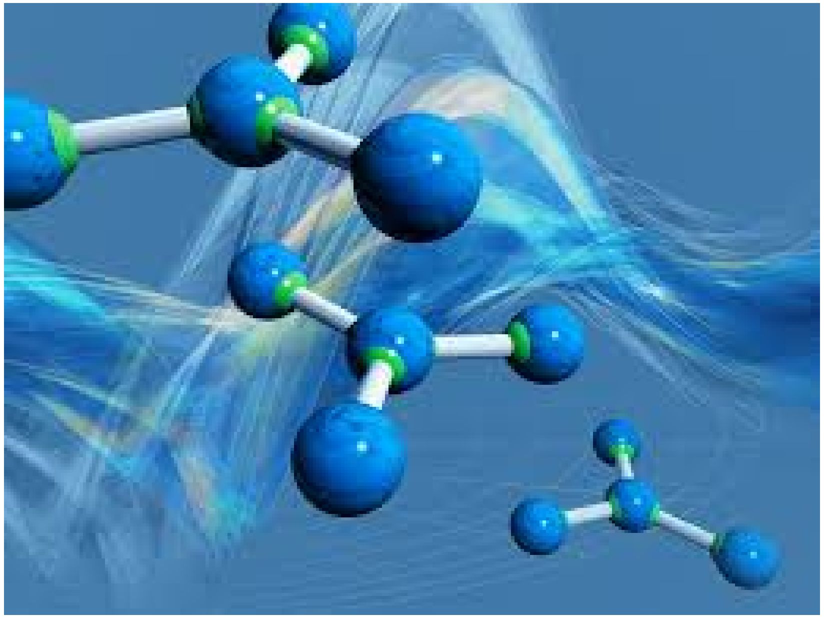
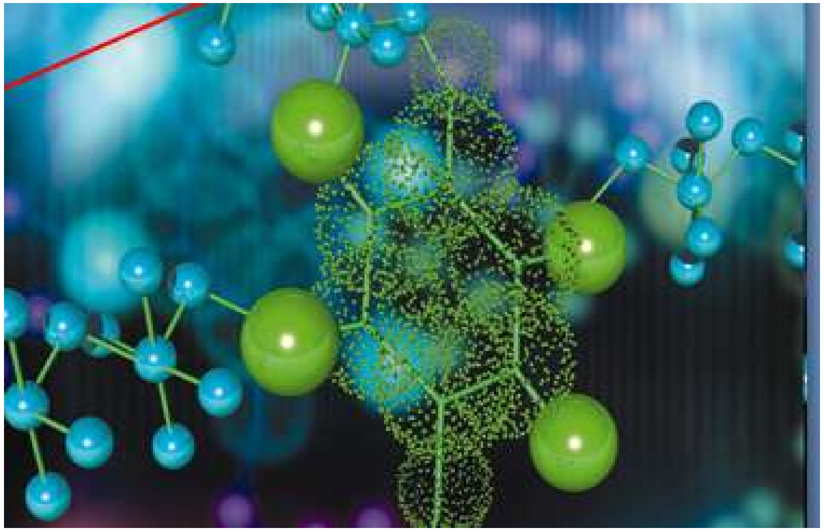




Chapter 8 – Basic Concepts of Chemical Bonding

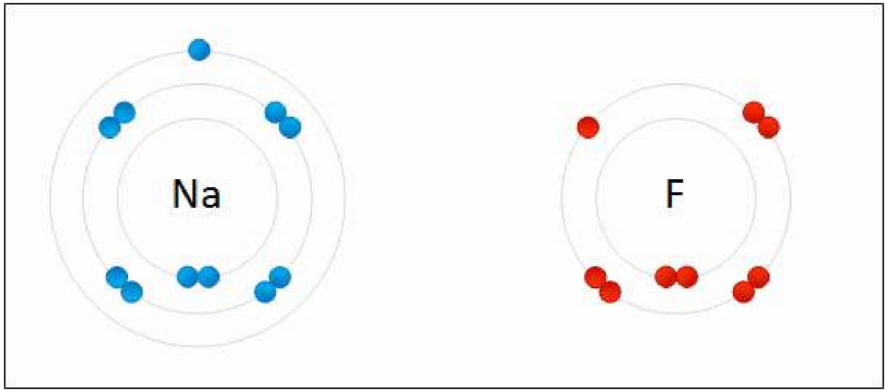
Jennie L. Borders

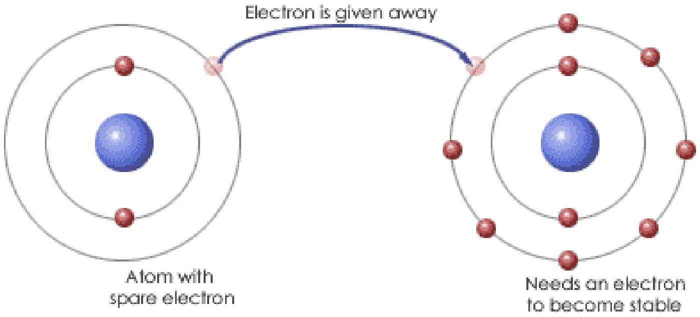
Section 8.1 – Chemical Bonds, Lewis Symbols, and the Octet Rule

- Whenever two atoms or ions are strongly attached to each other, we say there is a chemical bond between them.
- There are three general types of chemical bonds: ionic, covalent, and metallic.

Ionic Bond

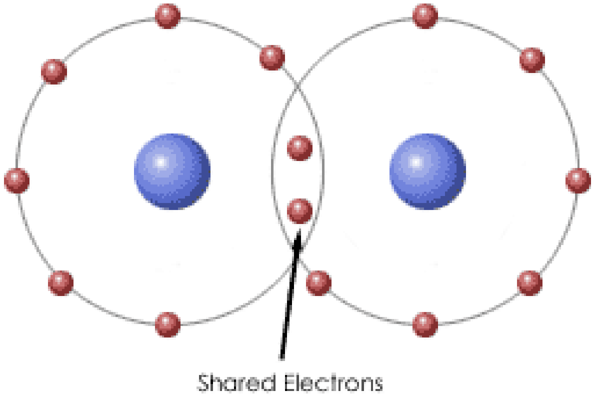
- An ionic bond is the electrostatic forces that exist between ions of opposite charge.
- Ionic bonds normally occur between a metal and a nonmetal.

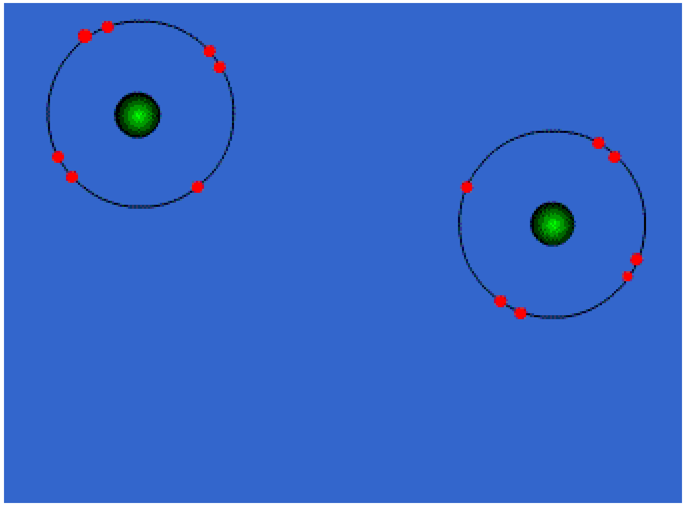




Covalent Bond

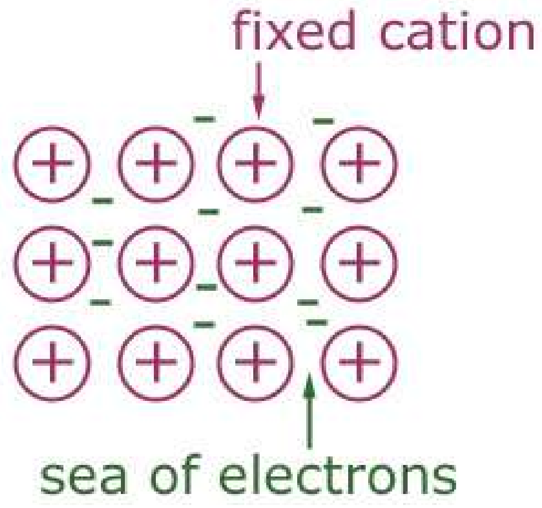
- A covalent bond results from the sharing of electrons between two atoms.
- Covalent bonds normally occur between two or more nonmetals.

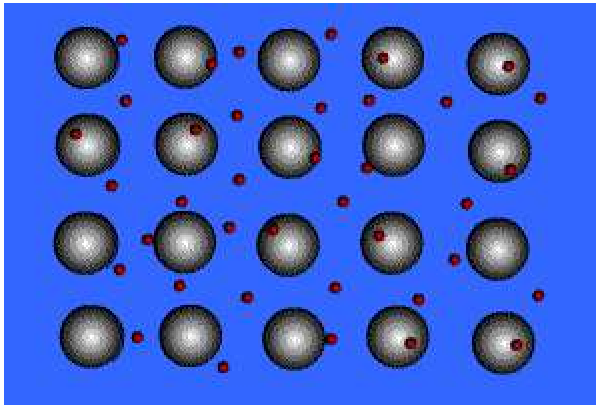




Metallic Bond

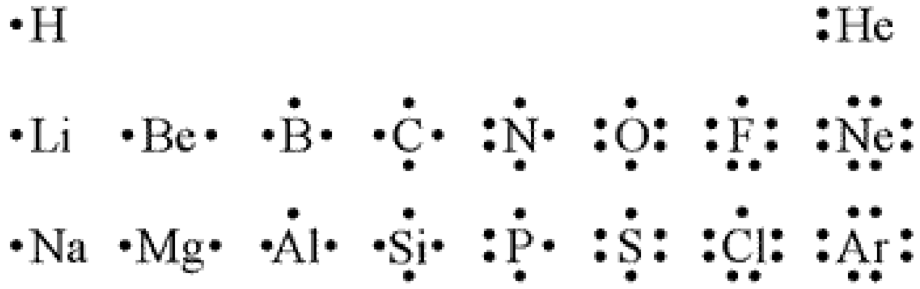
- Metallic bonds are the attractions between the positive nuclei of metal atoms and the sea of electrons.





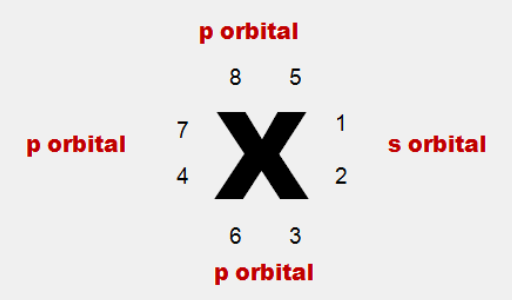
Lewis Symbols

- The electrons involved in chemical bonding are the valence electrons which are those residing in the outermost occupied shell of an atom.
- The Lewis symbol for an element consists of the chemical symbol for the element plus a dot for each valence electron.
- The number of valence electrons is the same for elements in the same group.



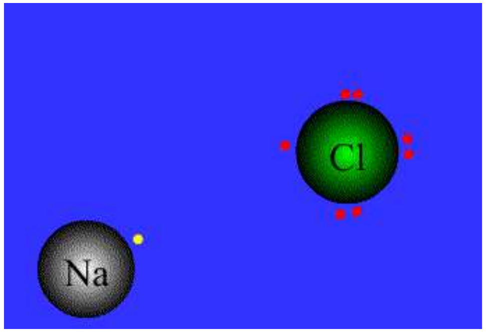
Octet Rule

- Most elements follow the octet rule which states that atoms tend to gain, lose, or share electrons until they are surrounded by eight valence electrons.
- An octet of electrons consists of full s and p subshells in an atom.
- Elements that do not follow the octet rule include hydrogen and helium. They follow the duet rule.



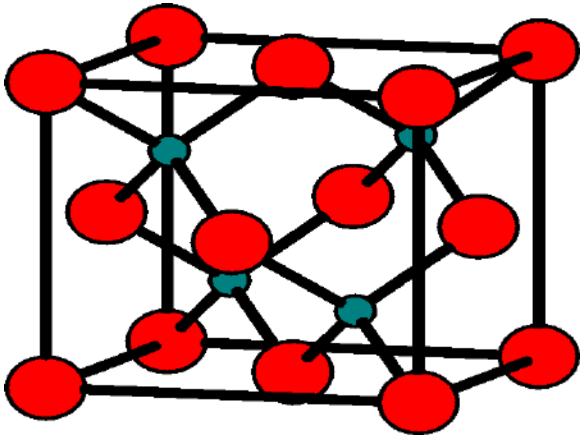
Section 8.2 – Ionic Bonding

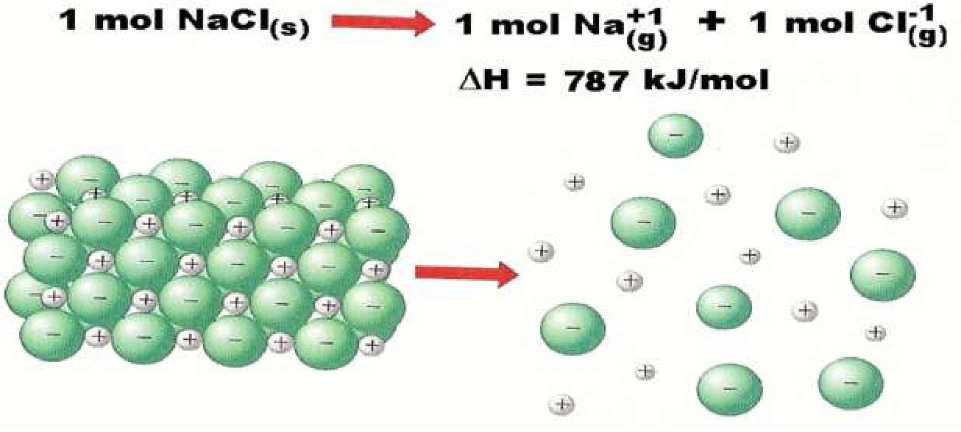
- An ionic bond involves the transfer or electrons between a cation and an anion.
- The loss of electrons is always an endothermic process.
- The gaining of electrons is generally an exothermic process.
- When ions come together, energy is released, so ionic compounds are stable.



Lattice Energy

- Lattice energy is the energy required to completely separate a mole of a solid ionic compound into its gaseous ions.
- All are large positive values, indicating that the ions are strongly attracted to one another in these solids.





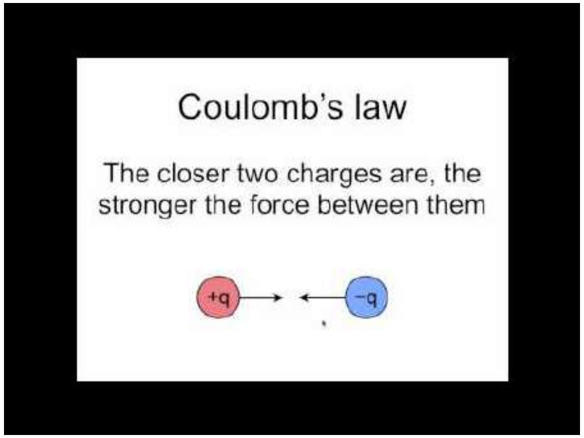
$1 \text{ mol NaCl}_{(s)} \rightarrow 1 \text{ mol Na}^{+1}_{(g)} + 1 \text{ mol Cl}^{-1}_{(g)}$

$\Delta H = 787 \text{ kJ/mol}$

Lattice Energy

- Coulomb's law is as follows:

$$E_{el} = \frac{\kappa Q_1 Q_2}{d}$$



Coulomb's law

The closer two charges are, the stronger the force between them

- Thus, for a given arrangement of ions, the lattice energy increases as the charges on the ions increase and as their radii decrease.

Sample Exercise 8.1

- Arrange the following ionic compounds in order of increasing lattice energy: NaF, CsI, and CaO.

Practice Exercise

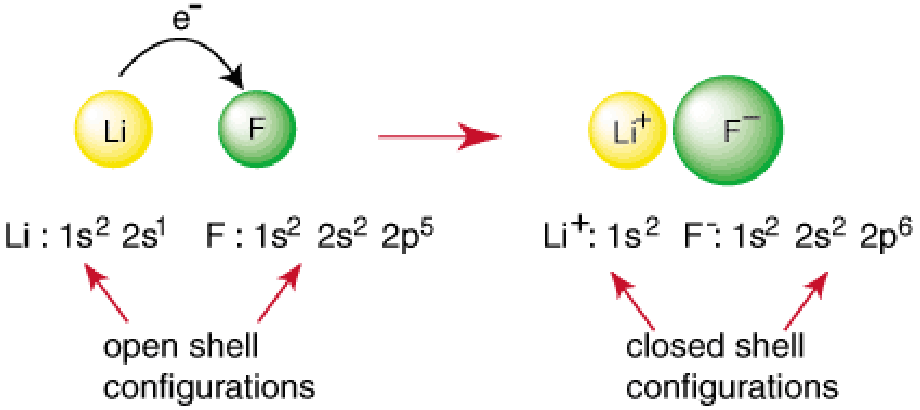
- Which substance would you expect to have the greatest lattice energy, MgF_2, CaF_2, or ZrO_2?

Ionic Bonds and Electrons

- Most atoms form ionic bonds in order to achieve noble gas configuration.

- Ex: Na = [Ne]$3s^1$, Na^+ = [Ne]

- Ex: Cl = [Ne]$3s^2 3p^5$, Cl^- = [Ar]



Sample Exercise 8.2

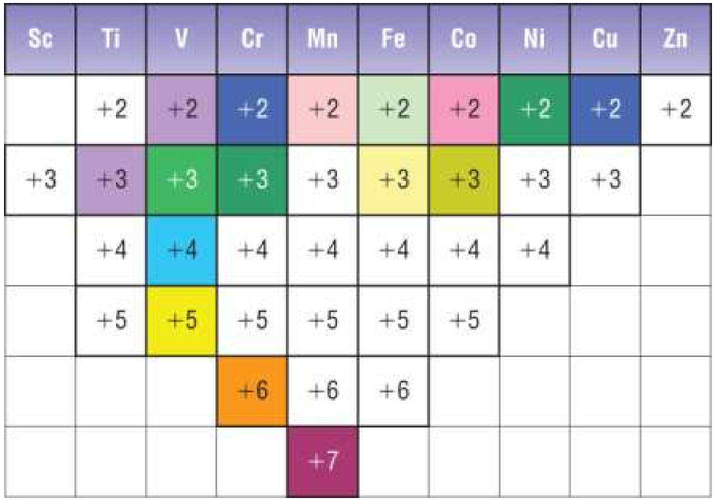
- Predict the ion generally formed by
  - a. Sr
  - b. S
  - c. Al

Practice Exercise

- Predict the charges on the ions formed when magnesium reacts with nitrogen.

Transition Metal Ions

- Since ionization energies increase rapidly for each successive electron removed, the lattice energies of ionic compounds are generally large enough to compensate for the loss of up to 3 electrons.
- This means that charges above 3+ are uncommon.



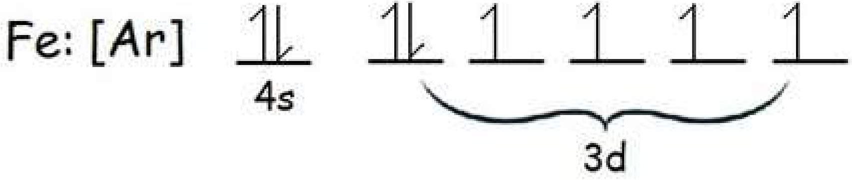
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	+2	+2	+2	+2	+2	+2	+2	+2	+2
+3	+3	+3	+3	+3	+3	+3	+3	+3	
	+4	+4	+4	+4	+4	+4	+4		
	+5	+5	+5	+5	+5	+5			
			+6	+6	+6				
				+7					

Transition Metal Ions

- Since transition metals have d sublevel electrons, they do not generally form ions that have a noble gas configuration.
- When forming ions, transition metals lose the valence-shell s electrons first, then as many d electrons as are required to reach the charge of the ion.
- Ex: Fe = [Ar]$3d^6 4s^2$

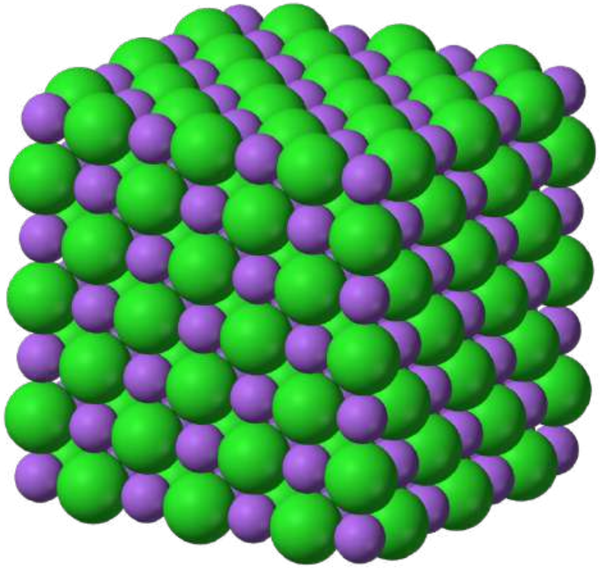
  Fe^{2+} = [Ar]$3d^6$

  Fe^{3+} = [Ar]$3d^5$



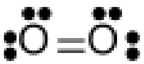
Section 8.3 – Covalent Bonding

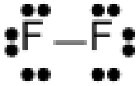
- Ionic compounds tend to be brittle, have high melting points, are crystalline, and can be cleaved (break with a smooth surface).

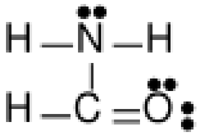


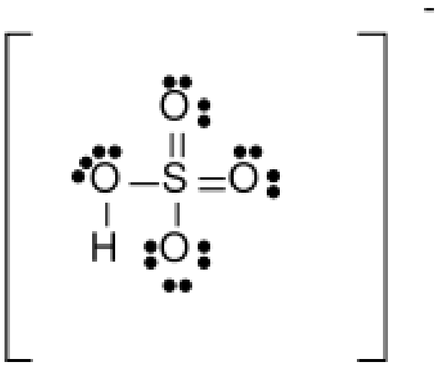
Lewis Structures

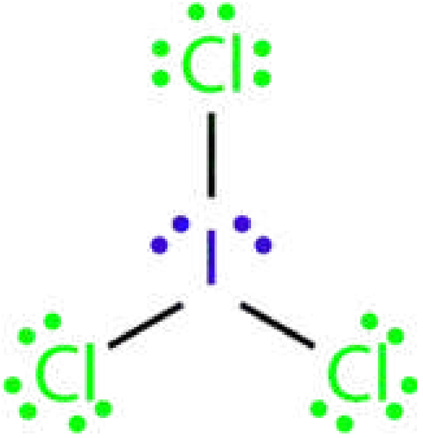
- The formation of covalent bonds can be represented using Lewis symbols.
- The unpaired electrons are drawn as dots, and the bonding electrons are drawn as a dash.











Sample Exercise 8.3

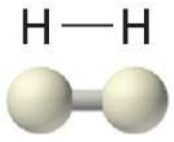
- Predict the formula of the stable binary compound formed when nitrogen reacts with fluorine, and draw its Lewis structure.

Practice Exercise

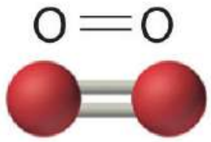
- Compare the Lewis symbol for neon with the Lewis structure for methane, CH_4. In what important way are the electron arrangements about neon and carbon alike? In what important respect are they different?

Multiple Bonds

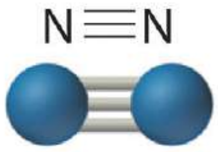
- A single bond consists of 1 pair of electrons.
- A double bond consists of 2 pairs of electrons.
- A triple bond consists of 3 pairs of electrons.



Single bond



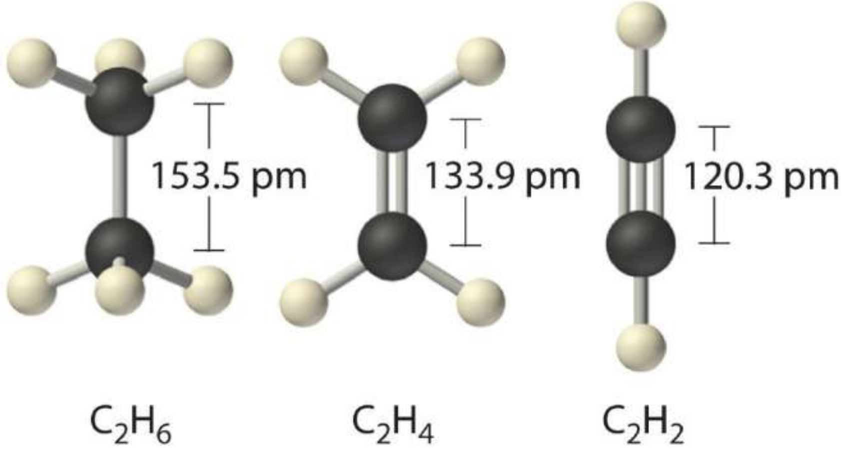
Double bond



Triple bond

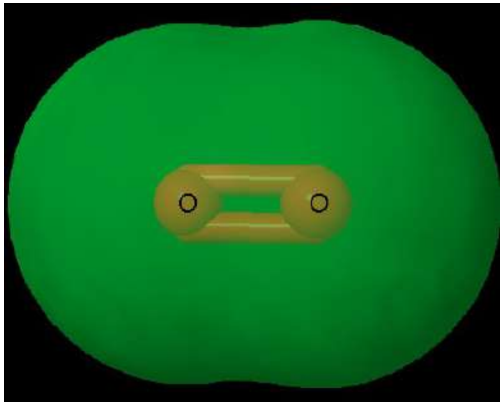
Bond Length

- The distance between the nuclei of the atoms involve in a bond is called the bond length for the bond.
- As a general rule, the distance between bonded atoms decreases as the number of shared electrons increases.



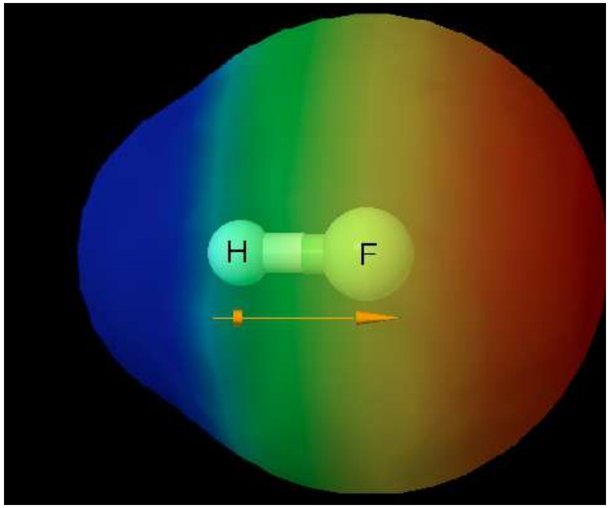
Section 8.4 – Bond Polarity and Electronegativity

- The concept of bond polarity helps describe the sharing of electrons between atoms.
- When two identical atoms bond, the electron pairs must be shared equally. (Ex. Cl_2 and H_2)
- A nonpolar covalent bond is one in which the electrons are shared equally.



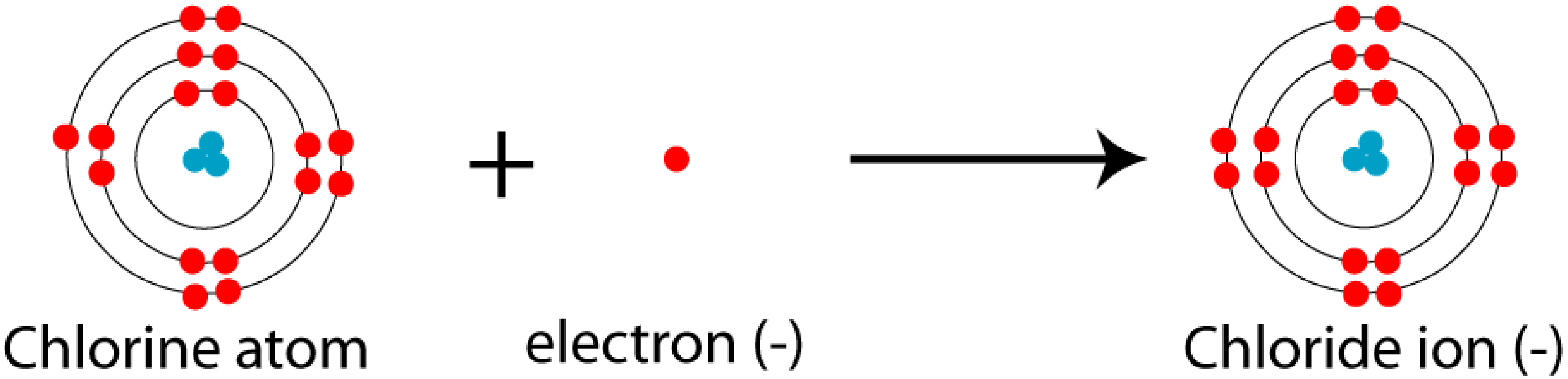
Polar Bond

- In a polar covalent bond, one of the atoms exerts a greater attraction for the bonding electrons than the other.
- If the difference in relative ability to attract electrons is large enough, an ionic bond is formed.



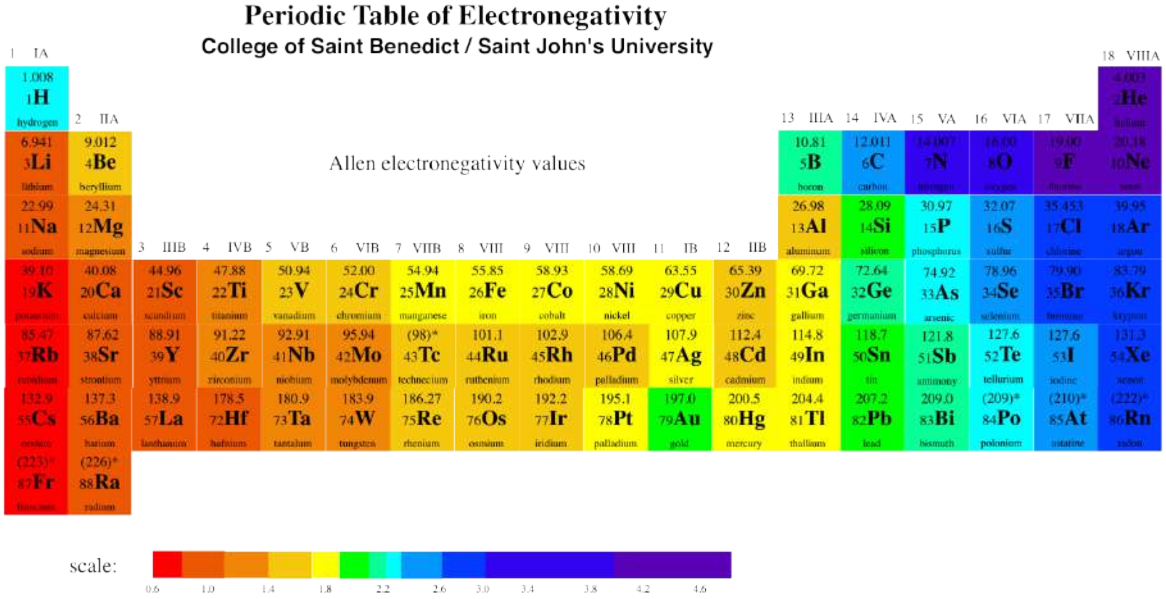
Electronegativity

- Electronegativity is the ability of an atom in a molecule to attract electrons to itself.



Electronegativity Trends

- When moving across a period there, is generally a steady increase in electronegativity.
- When moving down a group, there is a decrease in electronegativity.



Periodic Table of Electronegativity

College of Saint Benedict / Saint John's University

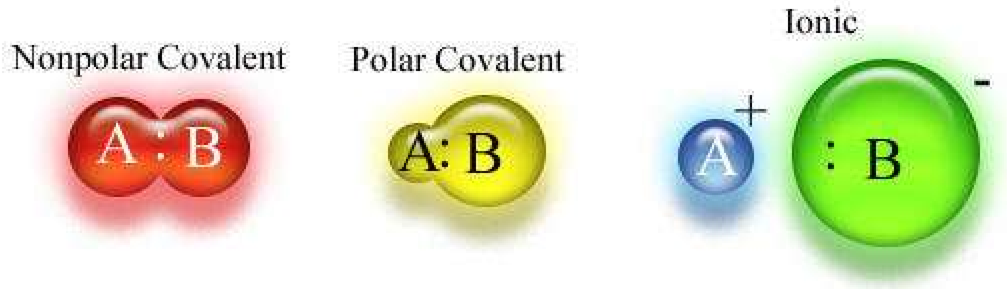
Allen electronegativity values

1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIII	9 VIII	10 VIII	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1.008 1**H** hydrogen																	4.003 2**He** helium
6.941 3**Li** lithium	9.012 4**Be** beryllium											10.81 5**B** hocon	12.011 6**C** carbon	14.007 7**N** nitrogen	16.00 8**O** oxygen	19.00 9**F** fluorine	20.18 10**Ne** neon
22.99 11**Na** sodium	24.31 12**Mg** magnesium											26.98 13**Al** aluminum	28.09 14**Si** silicon	30.97 15**P** phosphorus	32.07 16**S** sulfur	35.453 17**Cl** chlorine	39.95 18**Ar** argon
39.10 19**K** potassium	40.08 20**Ca** calcium	44.96 21**Sc** scandium	47.88 22**Ti** titanium	50.94 23**V** vanadium	52.00 24**Cr** chromium	54.94 25**Mn** manganese	55.85 26**Fe** iron	58.93 27**Co** cobalt	58.69 28**Ni** nickel	63.55 29**Cu** copper	65.39 30**Zn** zinc	69.72 31**Ga** gallium	72.64 32**Ge** germanium	74.92 33**As** arsenic	78.96 34**Se** selenium	79.90 35**Br** bromine	83.79 36**Kr** krypton
85.47 37**Rb** rubidium	87.62 38**Sr** strontium	88.91 39**Y** yttrium	91.22 40**Zr** zirconium	92.91 41**Nb** niobium	95.94 42**Mo** molybdenum	(98)* 43**Tc** technecium	101.1 44**Ru** ruthenium	102.9 45**Rh** rhodium	106.4 46**Pd** palladium	107.9 47**Ag** silver	112.4 48**Cd** cadmium	114.8 49**In** indium	118.7 50**Sn** tin	121.8 51**Sb** antimony	127.6 52**Te** tellurium	127.6 53**I** iodine	131.3 54**Xe** xenon
132.9 55**Cs** cesium	137.3 56**Ba** barium	138.9 57**La** lanthanum	178.5 72**Hf** hafnium	180.9 73**Ta** tantalum	183.9 74**W** tungsten	186.27 75**Re** rhenium	190.2 76**Os** osmium	192.2 77**Ir** iridium	195.1 78**Pt** palladium	197.0 79**Au** gold	200.5 80**Hg** mercury	204.4 81**Tl** thallium	207.2 82**Pb** lead	209.0 83**Bi** bismuth	(209)* 84**Po** polonium	(210)* 85**At** astatine	(222)* 86**Rn** radon
(223)* 87**Fr** francium	(226)* 88**Ra** radium																

Bond Polarity

- The greater the difference in electronegativity between two atoms, the more polar their bond.

Bond	Electronegativity Difference
nonpolar	<0.5
polar	0.5 – 2.0
ionic	>2



Sample Exercise 8.4

- In each case, which bond is more polar? Indicate in each case which atom has the partial negative charge.

a. B-Cl or C-Cl

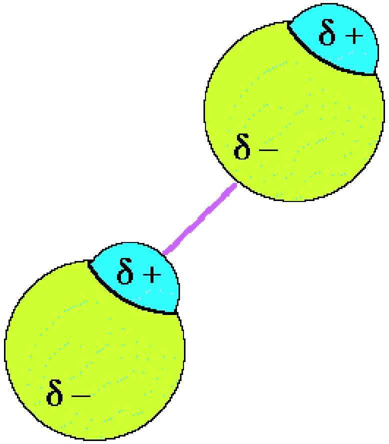
b. P-F or P-Cl

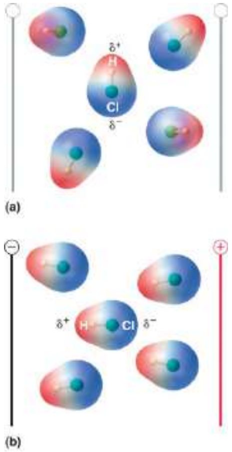
Practice Exercise

- Which of the following bonds is most polar:
  S-Cl, S-Br, Se-Cl, or Se-Br?

Polar Molecules

- A molecule such as HF, in which there is a partially positive and partially negative end, is called a polar molecule.
- Polar molecules align themselves with the negative end of the molecule and the positive end of another molecule attracting each other.





Dipole Moment

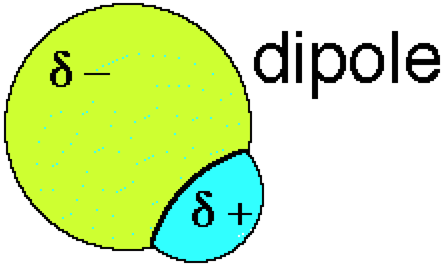
- Whenever a distance separates two electrical charges of equal magnitude but opposite sign, a dipole is established.
- The quantitative measure of the magnitude of a dipole is called the dipole moment (μ).

$$\mu = Qr$$

μ = dipole moment (debyes (D) = 3.34×10^{-30} coulomb-meters)

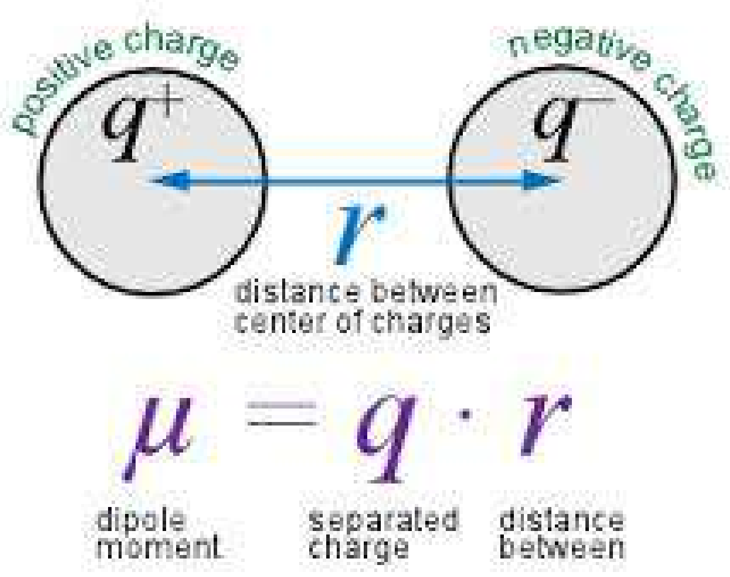
Q = charge (units of 1.60×10^{-19} C)

r = distance (m)



Dipole Moment

- The dipole moment increases as the magnitude of charge that is separated increases and as the distance between the charges increases.



Sample Exercise 8.5

- The bond length in the HCl molecule is 1.27Å.

a. Calculate the dipole moment, in debyes, that would result if the charges on the H and Cl atoms were 1+ and 1-, respectively.

b. The experimentally measured dipole moment of $HCl_{(g)}$ is 1.08D. What magnitude of charge, in units of e, on the H and Cl atoms would lead to this dipole moment?

Practice Exercise

- The dipole moment of chlorine monofluoride, $ClF_{(g)}$, is 0.88D. The bond length of the molecule is 1.63Å.

a. Which atom is expected to have the partial negative charge?

b. What is the charge on that atom, in units of e?

Bond Length

- As we proceed from HF to HI, the electronegativity difference decreases and the bond length increases.

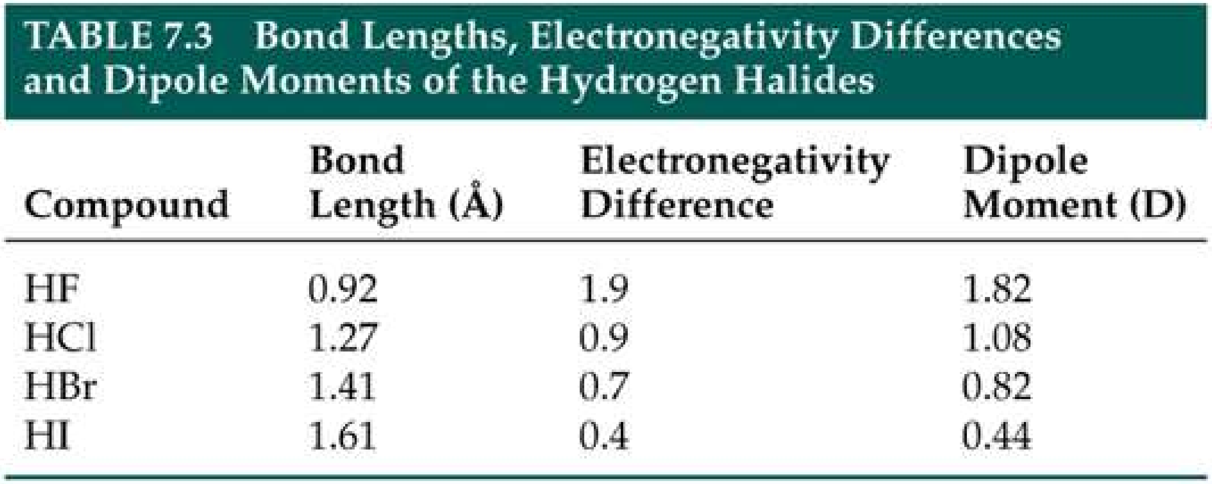
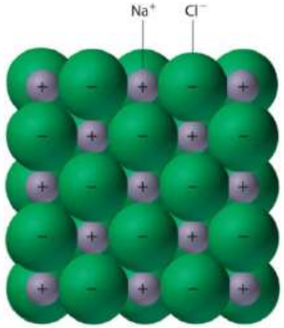


TABLE 7.3 Bond Lengths, Electronegativity Differences and Dipole Moments of the Hydrogen Halides

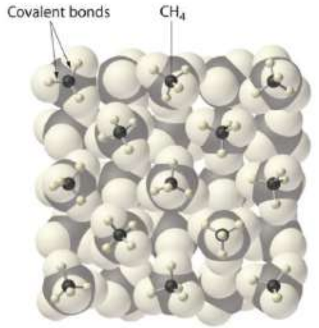
Compound	Bond Length (Å)	Electronegativity Difference	Dipole Moment (D)
HF	0.92	1.9	1.82
HCl	1.27	0.9	1.08
HBr	1.41	0.7	0.82
HI	1.61	0.4	0.44

Molecular Compounds

- When covalent bonding is dominant, most compounds exist as molecules, have low melting and boiling points, and exhibit nonelectrolyte behavior.
- When ionic bonding is dominant, most compounds are brittle solids, have a crystal lattice structure, have high melting points, and exhibit strong electrolyte behavior.



(a) Ionic solid: strong electrostatic interactions



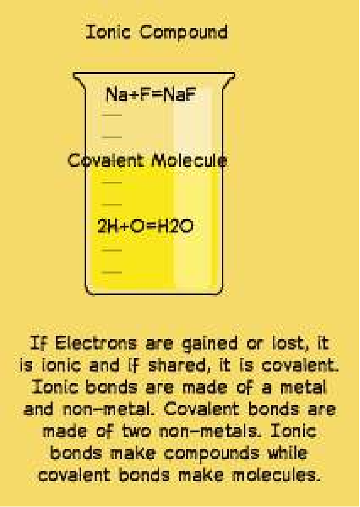
(b) Molecular solid: weak intermolecular forces

Ionic or Covalent?

- A simple approach to decide whether a bond is ionic or covalent is to assume that a bond between a metal and a nonmetal is ionic and a bond between two nonmetals is covalent.
- The problem with this approach is that there are many exceptions.

Ex: $SnCl_4$ = metal and nonmetal

= covalent

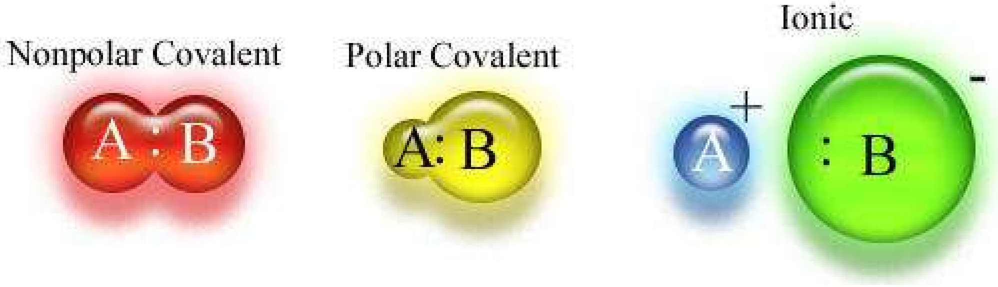


If Electrons are gained or lost, it is ionic and if shared, it is covalent. Ionic bonds are made of a metal and non-metal. Covalent bonds are made of two non-metals. Ionic bonds make compounds while covalent bonds make molecules.

Ionic or Covalent?

- Another approach to tell if a bond is ionic or covalent is to compare the electronegativity difference between the two bonded atoms.

Bond	Electronegativity Difference
Ionic	>2
Polar	0.5 – 2.0
Nonpolar	>0.5



Transition Metals

- The problem with this method is that there is no difference in the electronegativity values for the transition metals that have multiple charges.
- The rule of thumb is that the higher the charge (+4 or higher) on a transition metal, the more covalent the bond.

Section 8.5 – Drawing Lewis Structures

- Rules for drawing Lewis dot structures:

1. Add up valence electrons from all atoms.

2. Write the symbols for the atoms to show which atoms are attached to which, and connect them with a single bond.

**To know how the atoms will be arranged, use the following hints.

Sometimes the formula is written in the order that the atoms are bonded. Ex: HCN.

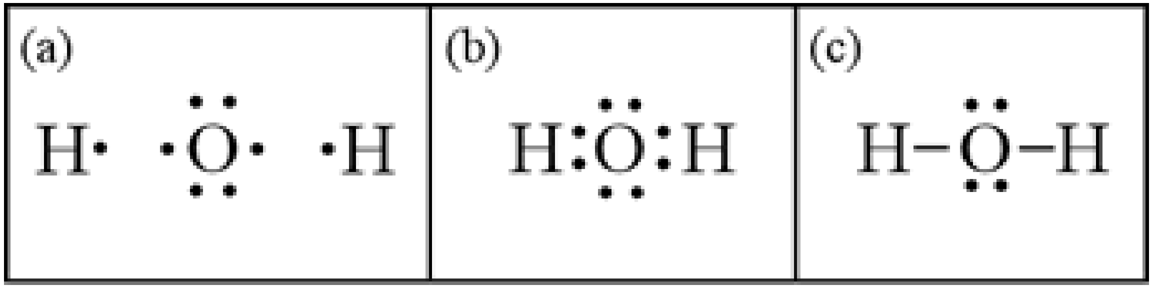
If there is a single atom, it is usually in the middle. Ex: SO4^{2-}.

Rules for Lewis Structures

3. Complete octets around all atoms bonded to the central atom. (Exception: Hydrogen only needs 1 bond so no extra electrons should ever be added.)

4. Place any leftover electrons on the central atom.

5. If there are not enough electrons to give the central atom an octet, try multiple bonds.



Sample Exercise 8.6

- Draw the Lewis structure for phosphorus trichloride, PCl_3.

Practice Exercise

- How many valence electrons should appear in the Lewis structure for CH_2Cl_2?

- Draw the Lewis structure.

Sample Exercise 8.7

- Draw the Lewis structure for HCN.

Practice Exercise

- Draw the Lewis structure for

  a. NO^+ ion

  b. C_2H_4

Sample Exercise 8.8

- Draw the Lewis structure for the BrO_3^- ion.

Practice Exercise

- Draw the Lewis structure for

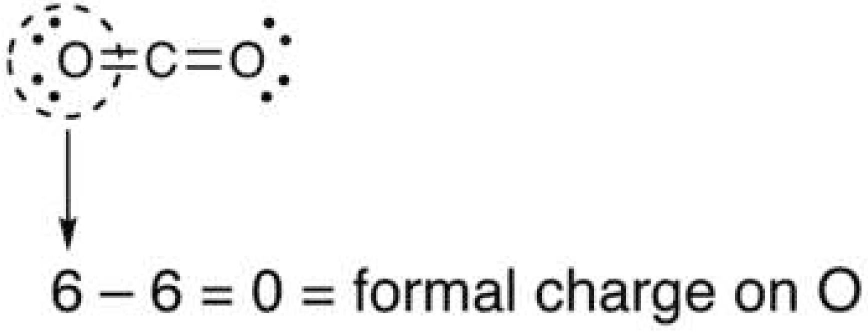
  a. ClO_2^- ion

  b. PO_4^{3-} ion

Formal Charge

- The formal charge of an atom in a molecule is the charge the atom would have if all the atoms in the molecule had the same electronegativity. (**Remember that formal charges are not real charges!)

Formal charge = valence electrons – electrons in Lewis structure



Formal Charge

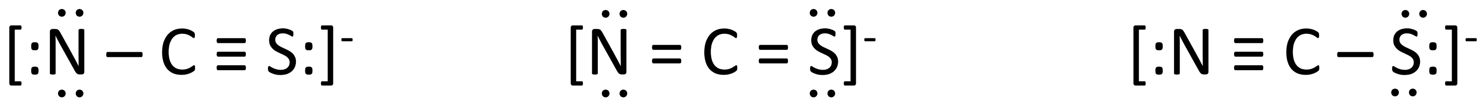
- When more than one Lewis structure can be drawn for a molecule, formal charges can be used to pick the most accepted structure.

1. We generally choose the Lewis structure in which the atoms bear formal charges closest to zero.
2. We generally choose the Lewis structure in which any negative charges reside on the more electronegative atoms.

	O	C	O	O	C	O
valence e⁻:	6	4	6	6	4	6
−(e⁻ assigned to atom):	6	4	6	7	4	5
formal charge:	0	0	0	−1	0	+1

Sample Exercise 8.9

- The following are three possible Lewis structures for the thiocyanate ion, NCS^-:
  a. Determine the formal charges of the atoms in each structure.



$[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}} - C \equiv S:]^-$ $[\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}} = C = \overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}]^-$ $[:N \equiv C - \overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}:]^-$

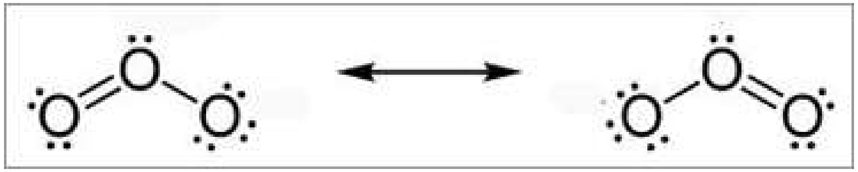
b. Which is the preferred structure?

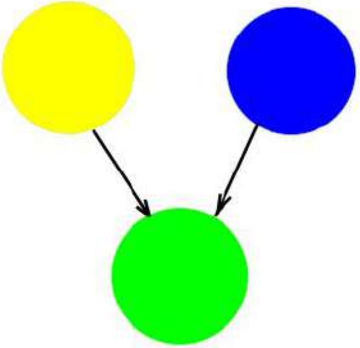
Practice Exercise

The cyanate ion (NCO^-) has three possible Lewis structures. Draw all three Lewis structures, label the formal charges on the atoms, and indicate the preferred structure.

Section 8.6 – Resonance Structures

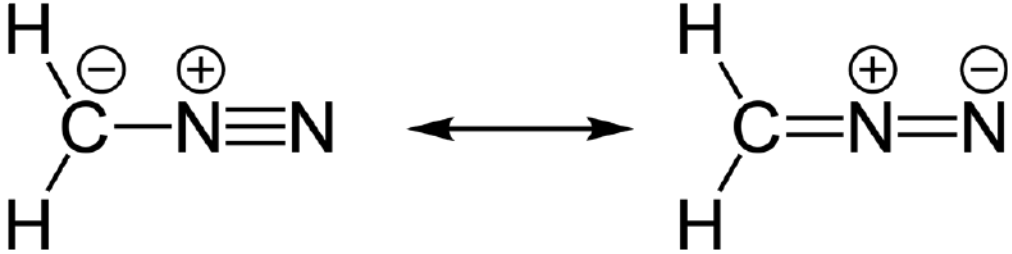
- Resonance structures in which the position of the atoms are the same but the placement of the electrons is different.
- Neither structure is correct on its own and the structure does not oscillate between the two.
- The true structure is a hybrid of the two structures because experimental evidences shows that the O-O bonds in O_3 are of equal length.





Resonance Structures

- In writing resonance structures, the same atoms are bonded to each other, so that the only difference is in the arrangement of the electrons.
- The resonance structures are separated by a double-headed arrow. (←→)



Sample Exercise 8.10

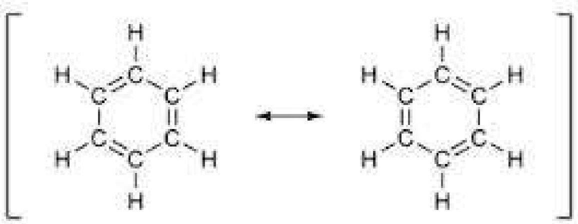
- Which is predicted to have the shorter sulfur-oxygen bonds, SO_3 or SO_3^{2-}?

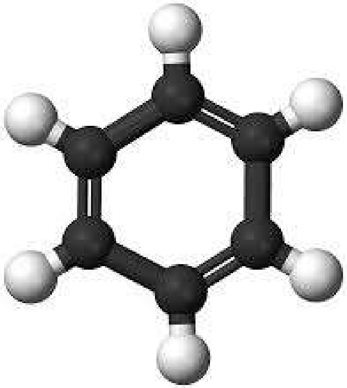
Practice Exercise

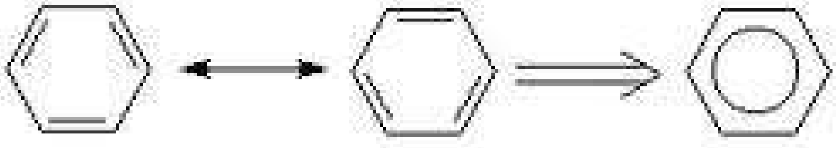
- Draw two equivalent resonance structures for the formate ion, HCO_2^-.

Resonance of Benzene

- Benzene is an aromatic (ring) organic molecule with the formula C_6H_6.
- The resonance of benzene is represented in many ways.

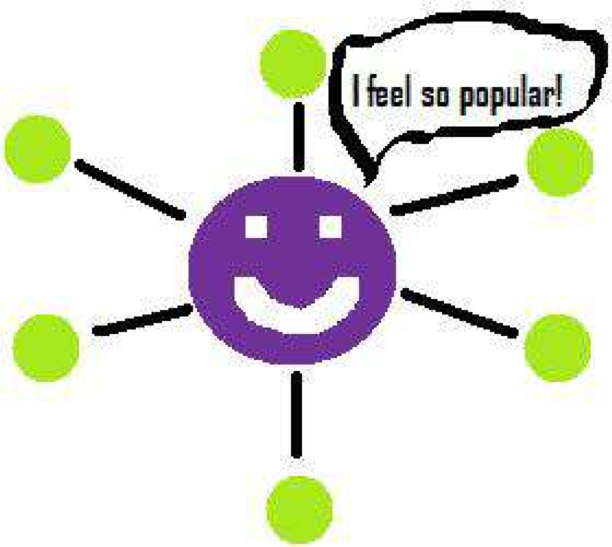


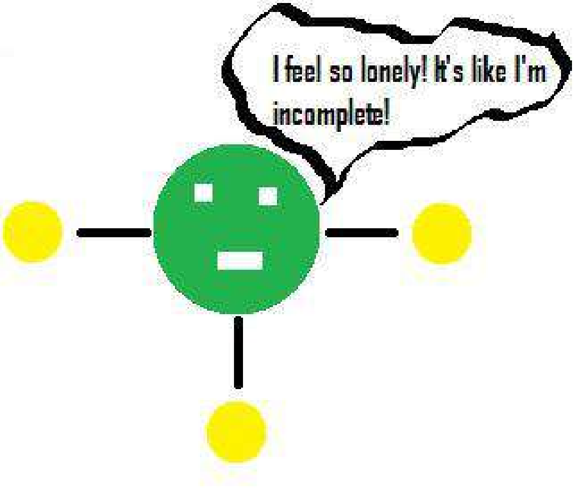




Section 8.7 – Exceptions to the Octet Rule

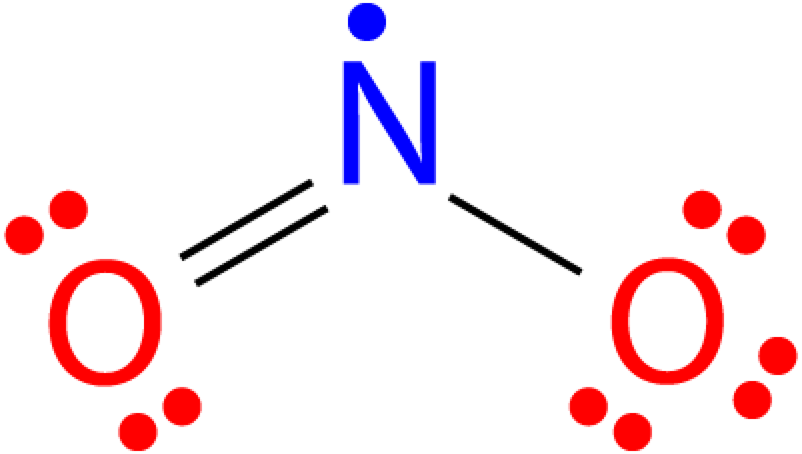
- There are 3 main categories of exceptions to the octet rule:
  1. Odd number of electrons
  2. Less than an octet
  3. More than an octet





Odd Number of Electrons

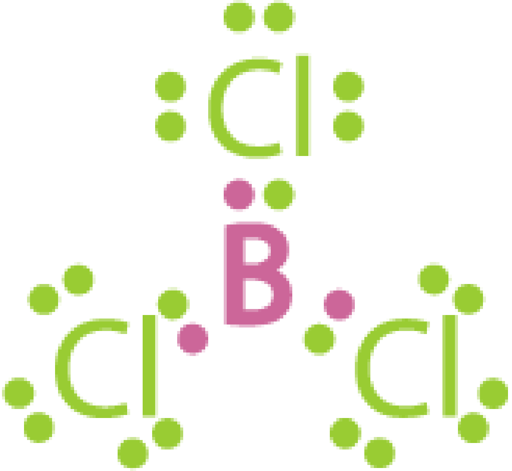
- When an odd number of electrons occurs, the central atom usually gets the unpaired electron.
- If there is no central atom, formal charges can be used to pick the correct structure.



Less than an Octet

- Molecules with less than an octet normally occur with boron and beryllium.

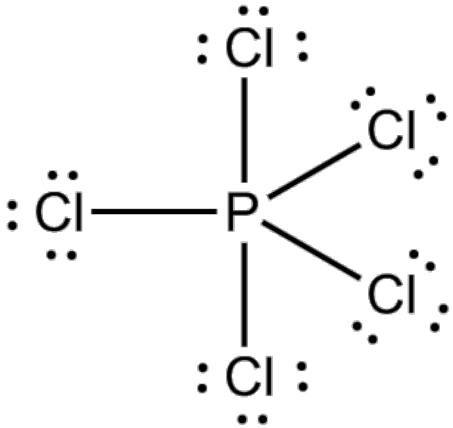
$BeCl_2$

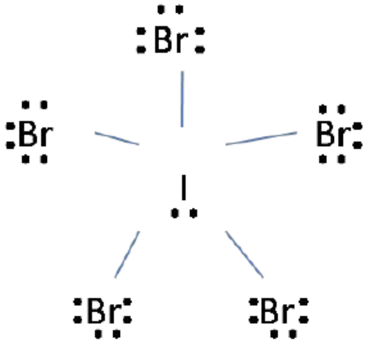


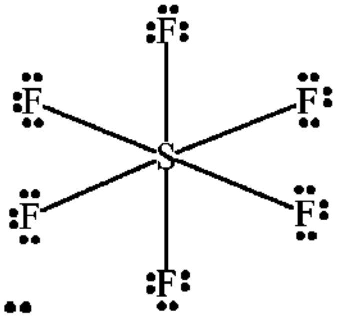
BCl_3

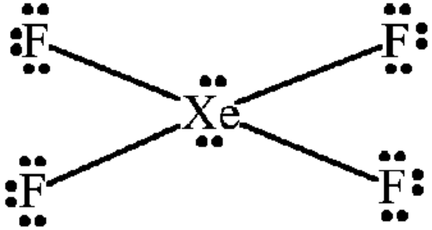
More than an Octet

- Molecules with more than an octet can only occur for atoms in the third period and beyond because of the d orbitals.
- Common elements that have more than an octet are S, P, As, some halogens, and some noble gases.









Sample Exercise 8.11

- Draw the Lewis structure for ICl_4^-.

Practice Exercise

a. Which of the following atoms is never found with more than an octet of valence electrons around it: S, C, P, or Br?

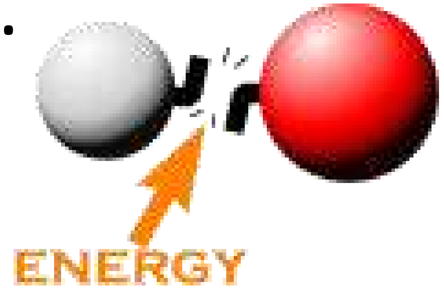
b. Draw the Lewis structure for XeF_2.

Multiple Structures

- In general, a Lewis dot structure where the octet rule is satisfied without using multiple bonds will be preferred. Ex: PO_4^{3-}

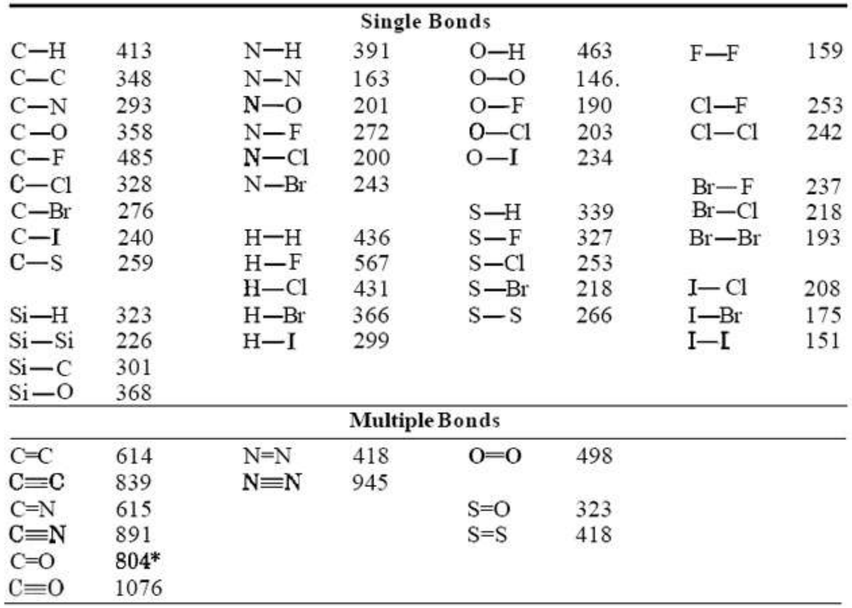
Section 8.8 – Strengths of Covalent Bonds

- The stability of a molecule is related to the strengths of the covalent bonds it contains.
- The strength of a covalent bond between two atoms is determined by the energy required to break that bond.
- The bond enthalpy is the enthalpy change, ΔH, for the breaking of a particular bond in one mole of a gaseous substance.



Bond Enthalpy

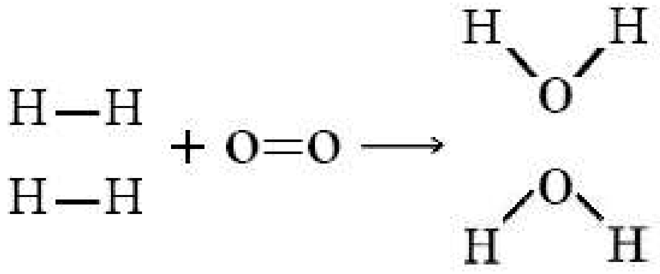
- We use the designation D(bond type) to represent the bond enthalpies.
- When molecules contain multiple identical bonds, then we use the average bond enthalpy.



Single Bonds							
C—H	413	N—H	391	O—H	463	F—F	159
C—C	348	N—N	163	O—O	146.		
C—N	293	N—O	201	O—F	190	Cl—F	253
C—O	358	N—F	272	O—Cl	203	Cl—Cl	242
C—F	485	N—Cl	200	O—I	234		
C—Cl	328	N—Br	243			Br—F	237
C—Br	276			S—H	339	Br—Cl	218
C—I	240	H—H	436	S—F	327	Br—Br	193
C—S	259	H—F	567	S—Cl	253		
		H—Cl	431	S—Br	218	I—Cl	208
Si—H	323	H—Br	366	S—S	266	I—Br	175
Si—Si	226	H—I	299			I—I	151
Si—C	301						
Si—O	368						
Multiple Bonds							
C=C	614	N=N	418	O=O	498		
C≡C	839	N≡N	945				
C=N	615			S=O	323		
C≡N	891			S=S	418		
C=O	804*						
C≡O	1076						

Bond Enthalpy

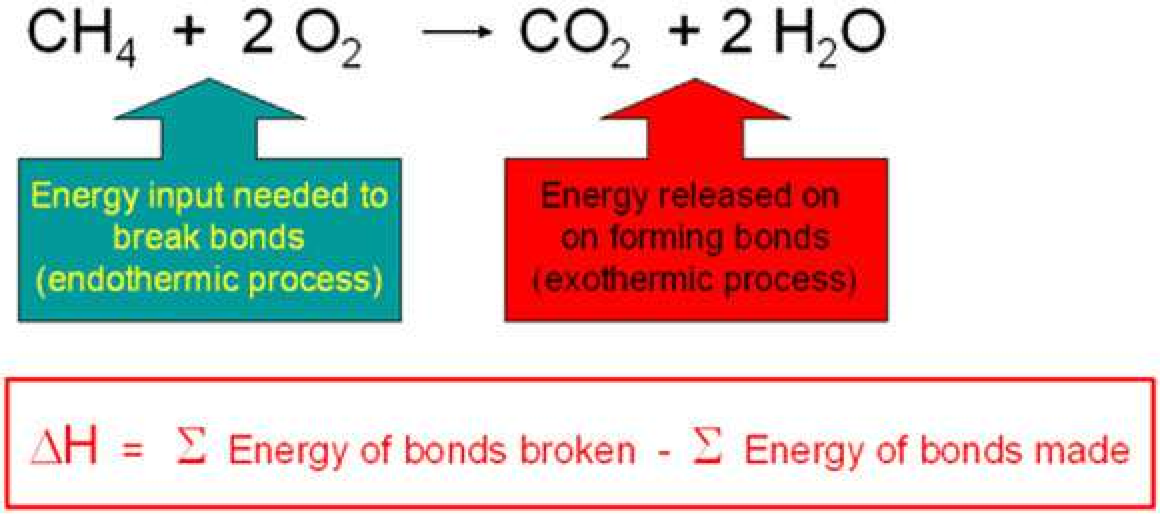
- The bond enthalpy is always a positive quantity; energy is always required to break chemical bonds.
- The greater the bond enthalpy is, the stronger the bond.
- A molecule with strong chemical bonds generally has less tendency to undergo chemical change than does one with weak bonds.



Bond Enthalpy and Reactions

- When calculating the ΔH of a reaction using bond enthalpies you use the following equation:

$$\Delta H_{rxn} = \Sigma(\text{bonds broken}) - \Sigma(\text{bonds formed})$$

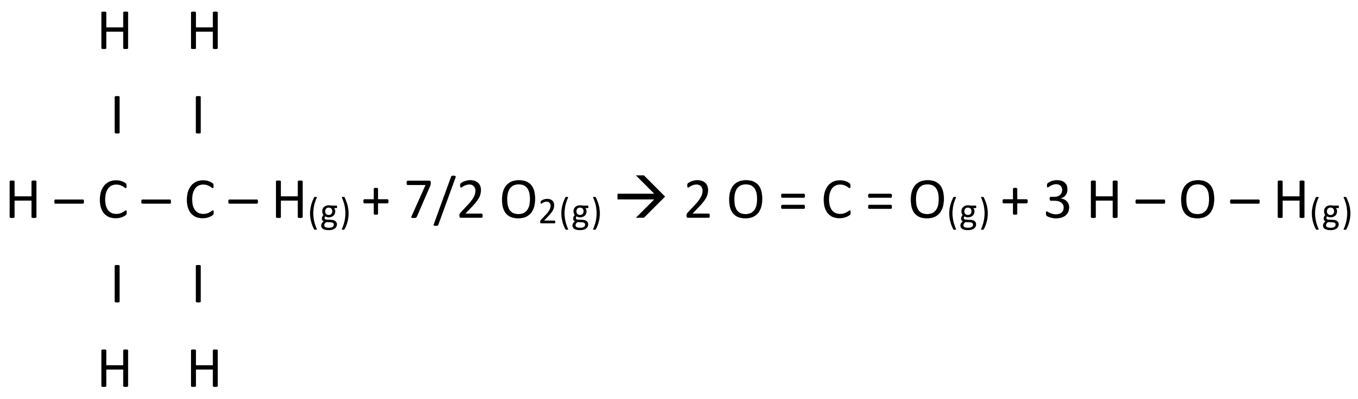


$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O$$

$$\boxed{\Delta H = \Sigma \text{ Energy of bonds broken} - \Sigma \text{ Energy of bonds made}}$$

Sample Exercise 8.12

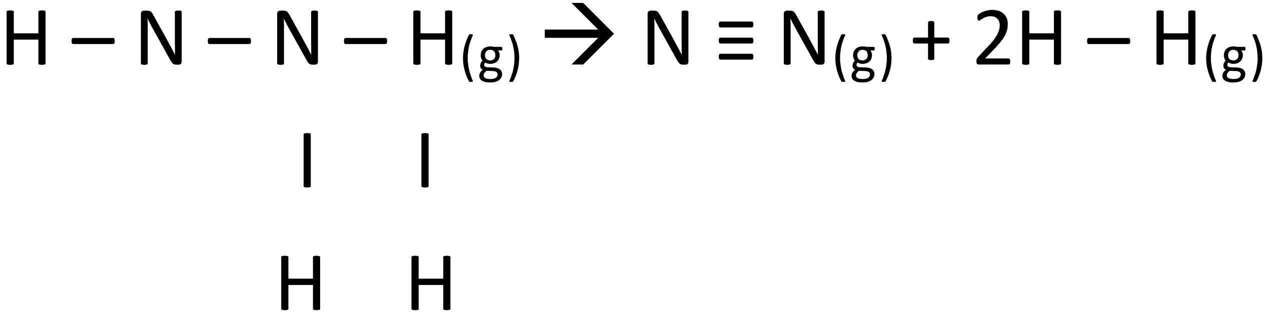
- Using Table 8.4, estimate ∆H for the following reaction:



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H_{(g)} \\ & & | & & | & & \\ & & H & & H & & \end{array} + 7/2\ O_{2(g)} \rightarrow 2\ O=C=O_{(g)} + 3\ H-O-H_{(g)}$$

Practice Exercise

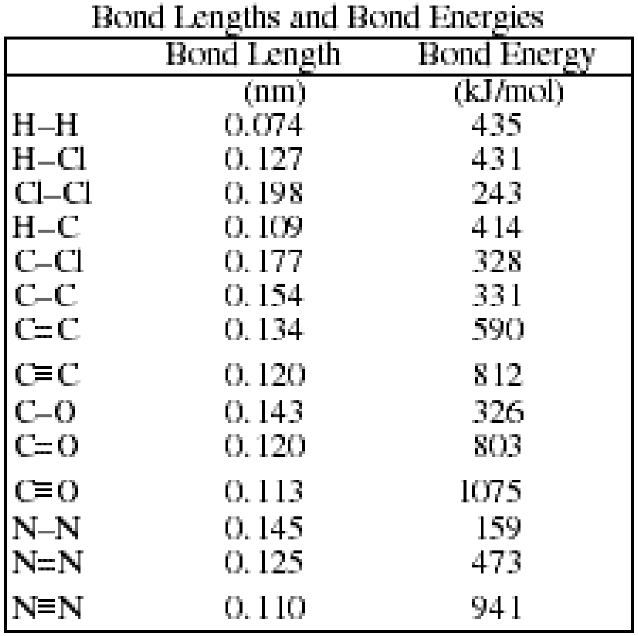
- Using Table 8.4, estimate ΔH for the following reaction:



$$\mathrm{H-\underset{\substack{|\\ H}}{N}-\underset{\substack{|\\ H}}{N}-H_{(g)} \rightarrow N\equiv N_{(g)} + 2H-H_{(g)}}$$

Bond Enthalpy and Bond Length

- As the number of bonds between the carbon atom increases, the bond enthalpy increases and the bond length decreases; that is, the carbon atoms are held more closely and more tightly together.
- In general, as the number of bonds between two atoms increases, the bond grows shorter and stronger.



Bond Lengths and Bond Energies

	Bond Length (nm)	Bond Energy (kJ/mol)
H–H	0.074	435
H–Cl	0.127	431
Cl–Cl	0.198	243
H–C	0.109	414
C–Cl	0.177	328
C–C	0.154	331
C=C	0.134	590
C≡C	0.120	812
C–O	0.143	326
C=O	0.120	803
C≡O	0.113	1075
N–N	0.145	159
N=N	0.125	473
N≡N	0.110	941

Sample Integrative Exercise

Phosgene has the following elemental composition: 12.41% C, 16.17% O, and 71.69% Cl by mass. Its molar mass is 98.9 g/mol.

a. Determine the molecular formula of this compound.

Sample Integrative Exercise

b. Draw three Lewis structures for the molecule that satisfy the octet rule for each atom.

Sample Integrative Exercise

c. Using formal charges, determine which Lewis structure is the most important one.

Sample Integrative Exercise

d. Using average bond enthalpies, estimate ΔH for the formation of gaseous phosgene from $CO_{(g)}$ and $Cl_{2(g)}$.