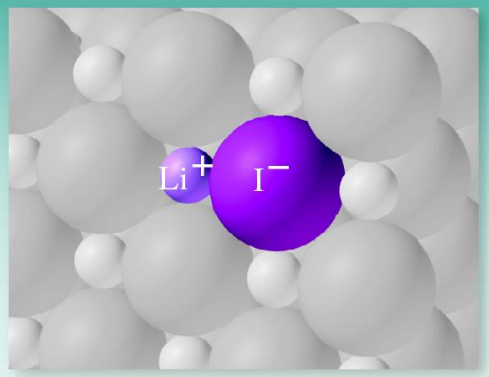
Q = amount of charge

d = distance of separation



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

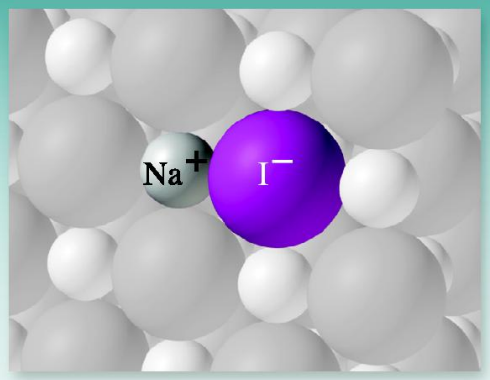
Lattice energies of alkali metal iodides



Li^+ 0.76 Å I^- 2.20 Å

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

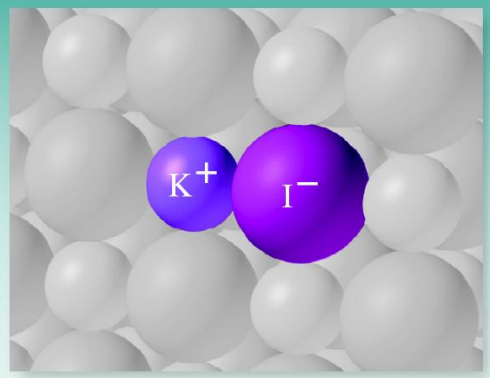
Largest lattice energy
(732 kJ/mol)



Na^+ 1.02 Å I^- 2.20 Å

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

Intermediate lattice energy
(686 kJ/mol)

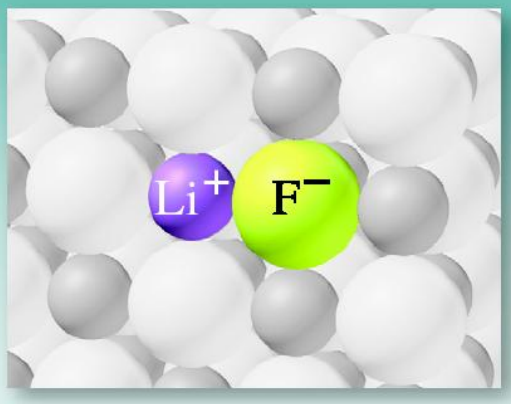


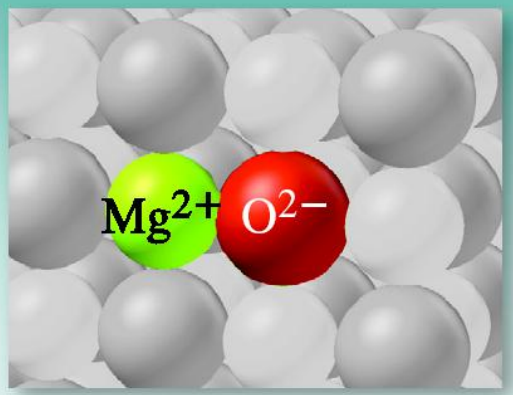
K^+ 1.38 Å I^- 2.20 Å

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

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^+ 0.76 Å F^- 1.33 Å

Mg^{2+} 0.72 Å O^{2-} 1.40 Å

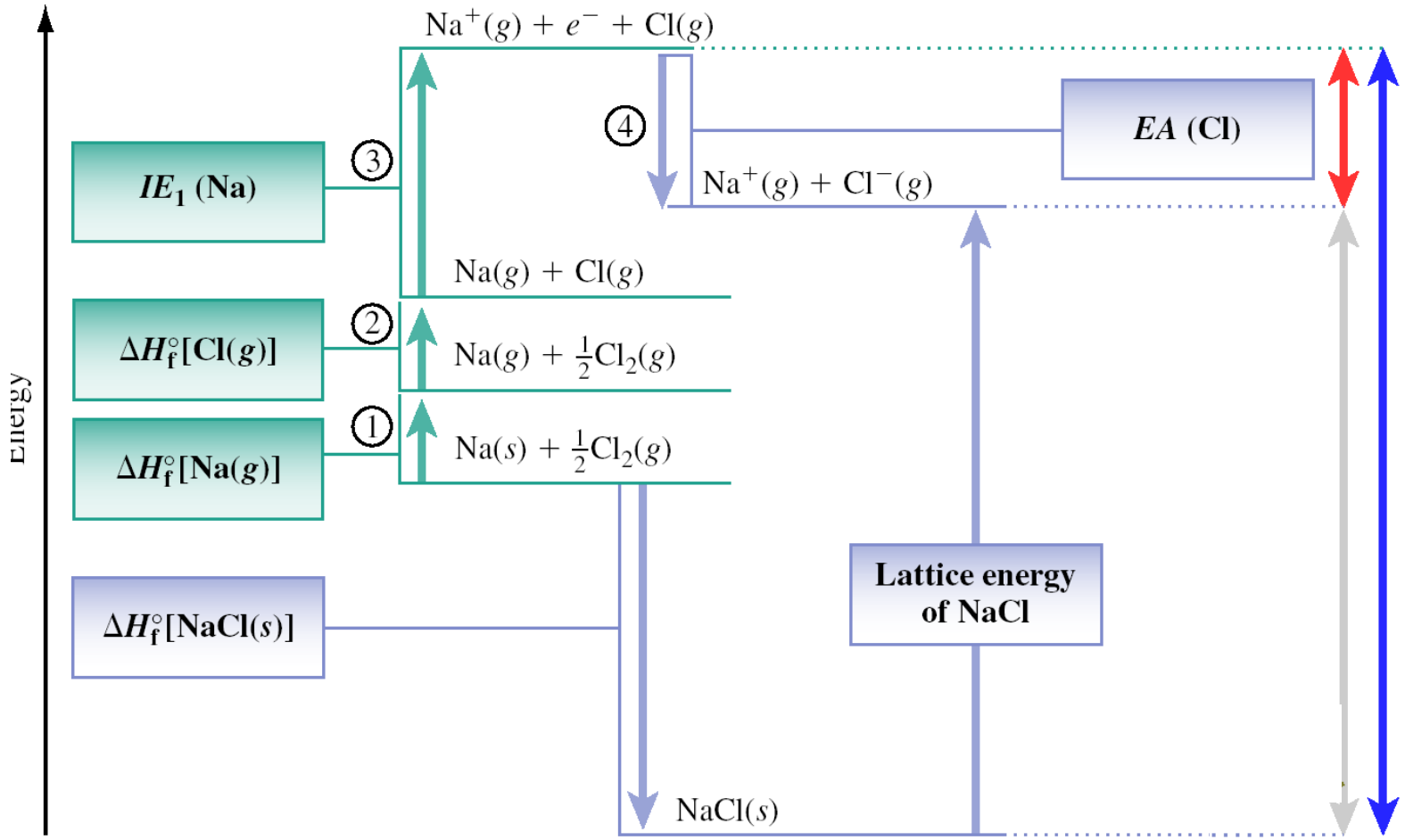
$$F \propto \frac{(+1) \times (-1)}{(0.76 + 1.33)^2} \propto -0.23$$

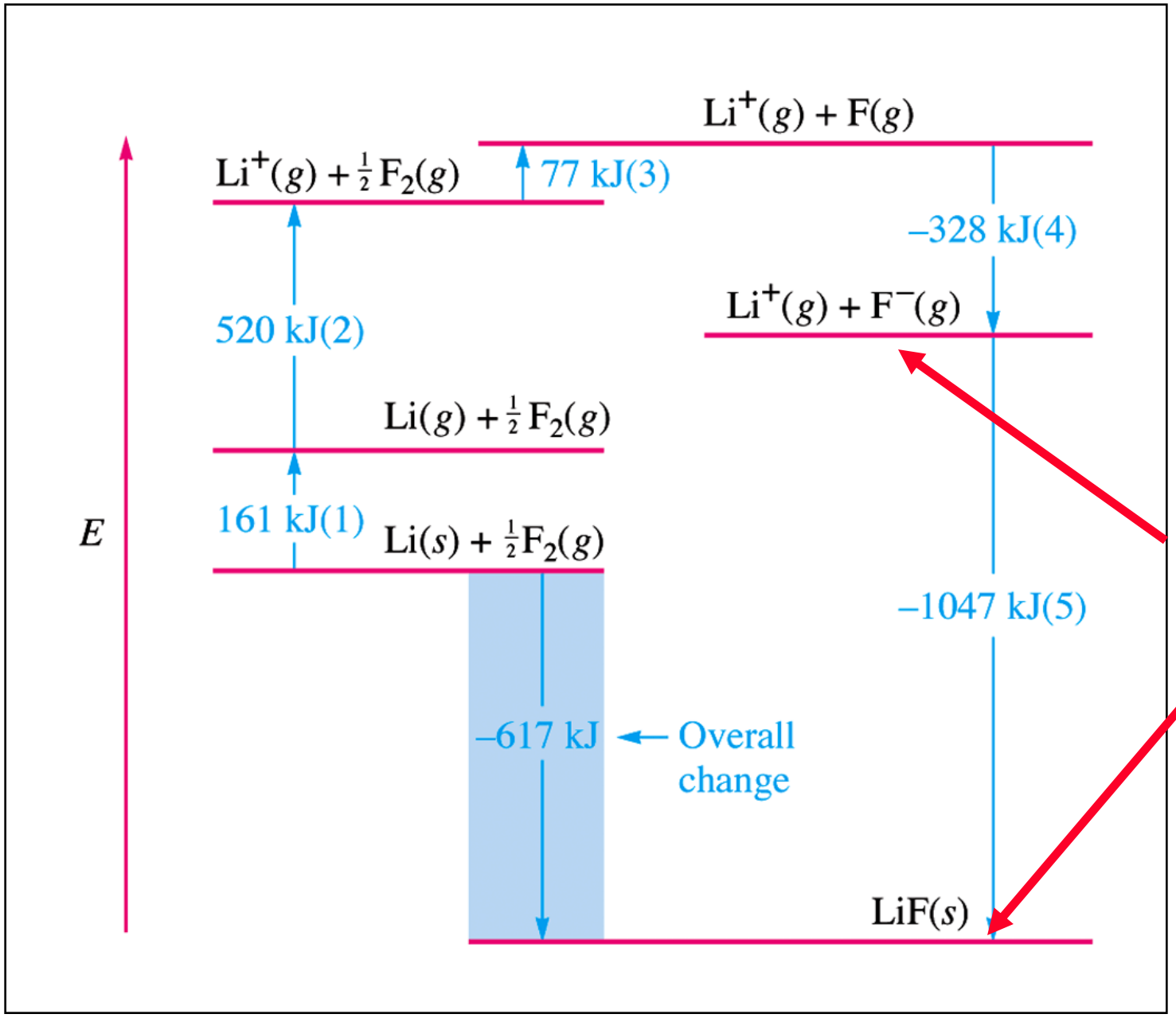
$$F \propto \frac{(+2) \times (-2)}{(0.72 + 1.40)^2} \propto -0.89$$

Smaller lattice energy (1017 kJ/mol)

Larger lattice energy (3890 kJ/mol)

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




$Li^+(g) + F(g)$
$Li^+(g) + \frac{1}{2}F_2(g)$
77 kJ(3)
–328 kJ(4)
$Li^+(g) + F^-(g)$
520 kJ(2)
$Li(g) + \frac{1}{2}F_2(g)$
161 kJ(1)
$Li(s) + \frac{1}{2}F_2(g)$
–1047 kJ(5)
–617 kJ
Overall change
$LiF(s)$
E
From Gas to Solid

Lattice Energy

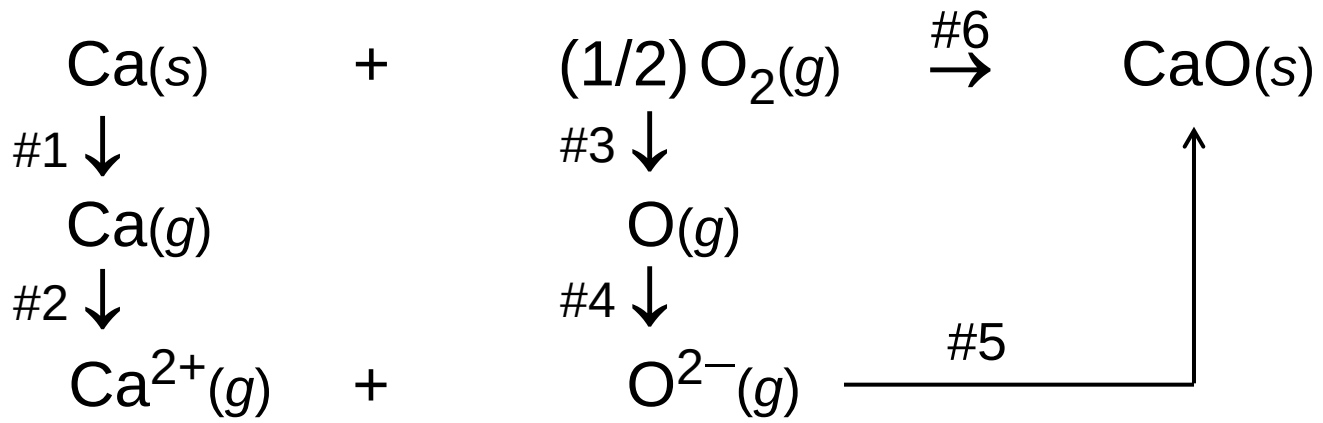
e.g., formation of LiF*(s)*:

Heat of formation: $Li\ (s) + \frac{1}{2} F_2\ (g) \rightarrow LiF\ (s)$

This equation is the result of the following:

1- ΔH_{sub}	= 161	Sublimation:	$Li(s)$	→	$Li(g)$
2- ΔH_{IE}	= 520	Ionization:	$Li(g)$	→	$Li^+(g) + e^-$
3- ΔH_{Dis}	= 77	Dissociation:	$\frac{1}{2} F_2(g)$	→	$F(g)$
4- ΔH_{EA}	= -328	Anion formation	$F(g) + e^-$	→	F^-
5- ΔH_{LE}	= -1047	Solid formation	$Li^+(g) + \frac{1}{2}F^-(g)$	→	$LiF(s)$
ΔH_{Total}	= -617	kJ/mol	$Li\ (s) + \frac{1}{2} F_2(g)$	→	$LiF\ (s)$

- Born-Haber cycle for CaO



#1 Heat of sublimation = $\Delta H_f^\circ[Ca(g)]$ = +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) = $\Delta H_f^\circ[O(g)]$ = +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)

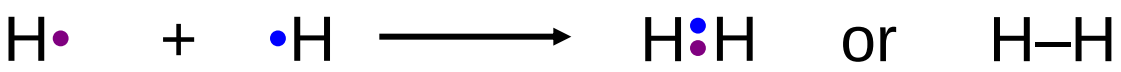
#6 Standard enthalpy of formation = $\Delta H_f^\circ[CaO(s)]$ = – 635 kJ/mol

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

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

8.3 Covalent Bonding

- Atoms share electrons to form covalent bonds.



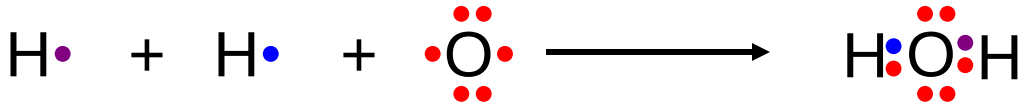
- In forming the bond the atoms achieve a more stable electron configuration.

- Often found between two nonmetals

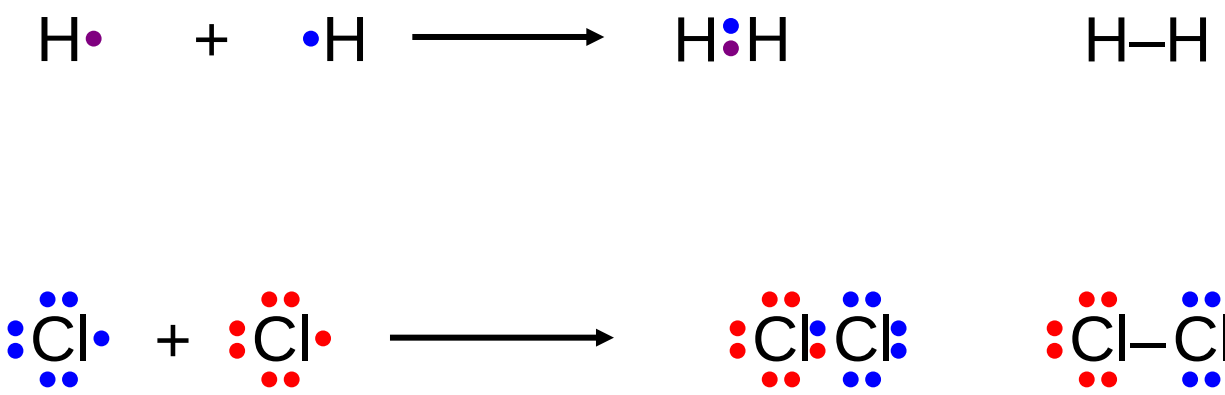
- **Octet:** Eight is a "magic" number of electrons.

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

Examples:



- Lewis Structures

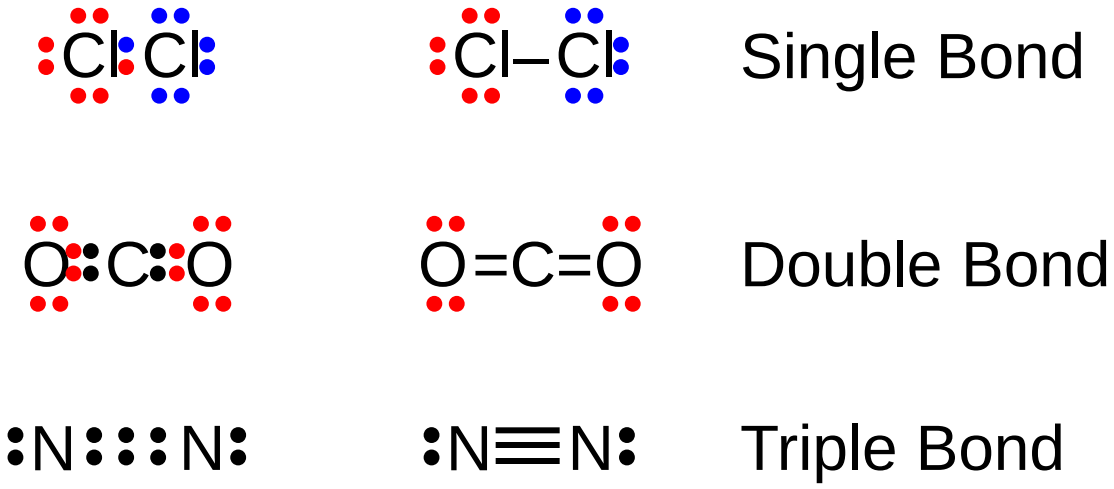


Shared electrons ⇒ Bonds

Non-bonding valence electrons ⇒ Lone pairs

- Multiple Bonds

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



- **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

Covalent Bond

- Often found between two nonmetals
- ***Covalent bond***: electrons are shared equally between two identical atoms.
- ***Ionic Bond:*** electrons transfer completely to form oppositely charged ions
- In between are ***polar covalent bonds.***
- The electrons are ***not shared equally***
- One end is ***slightly positive,*** the other is slightly ***negative.***

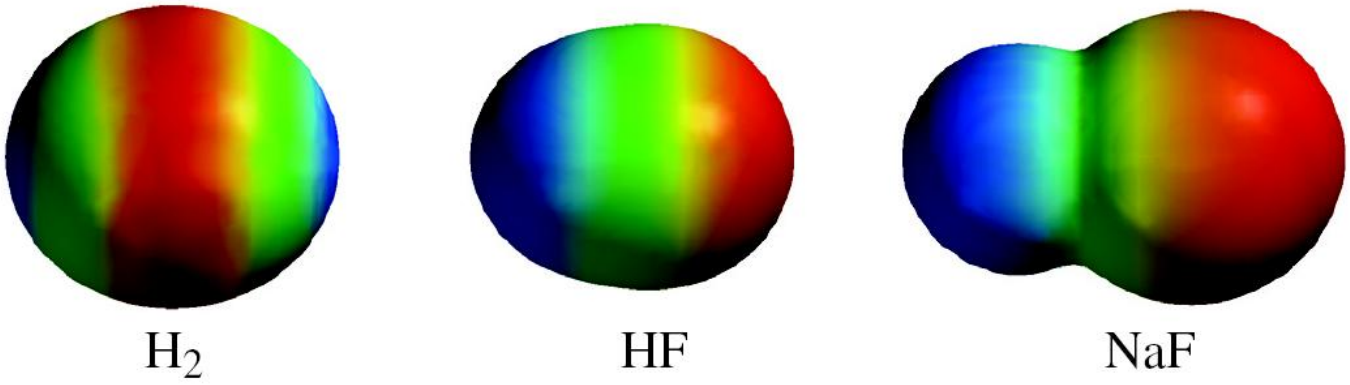
8.4 Electronegativity and Polarity

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

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

- Electron density distributions



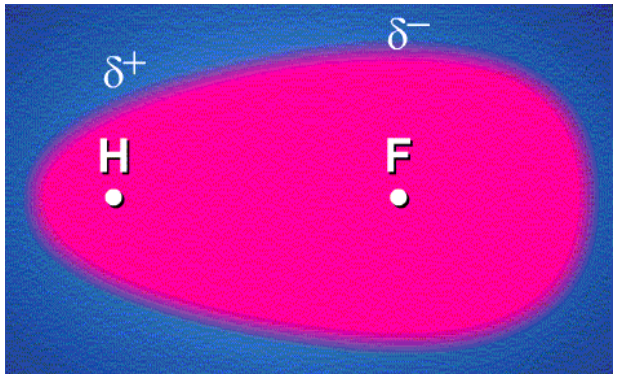
red ⇒ high electron density
green ⇒ intermediate electron density
blue ⇒ low electron density

$\delta+ \quad \delta-$
H – F

H – F

alternate representations

Polar covalent bond



δ+ δ-

H - F

The density of electron cloud is ***shifted*** towards one of the two bonded atoms

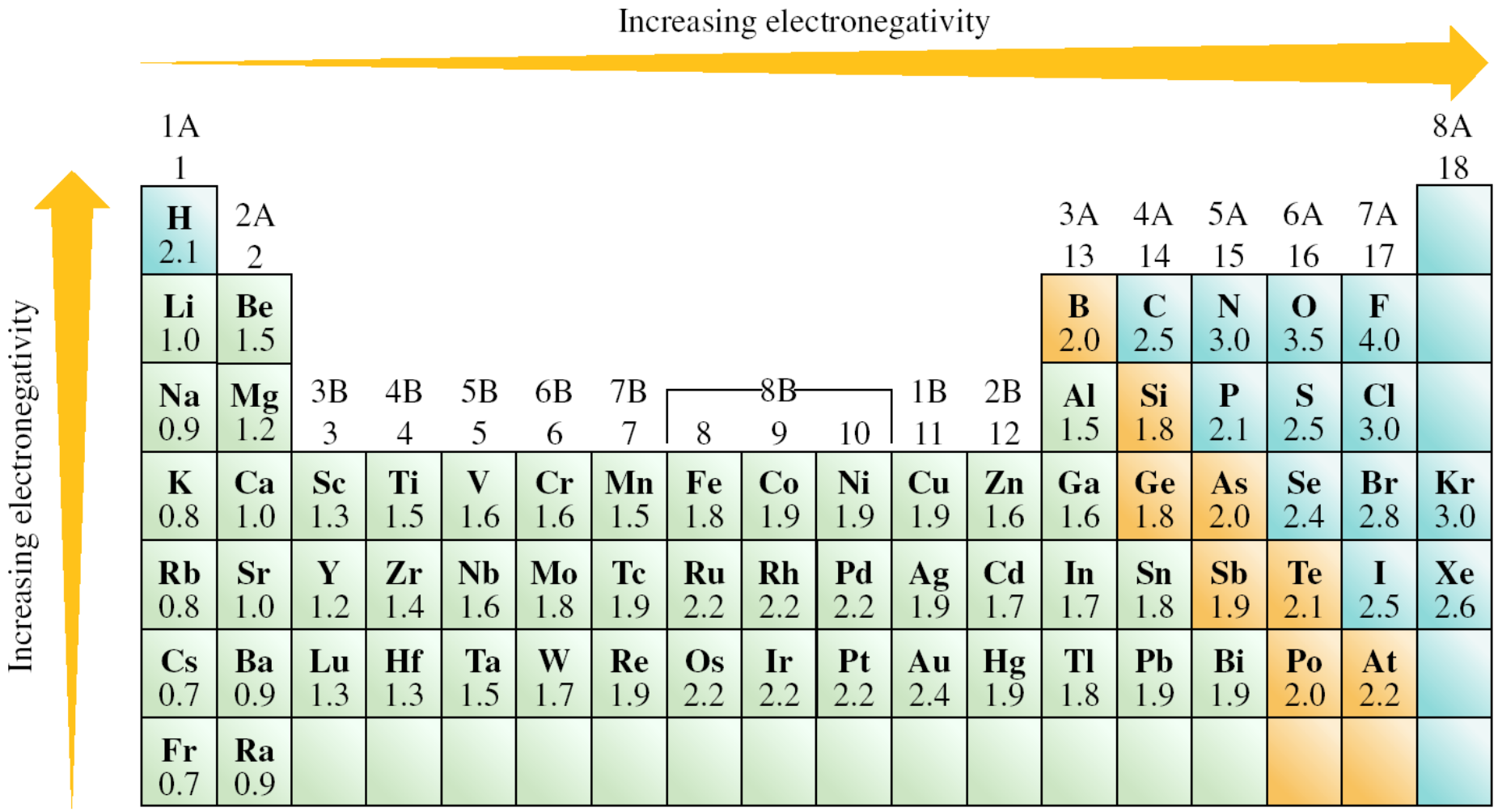
- Dipole Moment
- Polarity

- **Electronegativity: ability of an atom to draw shared electrons to itself.**

  - More electronegative elements attract electrons more strongly.

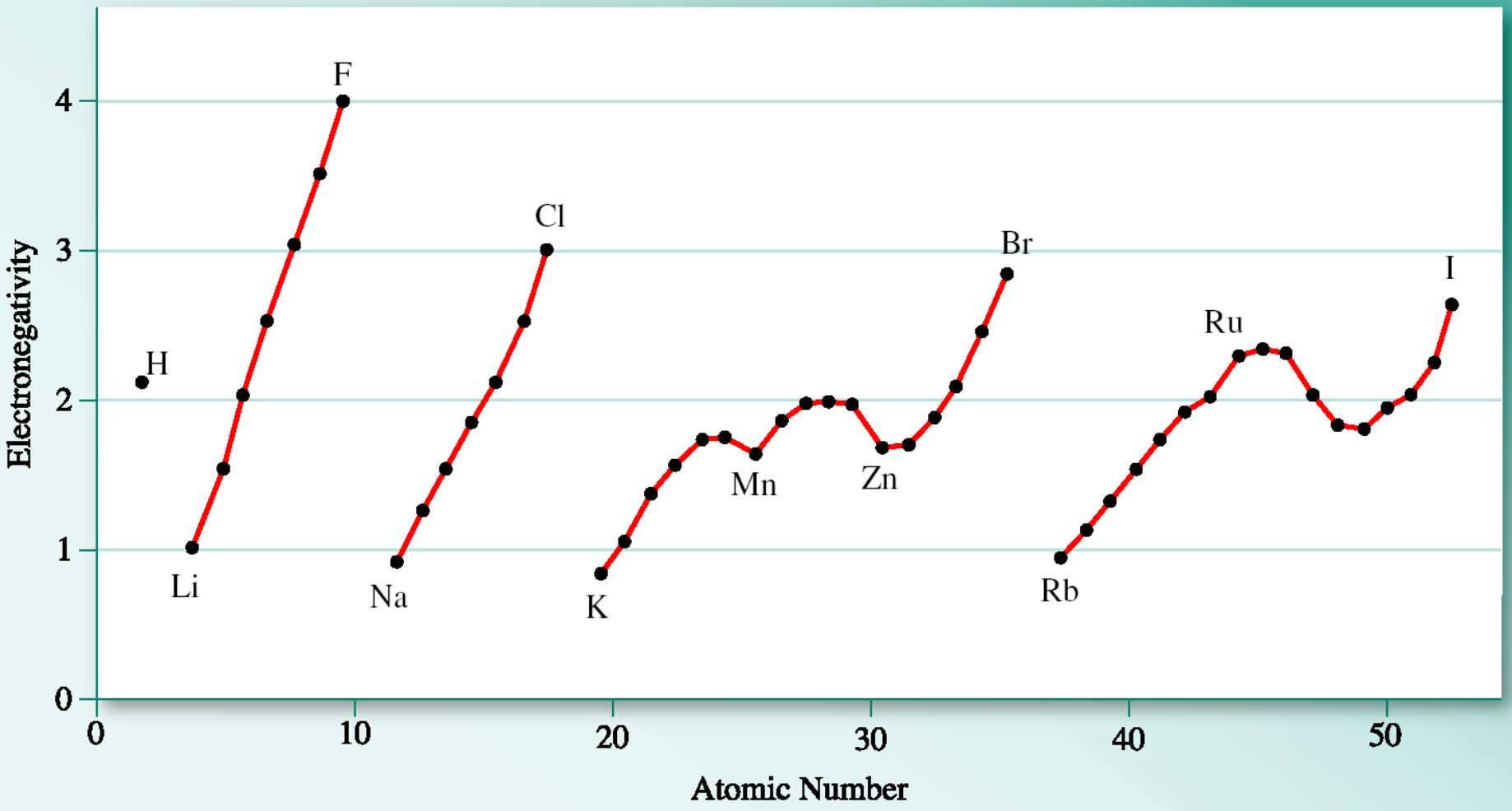
    - relative scale
    - related to *IE* and *EA*
    - unitless
    - smallest electronegativity: Cs 0.7
    - largest electronegativity: F 4.0

Electronegativity: The Pauling Scale

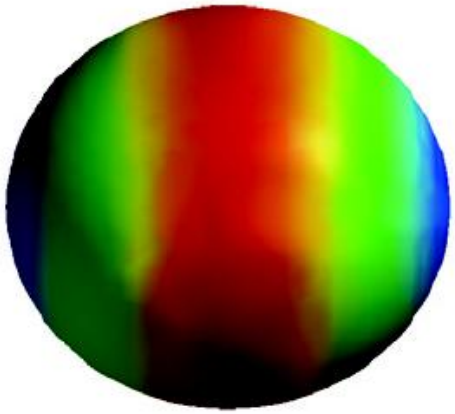


1A 1	2A 2	3B 3	4B 4	5B 5	6B 6	7B 7	8B 8	8B 9	8B 10	1B 11	2B 12	3A 13	4A 14	5A 15	6A 16	7A 17	8A 18
H 2.1																	
Li 1.0	**Be** 1.5											**B** 2.0	**C** 2.5	**N** 3.0	**O** 3.5	**F** 4.0	
Na 0.9	**Mg** 1.2											**Al** 1.5	**Si** 1.8	**P** 2.1	**S** 2.5	**Cl** 3.0	
K 0.8	**Ca** 1.0	**Sc** 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																

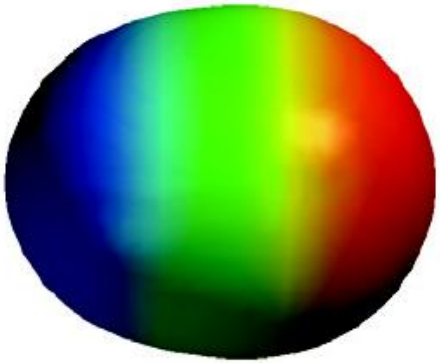
Variation in Electronegativity with Atomic Number



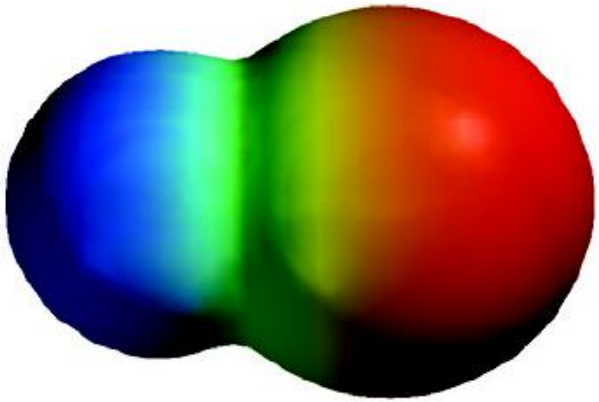
- Polar and nonpolar bonds



H_2



HF



NaF

2.1 - 2.1 = 0.0

nonpolar covalent

4.0 - 2.1 = 1.9

polar covalent

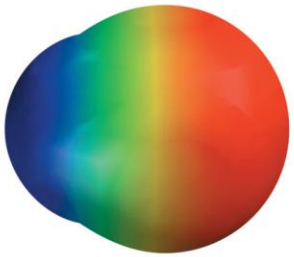
4.0 - 0.9 = 3.1

ionic

> 2.0 is ionic

Bond Polarity and Dipole Moment

F_2



HF

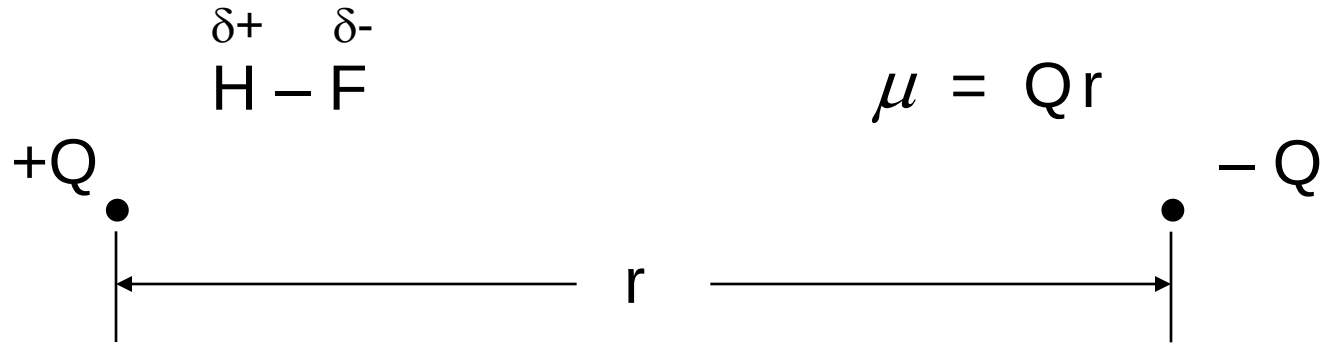
δ+ δ-

H - F

Compound	Bond Length (Å)	Electronegativity Difference	Dipole Moment (D)
HF	0.92	1.9	1.82
HCl	1.27	0.9	1.08
HBr	1.41	0.7	0.82
HI	1.61	0.4	0.44

The greater the difference in electronegativity, the ***more polar is the bond.***

- **Dipole moments and partial charges**
  - Polar bonds *often (not always)* result in polar molecules.
  - A polar molecule possesses a ***dipole.***
    - ***dipole moment (μ)*** = the quantitative measure of a dipole



SI unit: coulomb•meter (C•m)

common unit: debye (D)

$1\,D = 3.34 \times 10^{-30}\ C \cdot m$

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

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.

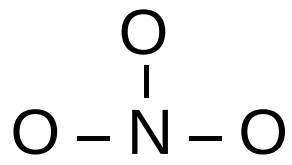
4) Complete electron octets for atoms bonded to the central atom except for hydrogen.

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.



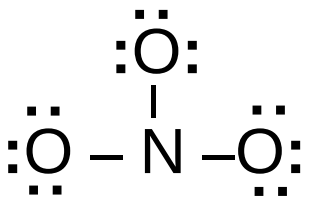
2) Sum valence electrons. Add 1 for each negative charge and subtract 1 for each positive charge.

$NO_3^- \Rightarrow (1 \times 5) + (3 \times 6) + 1 = 24$ valence e^- $\quad 24\,e^-$

3) Subtract 2 for each bond in the skeletal structure. $\quad -6\,e^-$

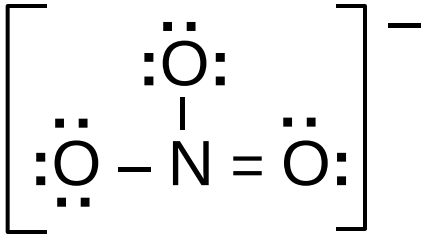
$\quad 18\,e^-$

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



5) Place extra electrons on the central atom.

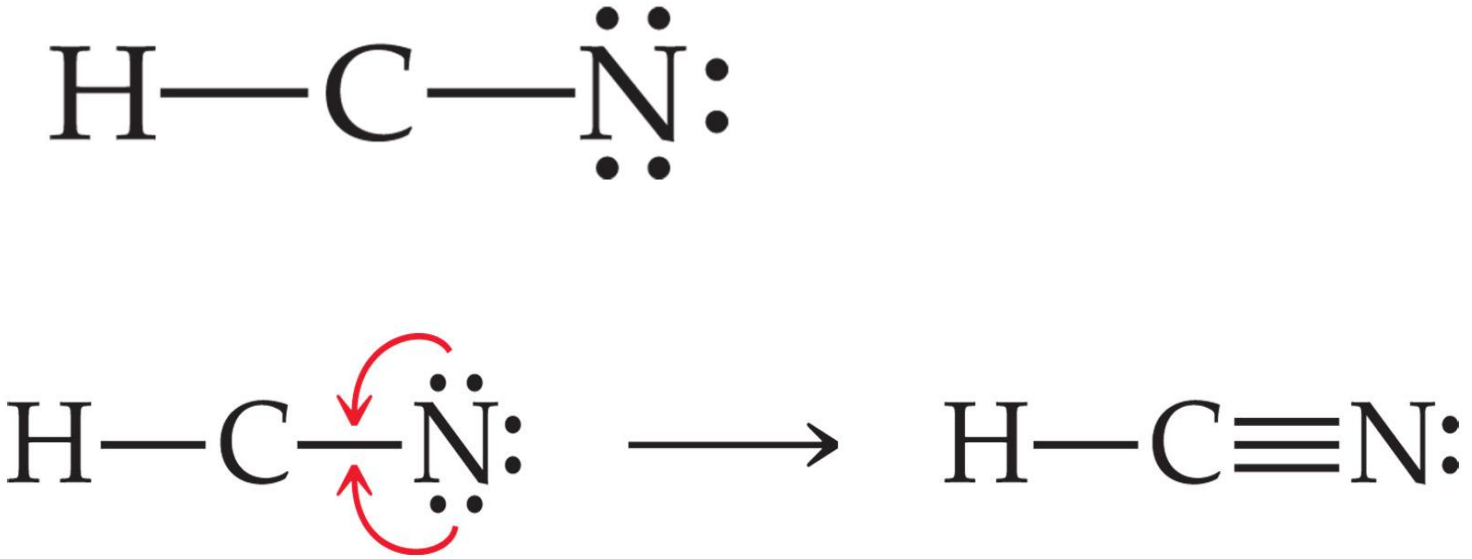
6) Add multiple bonds if atoms lack an octet.



$24\,e^-$

Example

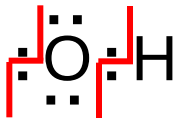
Write Lewis Structure for HCN



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.

$$\text{Formal Charge} = \text{Total valence electrons} - \text{Total non-bonding electrons} - \frac{1}{2}\left(\text{Total bonding electrons}\right)$$

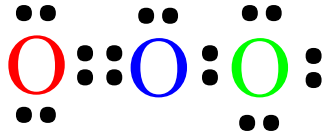
Example: H_2O = 

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.

Example: Formal charges on the atoms in ozone



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

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

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

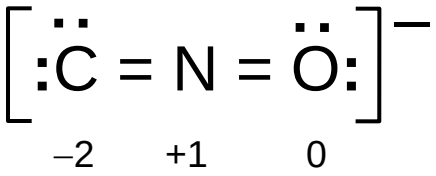
- **Formal charge guidelines**

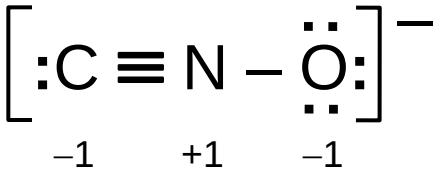
  - A Lewis structure with *no* formal charges is generally better than one with formal charges.

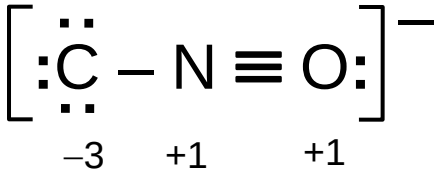
  - Small formal charges are generally better than large formal charges.

  - Negative formal charges should be on the more electronegative atom(s).

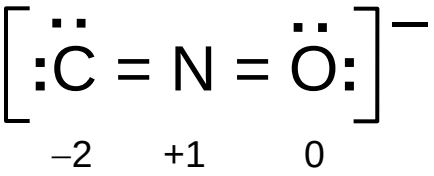
Identify the best structure for the isocyanate ion below:

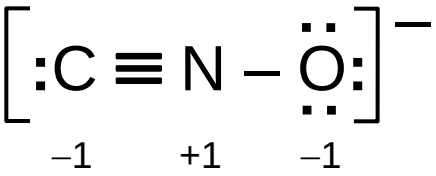
(a) 

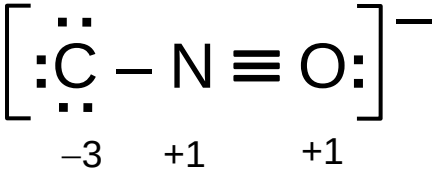
(b) 

(c) 

Identify the best structure for the isocyanate ion below:

(a) 

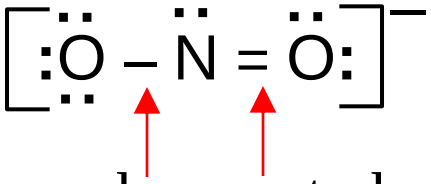
(b) 

(c) 

8.7 Resonance

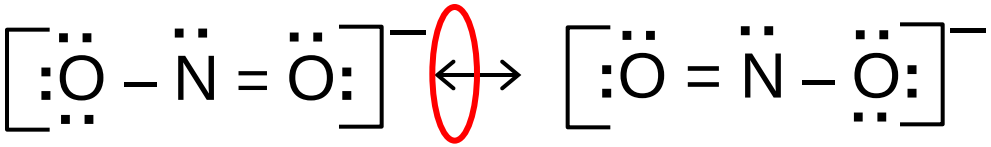
• ***Resonance*** structures are used when two or more equally valid Lewis structures can be written.

Example: NO_2



These two bonds are known to be identical.

Solution:



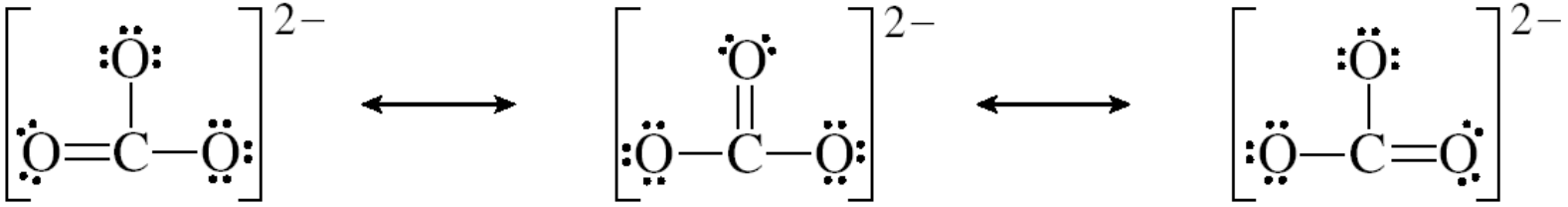
Two ***resonance structures***, their average or the ***resonance hybrid***, best describes the nitrite ion.

The double-headed arrow indicates resonance.

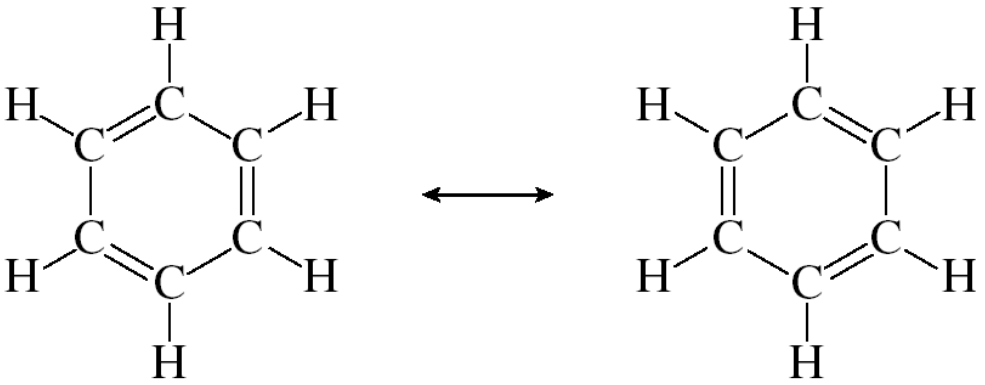
The electron pairs are not localized, but they are delocalized

Additional Examples

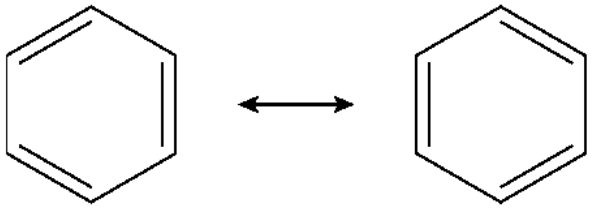
Carbonate: CO_3^{2-}



Benzene: C_6H_6



or



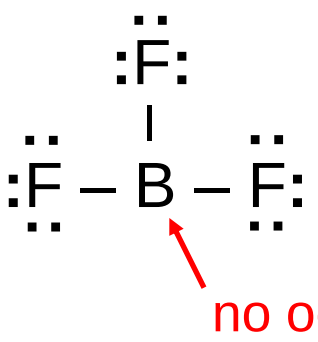
8.8 Exceptions to the Octet Rule

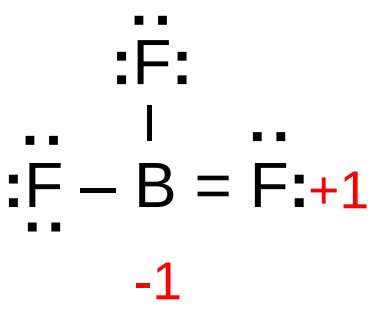
- **Exceptions to the octet rule fall into three categories:**
  - Molecules with an incomplete octet
  - Molecules with an odd number of electrons
  - Molecules with an expanded octet

- Incomplete Octets

Example: BF_3 (boron trifluoride)

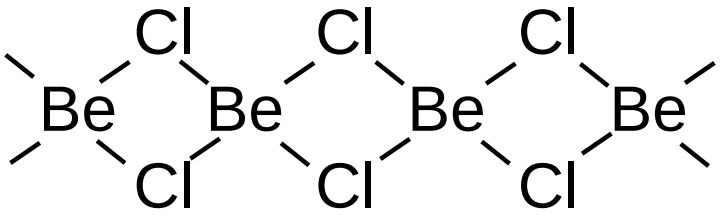
$$BF_3 \Rightarrow (1 \times 3) + (3 \times 7) = 24 \text{ val. } e^-$$





- Common with Be, B and Al compounds, but they often dimerize or polymerize.

Example:



Incomplete Octet

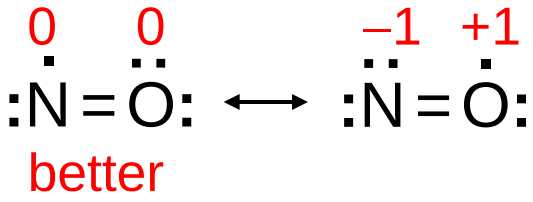
H—Be—H

$$\begin{array}{r} Be - 2e^- \\ 2H - 2x1e^- \\ \hline 4e^- \end{array}$$

- Odd Numbers of Electrons

Example: NO (nitrogen monoxide or nitric oxide)

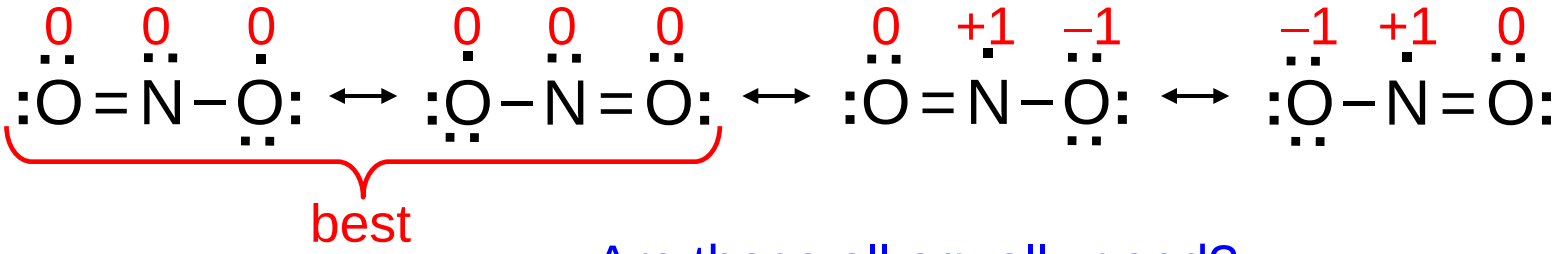
$$NO \Rightarrow (1 \times 5) + (1 \times 6) = 11 \text{ valence } e^-$$



Are these both equally good?

Example: NO_2 (nitrogen dioxide)

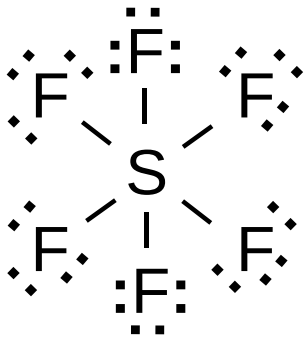
$$NO_2 \Rightarrow (1 \times 5) + (2 \times 6) = 17 \text{ val. } e^-$$



Are these all equally good?

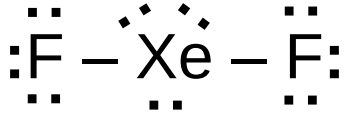
- Expanded Octet
  - Elements of the **3rd period** and beyond have ***d*-orbitals** that allow more than 8 valence electrons.

SF_6 =



48 valence e^-
(S has 12 valence electrons)

XeF_2 =



22 valence e^-
(Xe has 10 valence electrons)

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.

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

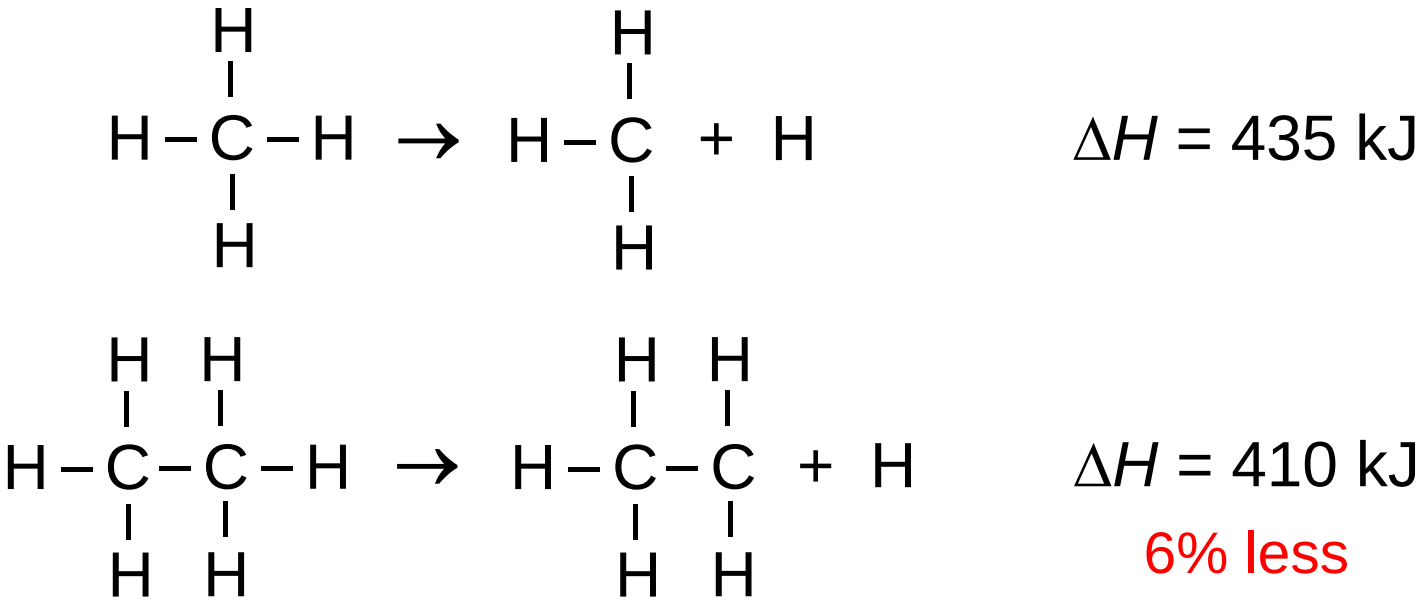
$HCl(g) \rightarrow H(g) + Cl(g) \quad \Delta H^o = 431.9\ kJ$

single bonds

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

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

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



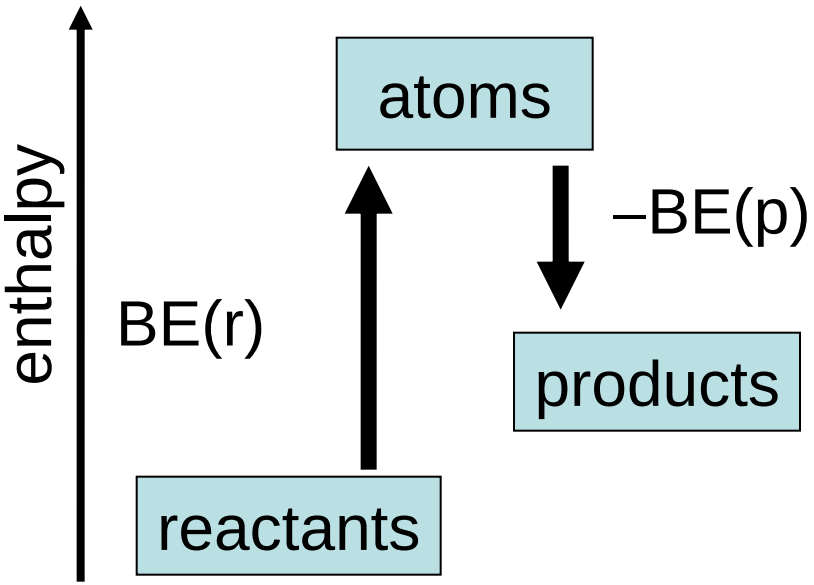
- Average bond enthalpies are used for polyatomic molecules.

  - **Provide only estimates**

Covalent bond energies and chemical reactions

- Consider stepwise decomposition of CH_4
- Each C-H bond has a different energy.
- $CH_4 \rightarrow CH_3 + H$ $\Delta H = 435$ kJ/mol
- $CH_3 \rightarrow CH_2 + H$ $\Delta H = 453$ kJ/mol
- $CH_2 \rightarrow CH + H$ $\Delta H = 425$ kJ/mol
- $CH \rightarrow C + H$ $\Delta H = 339$ kJ/mol
- Each bond is sensitive to its environment but in an unsymmetrical way
- **Average C-H bond energy = 1652/4=413kJ/mol**

- **Prediction of bond enthalpy**



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

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

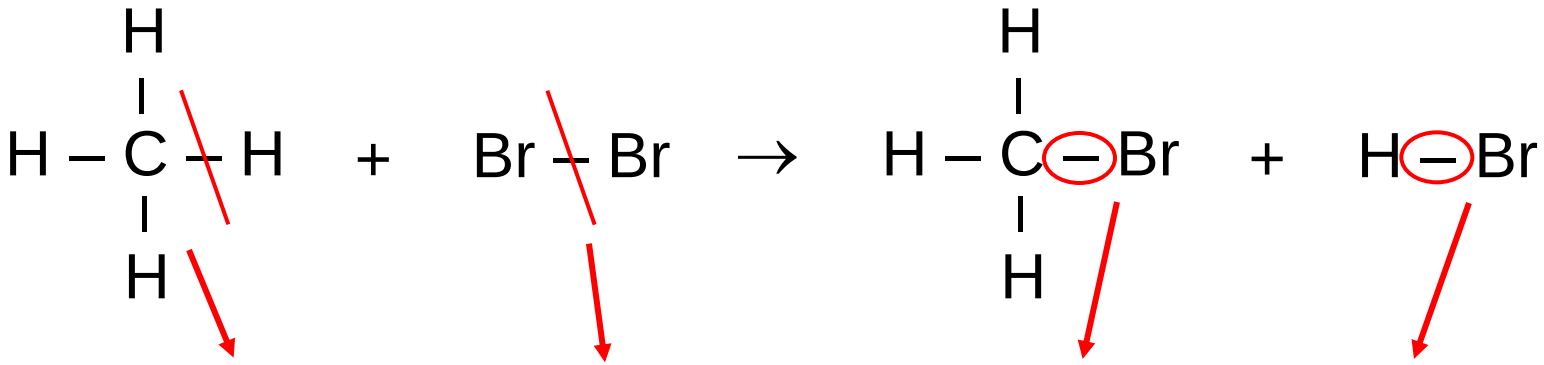
Type of bonds formed	Number of bonds formed	Bond energy (kJ/mol)	Energy change (kJ)
H—F	2	568.2	1136.4

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

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.



$$\Delta H_{rxn} = [BE(C{-}H) + BE(Br{-}Br)] - [BE(C{-}Br) + BE(H{-}Br)]$$

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

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

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

Key Points

- Electronegativity
- Dipole moment
- Drawing lewis structures
- Formal charge
- Resonance structures
- Incomplete octets
- Odd numbers of electrons
- Expanded octets
- Bond enthalpy