

Chapter 9: Chemical Bonding I: Lewis Theory

Homework:

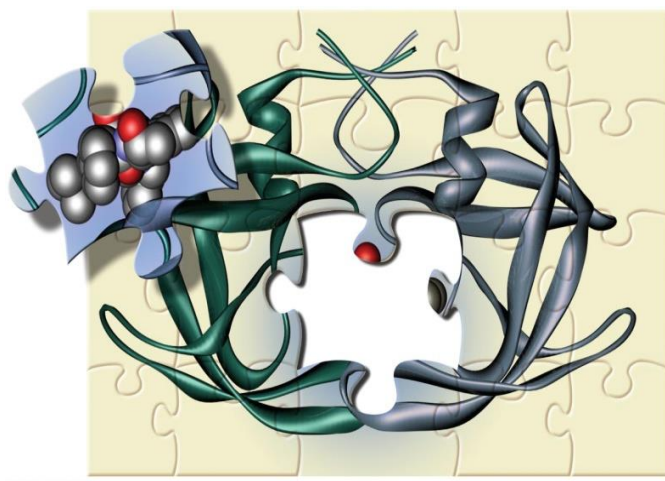
Read Chapter 9: Work out sample/practice exercises.

Check for the MasteringChemistry.com assignment and complete before due date

Chemical Bonding:

How atoms are connected together and the three dimensional shapes of molecules are very important. Many chemicals need to have the right shape to fit into the correct receptor or react the expected way. Finding the correct “fit” will allow manmade drugs to do a certain job. Artificial sweeteners have a shape that fits our receptors on the tongue to fool our brain into believing we taste something sweet.

The puzzle picture is showing the AIDS drug Indinavar as the missing piece depicting the protein HIV-protease. Pharmaceutical companies designed molecules that would disable HIV-protease by sticking to the molecule’s active site – **protease inhibitors**. To design such a molecule, researchers used **bonding theories** to simulate the shape of potential drug molecules and how they would interact with the protease molecule



Why do chemical bonds form?

- Chemical bonds form because they lower the potential energy between the particles that compose atoms
- A chemical bond forms when the potential energy of the bonded atoms is less than the potential energy of the separate atoms
- You need to consider the following interactions:
 1. nucleus-to-nucleus repulsions
 2. electron-to-electron repulsions
 3. nucleus-to-electron attractions

Lewis dot structures:

A UC Berkeley chemistry professor in 1916, Gilbert Lewis, developed a method to teach his beginning chemistry students how to understand chemical bonding that represents valence electrons with dots for main group elements.

Lewis structures allow us to predict many properties of molecules such as molecular stability, shape, size, polarity

Types of Bonding:

Types of Atoms	Types of Bond	Bond Characteristics
Metal to Nonmetal	Ionic	Electrons Transfer
Nonmetal to Nonmetal	Covalent	Electrons Shared
Metals to Metals	Metallic	Sea of Electrons

Ionic bonds occur between a cation (metal) and an anion (nonmetal). Ions are held together by electrostatic attraction, opposite charges (+, -) attracting each other. These attractions are quite *strong* and *increase with increasing charges and decreasing ionic sizes*. Ionic compounds must overcome large lattice energies to separate to melt or boil. Ionic compounds have *high melting points* due to a vast three dimensional network of attractions between ions.

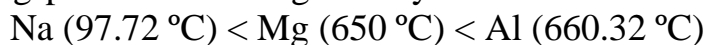
Covalent bonds occur when electrons are shared between nonmetal atoms. The *length of a bond increases as the bond order* decreases (triple < double < single). The amount of energy to break a chemical covalent bond in an isolated gas molecule is called the bond dissociation energy (BE or D). The *strength of the bond energy increases with increasing bond order* (single < double < triple bonds). Approximate Bond Energy values ($\pm 10\%$) can be found in reference sources. Note: Bond energy values assume starting and ending with gas substances. One can use these energies to find approximate enthalpies of reaction, ($\Delta H_{\text{reaction}} = \sum BE_{\text{reactants}} - \sum BE_{\text{products}}$). Covalent compounds have **low melting points**, the strong molecular bonds do not break apart when melting or boiling. *Covalent compounds are made of discrete molecules held together by weak intermolecular attractions.*

Metallic bonds: The low ionization energy of metals allows them to lose electrons easily. The simplest theory of metallic bonding involves the metal atoms

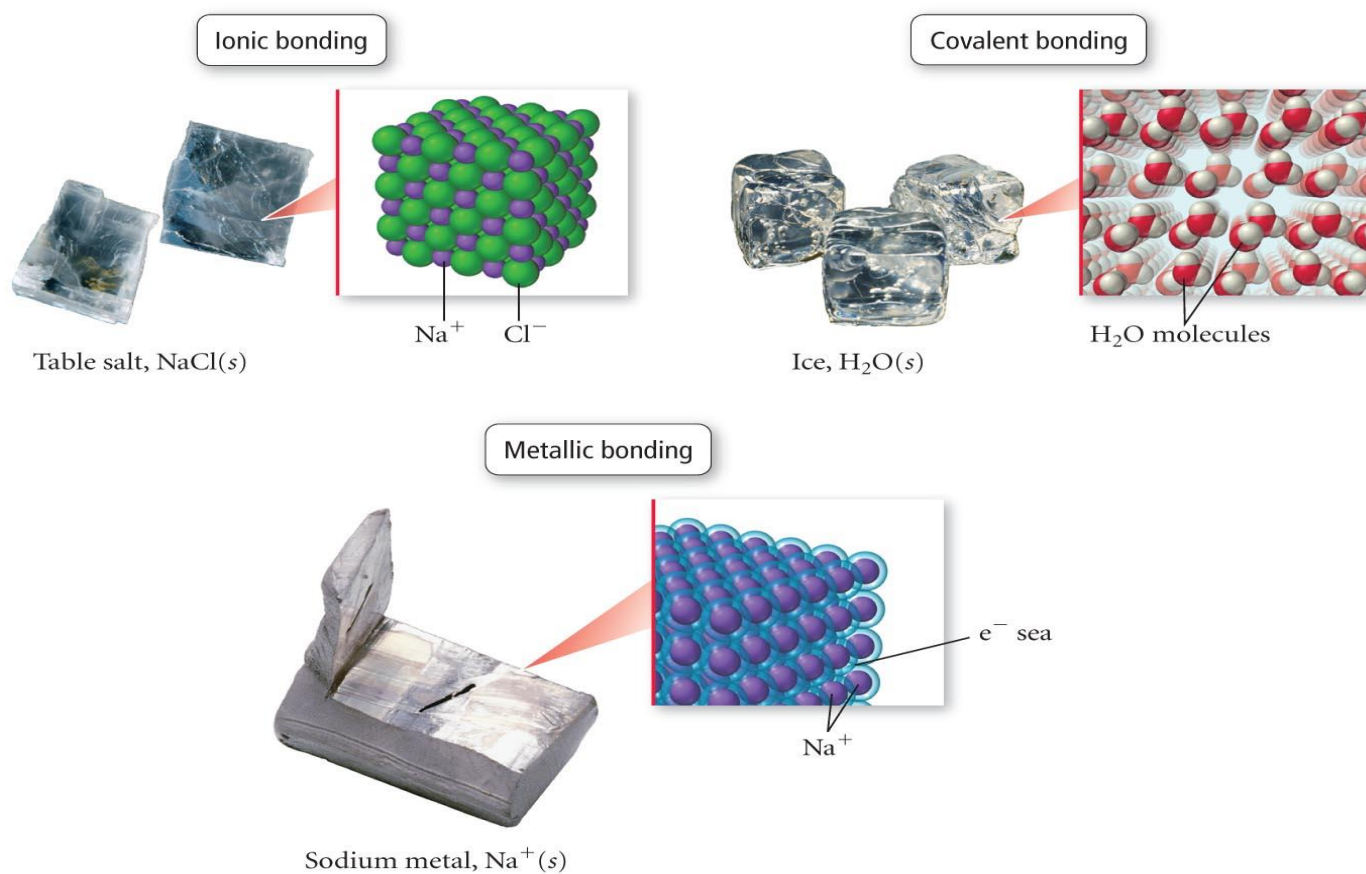
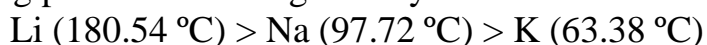
releasing *valence electrons to be shared by all atoms/ions* in the metal. Metal cations are surrounded by a *sea of electrons*. The electrons are delocalized throughout the metal structure. Bonding results from attraction of the cations for the delocalized electrons.

- Metallic solids conduct electricity well. As temperature increases, the electrical conductivity of metals decreases
- Metallic solids conduct heat well
- Metallic solids reflect light
- Metallic solids are malleable and ductile
- Metals generally have high melting points and boiling points, all but Hg are solids at room temperature

Melting points of metal generally increase left-to-right across period



Melting points of metals generally decrease down column



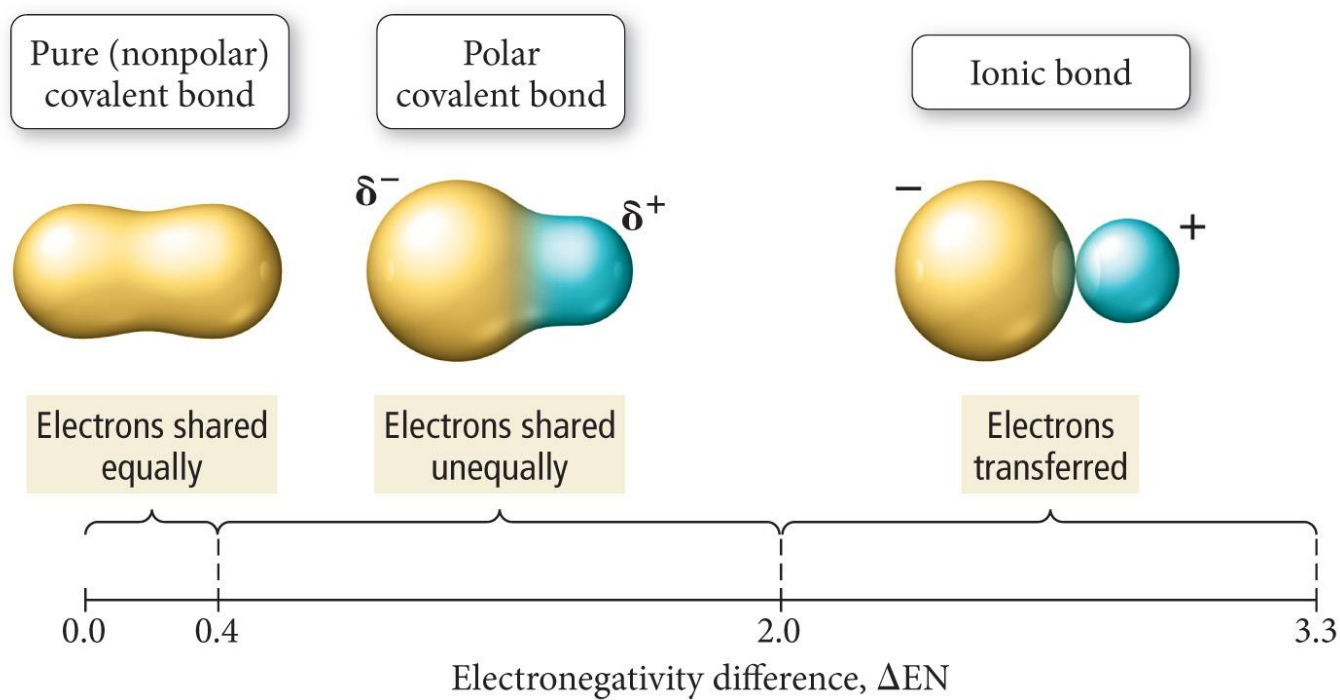
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Electronegativity (EN) is the ability of an atom to attract bonding electrons to itself.

Metals attract weakly while nonmetals attract electrons more strongly, especially as they become smaller and more nonmetallic. A way to remember stronger to weaker electronegativities is the term FONCIBrISCH.

- EN increases across period (left to right) and Decreases down group (top to bottom). Often noble gas atoms are not assigned values
 - Larger the difference in EN = more polar the bond
 - Negative end toward more EN atom
 - Most compounds are between the two extremes of ionic and pure covalent bonds sharing electrons unequally (**polar covalent bonds**).
1. If difference in electronegativity (ΔEN) between bonded atoms is 0, the bond is **pure covalent**. Share electrons equally such as O_2
 2. ΔEN is 0.1 to 0.4, the bond is **nonpolar covalent**. Share electrons nearly equal. Number ranges are approximate, C-H hydrocarbons are considered nonpolar covalent, while H_2S is polar covalent.
 3. ΔEN is 0.5 to 1.9, the bond is **polar covalent**. Unequally share electrons. Number ranges are approximate, a metal – nonmetal is considered ionic such as $MgBr_2$ whose $\Delta EN = 1.3$
 4. ΔEN atoms is larger than or equal to 2.0, the bond is **ionic**. Electrons are transferred as in NaCl

The Continuum of Bond Types



Electronegativity values of the elements (Pauling scale)																		He
H 2.1																	Ne	
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne	
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar	
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 1.8	Ni 1.8	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	La 1.1	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 1.8	Bi 1.9	Po 2.0	At 2.2	Rn 2.4	
Fr 0.7	Ra 0.7	Ac 1.1																
Ce 1.1	Pr 1.1	Nd 1.1	Pm 1.1	Sm 1.1	Eu 1.1	Gd 1.1	Tb 1.1	Dy 1.1	Ho 1.1	Er 1.1	Tm 1.1	Yb 1.1	Lu 1.2					
Th 1.3	Pa 1.5	U 1.7	Np 1.3	Pu 1.3	Am 1.3	Cm 1.3	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr					

Note: Bond Polarity is between two atoms, this is not the same as identifying whether a molecule is polar or nonpolar. For polarity of the overall substance we need 3D information found in the VSEPR and VB theories in Chapter 10.

Ionic Bonding:

Lewis theory predicts...

the attractions between ions are strong, ionic compounds should have high melting points and boiling points because breaking down the crystal should require a lot of energy

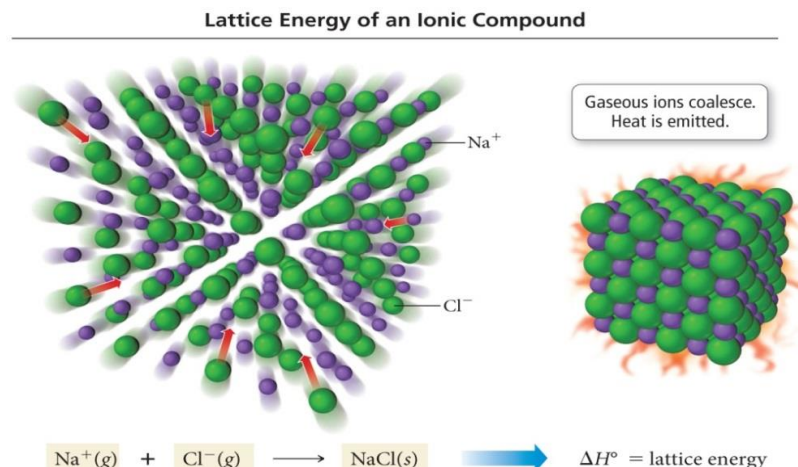
Stronger the attraction = Higher the melting point

Reality:

- High melting points and boiling points. $MP > 300\text{ }^{\circ}\text{C}$
- Solids at room temperature
- Relatively hard compared to most molecular solids
- Brittle. When struck they shatter
- Do not conduct electricity-ions are trapped in place in the solid
- Ionic compounds conduct electricity in the liquid state or when dissolved in water

Crystal Lattice Energy or Lattice Energy:

Crystal Lattice Energy is (-) energy given up when creating one mole of an ionic solid from its gaseous ions or (+) energy required to break up one mole of an ionic solid to its gaseous ions.



- Lattice energy is hard to measure directly, but can be calculated from knowledge of other processes
- Lattice energy depends directly on the size of charges and inversely on distance between ions following Coulombs Law.
- **Coulombs Law:** Force is $F = kQ_1Q_2/d^2$ and since Energy is force times distance, $E = kQ_1Q_2/d$
- The **Born–Haber cycle** is a hypothetical series of reactions that represents the formation of an ionic compound from its constituent elements.

Born-Haber Cycle: (pages 386-389)

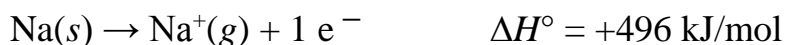
Born-Haber Cycle studies the formation of a solid ionic compound from its elements in its standard state of 1 atm pressure and 25°C.

ΔH_f = formation of solid ionic compound from elements in its standard state.

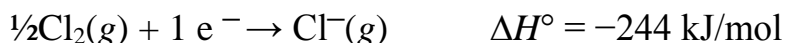
ΔH_{xtal} = formation of a solid ionic compound from ions in the gas state.

Forming an Ionic Compound from Elements:

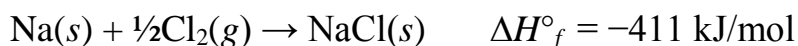
Ionization energy of a metal is endothermic.



Electron affinity of a nonmetal is generally exothermic.



Ionization energy of the metal is usually larger than electron affinity of the nonmetal; predicting that forming an ionic compound should be endothermic (+), but most are exothermic (-).

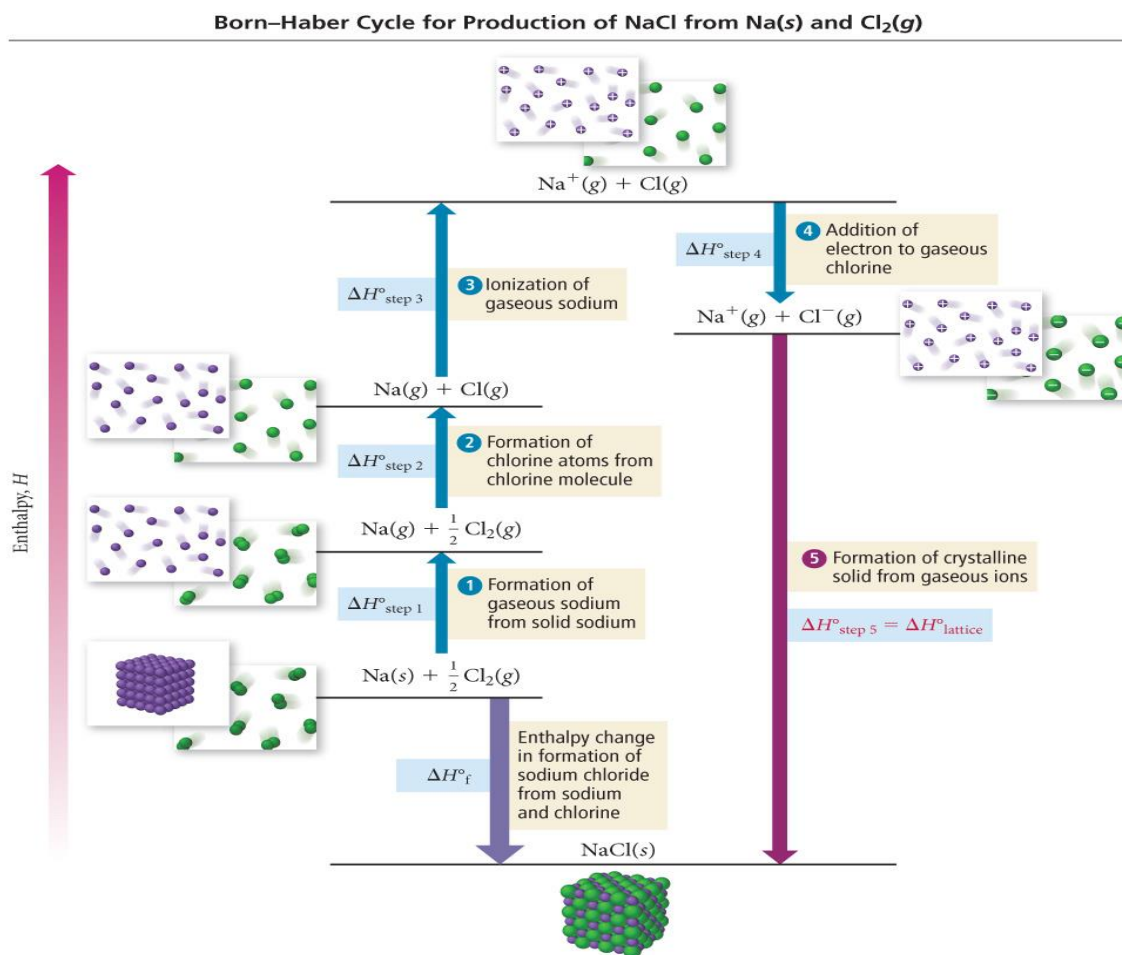


WHY?

Extra energy is released forming a structure in which every cation is surrounded by anions, and vice versa (**crystal lattice structure**).

Crystal lattice structure

- The crystal lattice maximizes attractions between cations and anions, leading to the most stable (lowest energy) arrangement.
- Electrostatic attraction is nondirectional with no direct anion–cation pair. There is **no ionic molecule**, the chemical formula is an empirical formula of the ratio of ions based on charge balance.



Change in enthalpy (ΔH) of each reaction is known by experiments, except for the lattice energy. Use Hess's law to add up enthalpy changes to determine the lattice energy.

$$\Delta H^\circ_{\text{xtal}} = \Delta H^\circ_f - \text{all others}$$

Try problem Ch 9:48

Use the Born-Haber cycle and data to calculate the lattice energy of CaO.
Write the reactants and products for each reaction of given information.

Given: ΔH_{subl} for Ca solid = 178 kJ/mole
BE for O₂ gas = 498 kJ/mole ($\frac{1}{2}$ mole O₂ in CaO)
IE₁ for Ca gas = 590 kJ/mole
IE₂ for Ca gas = 1145 kJ/mole
EA₁ for O gas = -141 kJ/mole
EA₂ for O gas = +744 kJ/mole
 ΔH_{xtal} for CaO solid = _____ kJ/mole

Coulomb's Law: $F = kQ_1Q_2/d^2$ since Energy is force times distance, $E = kQ_1Q_2/d$

Trends in Lattice Energy:

- The **force of attraction** between charged particles is **inversely** proportional to the **distance** between them. Larger ions mean the center of positive charge (nucleus of the cation) is farther away from the negative charge (electrons of the anion)

Larger ion = weaker attraction = smaller lattice energy

- The **force of attraction** between charged particles is **directly** proportional to the **charges** on the ions.

Larger charge = stronger attraction = larger lattice energy

- Ion charge is **generally** more important than size

Examples of Lattice Energy:

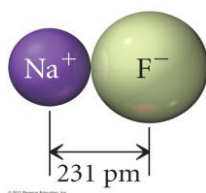
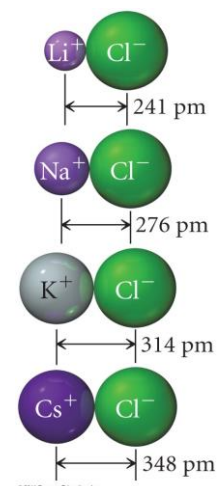
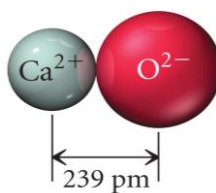
A) Same charge:

All charges are +1 and -1

Larger ion = Weaker attraction

B) Larger charge = Stronger attraction

Metal Chloride	Lattice Energy (kJ/mol)
LiCl	-834
NaCl	-787
KCl	-701
CsCl	-657

Lattice Energy =
-910 kJ/molLattice Energy =
-3414 kJ/mol

Example 1: Order the following ionic compounds in order of increasing magnitude of lattice energy: **MgS, NaBr, LiBr, SrS**

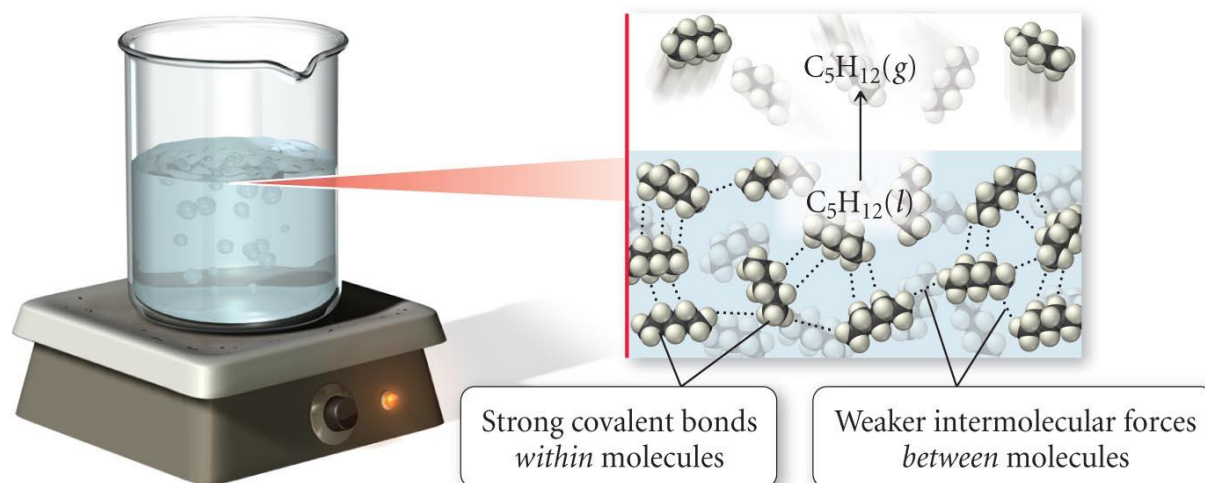
Covalent Bonding:**Lewis theory predicts...**

- Some combinations should be stable, others should not. Most stable combinations result in “octets”, which assists in predicting the formulas of molecules of covalently bonded substances
- Covalent attractions between atoms are directional; shared electrons are most stable between the bonding atoms. Covalently bonded compounds are individual molecules rather than an array like ionic compounds
- Weak attractions between the molecules are broken, not the covalent bonds, when melting and boiling molecular compounds so melting points are low
- The hardness and brittleness of molecular compounds vary depending on the strength of intermolecular attractive forces.
- Neither molecular solids nor liquids conduct electricity, no charged particles.
- The more electrons two atoms share, the stronger and shorter the bond should be.

Reality of Covalent Bonding:

- Compounds of nonmetals are made of individual molecule units
- Molecular compounds have low melting points and boiling points. MP generally $< 300\text{ }^{\circ}\text{C}$. Molecular compounds are found in all three states at room temperature

Molecular Compound



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- Some molecular solids are brittle and hard, but many are soft and waxy
- Molecular compounds do not conduct electricity in the solid or liquid state. Molecular acids conduct electricity when dissolved in water, but not in the solid or liquid state, due to them being ionized by the water
- Bond strength is measured by how much energy must be added into the bond to break it in half. In general, triple bonds are stronger than double bonds, and double bonds are stronger than single bonds.
- Bond length is determined by measuring the distance between the nuclei of bonded atoms. Triple bonds are shorter than double bonds, and double bonds are shorter than single bonds between the same atoms. Bond Length increases down a column with size.
- In general, as bonds get longer, their strength gets weaker.

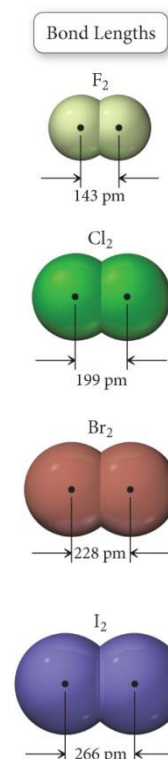


TABLE 9.4 Average Bond Lengths

Bond	Bond Length (pm)	Bond	Bond Length (pm)	Bond	Bond Length (pm)
H—H	74	C—C	154	N—N	145
H—C	110	C=C	134	N=N	123
H—N	100	C≡C	120	N≡N	110
H—O	97	C—N	147	N—O	136
H—S	132	C=N	128	N=O	120
H—F	92	C≡N	116	O—O	145
H—Cl	127	C—O	143	O=O	121
H—Br	141	C=O	120	F—F	143
H—I	161	C—Cl	178	Cl—Cl	199
				Br—Br	228
				I—I	266

Dipole Moment:

Dipole moment, μ , is a measure of the net molecular polarity; $\mu = (q)(r)$

Measured in Debyes, $D = 3.336 \times 10^{-30} \text{ C}\cdot\text{m}$ (Coulomb · meter)

Dipole has a + and – end. Generally, the more electrons two atoms share and the larger the atoms are, the larger the dipole moment.

(q) = the magnitude of the equal, but opposite charges between particles. For a proton/electron (± 1), $q = 1.60 \times 10^{-19} \text{ C}$

(r) = distance between particles

Dipole Moments of Several Gas Molecules

Molecule	ΔEN	Dipole Moment (D)
Cl_2	0	0
CO_2	1.0 (opposite directions)	0
CO	1.0	0.112
ClF	1.0	0.88
H_2O	1.4 (bent two bonds)	1.85
KBr	2.0	10.41
LiF	3.0	6.33

Example 2: Explain why LiF has a smaller dipole moment than KBr even though the ΔEN is greater in LiF. Explain CO vs ClF.

Percent Ionic Character:

Substances have a continuous range between sharing electrons equally (nonpolar covalent bonding) to transferring electrons (ionic bonding). The dipole moment of a substance allows one to estimate the % ionic character by dividing the measured dipole moment by the calculated dipole moment (assume 100% ionic character.)

$$\% \text{ ionic character} = (\text{measured } \mu) / (\mu \text{ if } e^{-1} \text{ completely transferred}) * 100\%$$

Example 3:

- a) The HCl (g) molecule has a measured dipole moment of 1.08 D. Solve for the dipole moment if an electron is completely transferred (100% ionic). One proton (H^{+1}) and one negative charge (Cl^{-1}) separated by 127 pm bond...

$$\mu = (1.60 \times 10^{-19} \text{ C}) \times (1.27 \times 10^{-10} \text{ m}) \times (1 \text{ D} / 3.336 \times 10^{-30} \text{ C}\cdot\text{m}) = \underline{\quad} \text{ D}$$

- b) Determine its percent ionic character. (Measured D/ionic D) x 100

Example 4:

The dipole moment of HF is $\mu = 1.82 \text{ D}$, and the bond length is 92 pm. Calculate the % ionic character of the H-F bond.

Electron dot structures (Lewis Structures) show us a way to draw pictures of compounds using all the valence electrons. Remember the valence electrons are the outermost s and p electrons. Two s electrons (duet, He) plus six p electrons (other noble gas configurations) have a maximum of eight (octet). The Lewis structures show bonding electrons as single, double, and triple lines (two electrons per line); nonbonding electrons as individual or pairs of dots; and ions inside of square brackets with a charge on the outside.

Simple example for H_2 is H-H

Example 5: Count valence electrons by the main group vertical column.

H-1, Be-2, B-3, C-4, N-5, O-6, F-7, Ne-8

Four regions have a maximum of two dots each = 8 maximum.

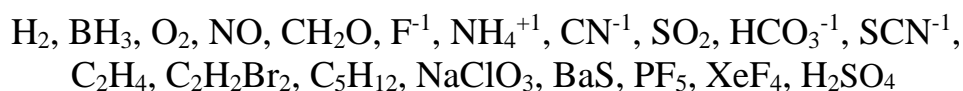
Lewis Dot Structure Guidelines:

- Count all valence electrons.
For ions:
 - 1) add electrons for negative charges (anions)
 - 2) subtract electrons for positive charges (cations)
- Two-Dimensional drawing, four sides (up, down, right, left)
- Octet and Duet rules are generally followed. Main group elements tend to undergo reactions that leave them with 8 outer shell electrons, obtaining the noble gas configuration, or 2 electrons for the elements near helium.
- Many formulas tend to be symmetrical, when a formula has many of the same element, they are often in terminal positions.
- Generally O will not bond to O except in oxygen (O_2), ozone (O_3), and peroxide or superoxides (O_2^{-2} , O_2^{-1}).
- Octet deficient atoms include: H-2, Be-4, B-6
- Odd number of electrons will not have a complete octet (single dot)
- Extended octets may occur with P or larger nonmetals (10 or 12 electrons).
- Coordinate covalent bonds occur when both electrons of a bond come from just one of the atoms as the bond between N and B in the molecule H_3NBH_3 , where the two nonbonding electrons on the nitrogen in NH_3 share with boron to increase the 6 shared electrons in BH_3 to an octet
- Single bonds can twist and rotate, but double and triple bonds cannot rotate. This fact causes molecules with a $C=C$ double bond to have structural isomers when the other two groups attached to each carbon are different.
- Use Electronegativity values to identify bond polarity (ionic, polar covalent, nonpolar covalent)
- Resonance occurs by moving electrons without moving atom locations. Resonance adds stability to a structure.
- Structural isomers occur by moving atoms to create new connections making a new substance
- Formal Charge = group number – (lines + dots) around each atom
- Octet rule is preferred over extended octet
- Lowest formal charges are preferred. All else being equal the more electronegative atom prefers to have the negative formal charge
- Count the number of electron regions: (a) any bond (single, double, triple) counts as just one region, (b) a lone pair of nonbonding electrons or a single dot for an odd number of electrons count as one electron region.

- Mirror images have different structural isomers if all four groups attached to the central carbon atom are different.

Rules to Draw the Lewis Structure:

- 1) Start with skeleton drawing structure. Choose an appropriate center atom, the one that desires multiple bonds such as C or N.
- 2) Bonded H will be a terminal atom bonded with a single line and no dots to fulfill the duet rule.
- 3) First connect all atoms with single bonds or ion brackets.
- 4) Work outside towards the center adding dots to fulfill octet/duet rule.
- 5) If you need more electrons then move nonbonding electrons to create double or triple bonds.
- 6) Ions are inside square brackets with its charge outside the brackets
- 7) The best structure will minimize formal charges and may have resonances. Octets are generally preferred, but reducing formal charges through resonances may cause extended octets.
- 8) Structural isomers may occur.
- 9) If you have too many electrons, the center has an extended octet and gets the extra electrons.

Example 6: Lewis Structures:

Count valence electrons, draw skeleton structure, solve for the best Lewis Structure(s) following the guidelines. Identify ionic vs. covalent compounds; bonding types; dipole arrows; resonances; structural isomers; formal charges; count the number of electron regions.

Bond Energies:

- Chemical reactions involve breaking bonds in reactant molecules and making new bonds to create the products.
 - Bond breaking is endothermic, $\Delta H = (+)$.
 - Bond making is exothermic, $\Delta H = (-)$
- $\Delta H^\circ_{\text{reaction}}$ may be estimated from bond energies involved in breaking old bonds and making new bonds in the gas state.
 - $\Delta H_{\text{rxn}} = \sum (\Delta H(\text{bonds broken})) + \sum (\Delta H(\text{bonds formed}))$
- Use average bond energies to estimate the ΔH_{rxn} . The actual bond energy depends on the surrounding atoms and other factors.

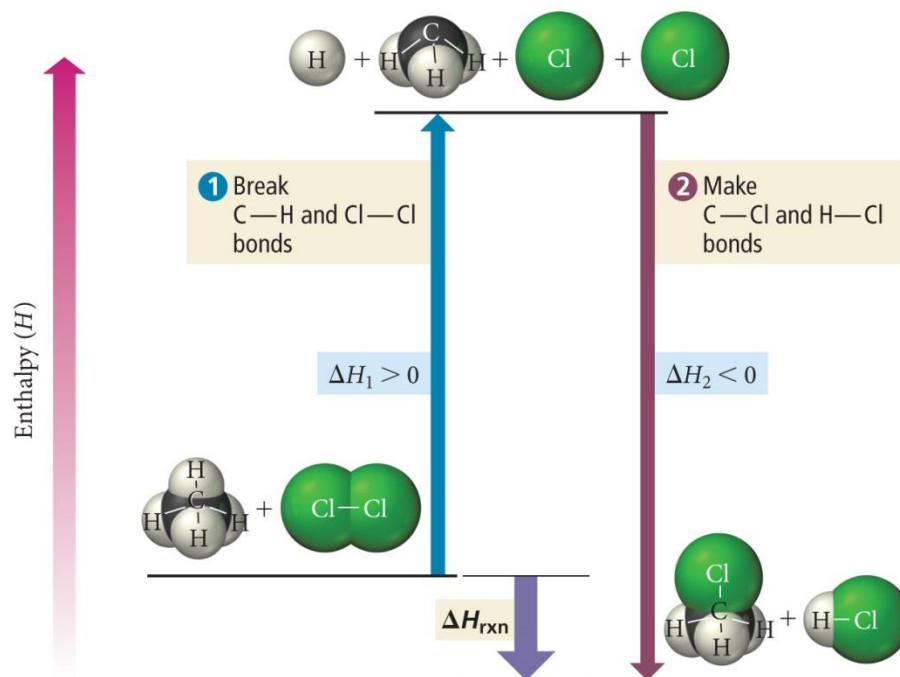
TABLE 9.3 Average Bond Energies

Bond	Bond Energy (kJ/mol)	Bond	Bond Energy (kJ/mol)	Bond	Bond Energy (kJ/mol)
H—H	436	N—N	163	Br—F	237
H—C	414	N=N	418	Br—Cl	218
H—N	389	N≡N	946	Br—Br	193
H—O	464	N—O	222	I—Cl	208
H—S	368	N=O	590	I—Br	175
H—F	565	N—F	272	I—I	151
H—Cl	431	N—Cl	200	Si—H	323
H—Br	364	N—Br	243	Si—Si	226
H—I	297	N—I	159	Si—C	301
C—C	347	O—O	142	S—O	265
C=C	611	O=O	498	Si=O	368
C≡C	837	O—F	190	S=O	523
C—N	305	O—Cl	203	Si—Cl	464
C=N	615	O—I	234	S=S	418
C≡N	891	F—F	159	S—F	327
C—O	360	Cl—F	253	S—Cl	253
C=O	736*	Cl—Cl	243	S—Br	218
C≡O	1072			S—S	266
C—Cl	339				

*799 in CO₂

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Estimating the Enthalpy Change of a Reaction from Bond Energies



Example 7:

Estimate ΔH_{rxn} for the reaction of $\text{CH}_4(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{CH}_3\text{Cl}(\text{g}) + \text{HCl}(\text{g})$

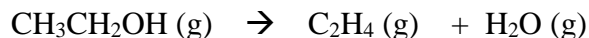
Example 8:

- Balance the reaction for the combustion of normal butane, all gases.

$$\text{C}_4\text{H}_{10}(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$$
- Draw Lewis structures and calculate an approximate heat of combustion for your balanced equation of the combustion of butane.

Practice Problems:

1. Draw the Lewis structure for carbon monoxide and indicate any formal charges.
2. Ethyl alcohol can undergo a dehydration reaction



Draw Lewis Structures and calculate the approximate heat of reaction for the dehydration of ethyl alcohol.

3. List several characteristic properties for each.

ionic compounds

molecular covalent compounds

metals

4. Predict whether the bonding between the following pairs of elements would be ionic, polar covalent, or pure/nonpolar covalent or metallic. If polar covalent indicate the direction of polarity with arrow.
 - a) O and O
 - b) H and N
 - c) F and H
 - d) Cu and Zn
 - e) Ca and Br
5. Draw two different Lewis structural isomers for the molecule $\text{C}_4\text{H}_8\text{O}_2$ (formal charges should all be zero)
6. Draw a Lewis structure and classify all the **bonding** types within the compound KCN.
7. Draw and identify the cis and trans isomers for 1,2-dichloroethene, $\text{C}_2\text{H}_2\text{Cl}_2$
8. Identify elements which **can** follow...(a) duet rule, (b) octet rule, (c) extended octet

H

P

Br

C

F