

Chapter 8
Bonding:
General Concepts

Bonds

- Forces that hold groups of atoms together and make them function as a unit.

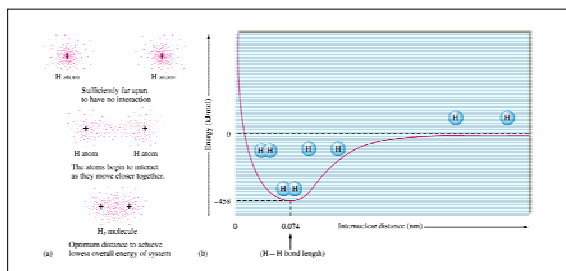
Bond Energy

- ▣ It is the energy required to break a bond.
- ▣ It gives us information about the strength of a bonding interaction.

Bond Length

- The **distance** where the **system** energy is a minimum.

Figure 8.1: (a) The interaction of two hydrogen atoms. (b) Energy profile as a function of the distance between the nuclei of the hydrogen atoms.



Covalent Bonds

- When two nonmetals bond, they often share electrons since they have similar attractions for them. This sharing of valence electrons is called the **covalent bond**.
- These atoms will share sufficient numbers of electrons in order to achieve a noble gas electron configuration (that is, eight valence electrons).

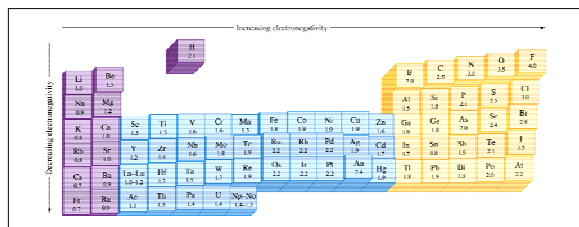
Polar Covalent Bonds

- A **polar covalent bond** is one in which the bonding electrons spend more time near one of the two atoms involved.
 - When the atoms are alike, as in the H-H bond of H₂, the bonding electrons are shared equally (a **nonpolar covalent bond**).
 - When the two atoms are of different elements, the bonding electrons need not be shared equally, resulting in a **“polar” bond**.

Polar Covalent Bonds

- **Electronegativity** is a measure of the ability of an atom in a molecule to draw bonding electrons to itself.
 - In general, electronegativity increases from the lower-left corner to the upper-right corner of the periodic table.
 - The current electronegativity scale, developed by Linus Pauling, assigns a value of 4.0 to fluorine and a value of 0.7 to cesium.

Figure 8.3: The Pauling electronegativity values. Electronegativity generally increases across a period and decreases down a group.



For the C=O bond: 3.5 - 2.5 = 1.0 electronegativity difference

Electronegativity

- The ability of an atom in a molecule to attract shared electrons to itself. Calculated using difference between experimental bond energy and expected bond energy

$$\Delta = (H - X)_{\text{actual}} - (H - X)_{\text{expected}}$$

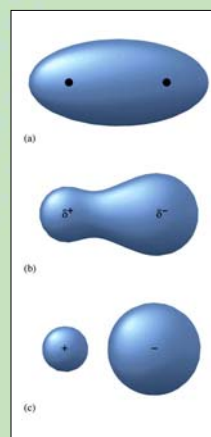
$$\text{Expected H-X bond energy} = \frac{\text{H-H b.e.} + \text{X-X b.e.}}{2}$$

TABLE 8.1 The Relationship Between Electronegativity and Bond Type

Electronegativity Difference in the Bonding Atoms	Bond Type
Zero	Covalent
Intermediate	Polar covalent
Large	Ionic

Figure 8.11: The three possible types of bonds

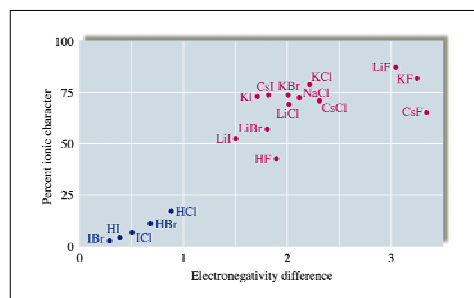
- a covalent bond formed between identical atoms
- a polar covalent bond, with both ionic and covalent components;
- an ionic bond with no electron sharing.



Polar Covalent Bonds

- The absolute value of the difference in electronegativity of two bonded atoms gives a rough measure of the **polarity** of the bond.
 - When this difference is small (less than 0.5), the bond is **nonpolar**.
 - When this difference is large (greater than 0.5), the bond is considered **polar**.
 - If the difference exceeds approximately 1.8, sharing of electrons is no longer possible and the bond becomes **ionic**.

Figure 8.12: The relationship between the ionic character of a covalent bond and the electronegativity difference of the bonded atoms.



Polarity

- A molecule, such as HF, that has a center of positive charge and a center of negative charge is said to be **polar**, or to have a **dipole moment**.

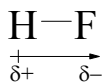


Figure 8.2: The effect of an electric field on hydrogen fluoride molecules.

- When no electric field is present, the molecules are randomly oriented.
- When the field is turned on, the molecules tend to line up with their negative ends toward the positive pole and their positive ends toward the negative pole.

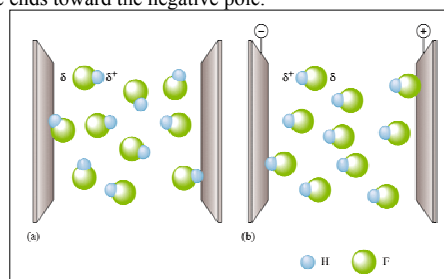
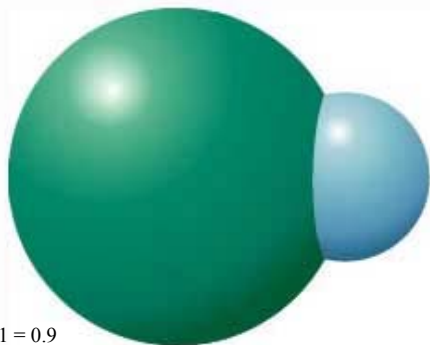


Figure 9.14: The HCl molecule.

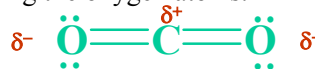


$$3.0 - 2.1 = 0.9$$

Bond is polar covalent - and the HCl molecule is also polar

Polar Covalent Bonds

- For example, the bond between carbon and oxygen in CO_2 is considered polar because the shared electrons spend more time orbiting the oxygen atoms.



- The result is a partial negative charge on the oxygens (denoted δ^-) and a partial positive charge on the carbon (denoted δ^+). The $\text{C}=\text{O}$ bond is polar - but the molecule is not.

Figure 8.6: (a) The carbon dioxide molecule. (b) The opposed bond polarities cancel out, and the carbon dioxide has no dipole moment.

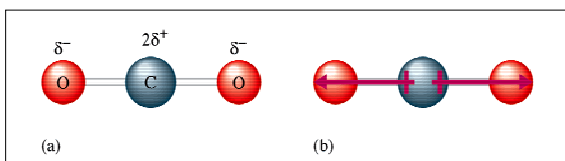


Figure 8.4: (a) The charge distribution in the water molecule. (b) The water molecule in an electric field.

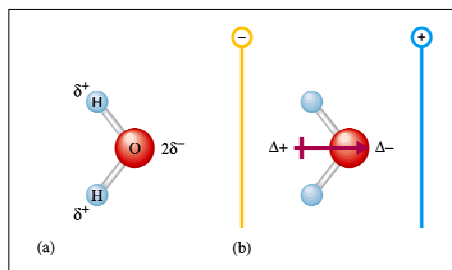


Figure 8.5: (a) The structure and charge distribution of the ammonia molecule. The polarity of the N—H bonds occurs because nitrogen has a greater electronegativity than hydrogen. (b) The dipole moment of the ammonia molecule oriented in an electric field.

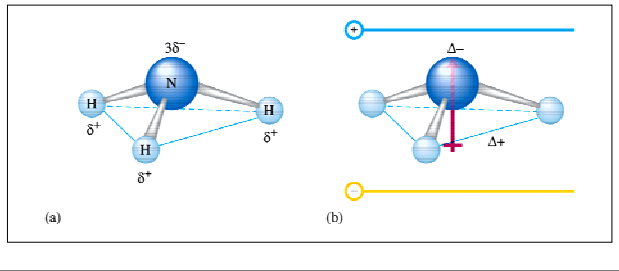


TABLE 8.2 Types of Molecules with Polar Bonds but No Resulting Dipole Moment			
Type	Cancellation of Polar Bonds	Example	Ball-and-Stick Model
Linear molecules with two identical bonds	B—A—B ←---+ +--->	CO ₂	
Planar molecules with three identical bonds 120° apart	 120°	SO ₂	
Tetrahedral molecules with four identical bonds 109.5° apart	 109.5°	CCl ₄	

Ionic Bonds

- Formed from electrostatic attractions of closely packed, oppositely charged ions.
- Formed when an atom that easily loses electrons reacts with one that has a high electron affinity.

Ionic Bonds

$$E = 2.31 \times 10^{-19} \text{ J nm } (Q_1 Q_2 / r)$$

- Q_1 and Q_2 = numerical ion charges
- r = distance between ion centers (in nm)

Valence Electrons - an electron in an atom outside the noble gas or pseudo-noble gas core.

Pseudo-noble gas core: refers to the noble gas + $(n-1)d^{10}$ configuration. Example: As has configuration $[\text{Ar}]3d^{10}4s^24p^3$ and has 5 valence electrons

Ionic Bonds - a chemical bond formed by the electrostatic attraction between positive and negative ions

Achieving Noble Gas Electron Configurations (NGEC)

- Two nonmetals react: They share electrons to achieve NGEC.
- A nonmetal and a representative group metal react (ionic compound): The valence orbitals of the metal are emptied to achieve NGEC. The valence electron configuration of the nonmetal achieves NGEC.

TABLE 8.3 Common Ions with Noble Gas Configurations in Ionic Compounds

Group 1A	Group 2A	Group 3A	Group 6A	Group 7A	Electron Configuration
H, Li ⁺	Be ²⁺				[He]
Na ⁺	Mg ²⁺	Al ³⁺	O ²⁻	F ⁻	[Ne]
K ⁺	Ca ²⁺		S ²⁻	Cl ⁻	[Ar]
Rb ⁺	Sr ²⁺		Se ²⁻	Br ⁻	[Kr]
Cs ⁺	Ba ²⁺		Te ²⁻	I ⁻	[Xe]

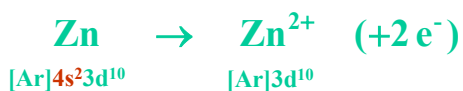
Electron Configurations of Ions

- As metals lose electrons to form **cations** and establish a “noble gas” configuration, the electrons are lost from the valence shell first.
- For example, magnesium generally loses two electrons from its 3s subshell to look like neon.



Electron Configurations of Ions

- Transition metals also lose electrons from the valence shell first, which is not the last subshell to fill according to the aufbau sequence.
- For example, zinc generally loses two electrons from its 4s subshell to adopt a “**pseudo**”-noble gas configuration.



Isoelectronic Ions

- Ions containing the the same number of electrons
 - (O²⁻, F⁻, Na⁺, Mg²⁺, Al³⁺)
 - O²⁻ > F⁻ > Na⁺ > Mg²⁺ > Al³⁺
 - largest smallest

Describing Ionic Bonds

- An **ionic bond** is a chemical bond formed by the electrostatic attraction between positive and negative ions.
- This type of bond involves the **transfer** of electrons from one atom (usually a metal) to another (usually a nonmetal).
- The number of electrons lost or gained by an atom is determined by its need to be “**isoelectronic**” with a noble gas.

Figure 9.8:
Comparison
of atomic and
ionic radii.

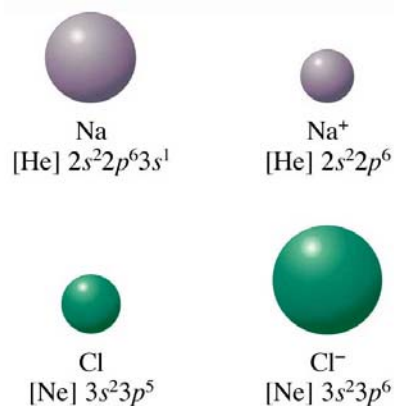
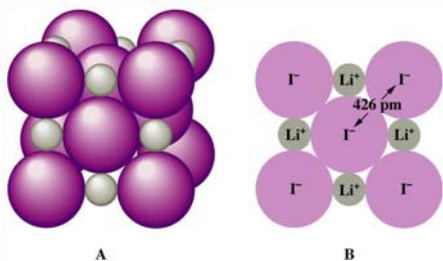


Figure 9.7: Determining the iodine ion radius in the lithium iodide (LiI) crystal.



1. Ionic radii increase down any column (group) because of the addition of electron shells.
2. In general, ions on the left and right sides of the periodic table lose or gain electrons to become **isoelectronic** with their noble gas core. Isoelectronic refers to different species which have the same number of electrons.

Ionic Radii

- Within an **isoelectronic group of ions**, the one with the greatest nuclear charge (positive) will be the smallest.
 - For example, look at the ions listed below.



All have 18 electrons

- Note that they all have the same number of electrons, but different numbers of protons.

Ionic Radii

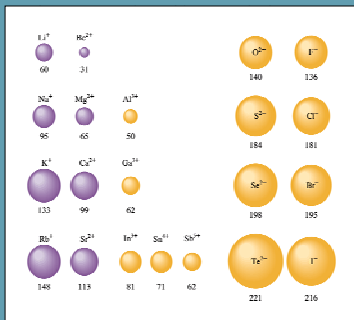
- In this group, calcium has the greatest nuclear charge and is, therefore, the smallest.



All have 18 electrons

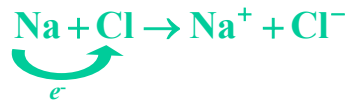
- Sulfur has only 16 protons to attract its 18 electrons and, therefore, has the largest radius.

Figure 8.7: Sizes of ions related to positions of the elements on



Describing Ionic Bonds

- Consider the transfer of valence electrons from a sodium atom to a chlorine atom.



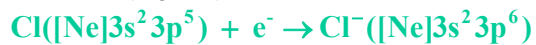
- The resulting ions are electrostatically attracted to one another.
- The attraction of these oppositely charged ions for one another is the **ionic bond**.

Describing Ionic Bonds

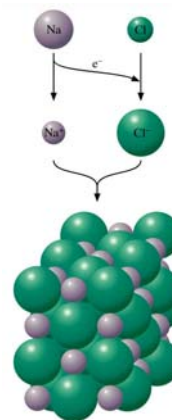
- Such noble gas configurations and the corresponding ions are particularly stable.
 - The atom that loses the electron becomes a **cation** (positive).



- The atom that gains the electron becomes an **anion** (negative).

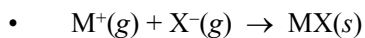


Reaction of Na and Cl to form NaCl.



Lattice Energy

- The change in energy when separated gaseous ions are packed together to form an ionic solid.



- Lattice energy is negative (exothermic) from the point of view of the system.

Formation of an Ionic Solid

- 1. Sublimation of the solid metal
 - $M(s) \rightarrow M(g)$ [endothermic]
- 2. Ionization of the metal atoms
 - $M(g) \rightarrow M^+(g) + e^-$ [endothermic]
- 3. Dissociation of the nonmetal
 - $1/2X_2(g) \rightarrow X(g)$ [endothermic]

Formation of an Ionic Solid

(continued)

- 4. Formation of X^- ions in the gas phase:
 - $X(g) + e^- \rightarrow X^-(g)$ [exothermic]
- 5. Formation of the solid MX
 - $M^+(g) + X^-(g) \rightarrow MX(s)$ [quite exothermic]
 -

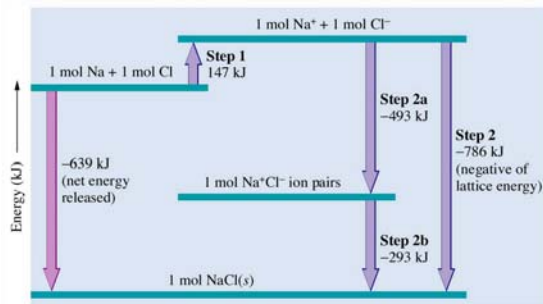
$$\text{Lattice Energy} = k(Q_1Q_2 / r)$$

- Q_1, Q_2 = charges on the ions
- r = shortest distance between centers of the cations and anions

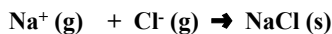
Energy Involved in Ionic Bonding

- The transfer of an electron from a sodium atom to a chlorine atom is not in itself energetically favorable; it requires 147 kJ/mol of energy.
- However, 493 kJ of energy is released when these oppositely charged ions come together.
- An additional 293 kJ of energy is released when the ion pairs solidify.
- This “**lattice energy**” is the negative of the energy released when gaseous ions form an ionic solid. The next slide illustrates this.

Figure 9.2: Energetics of ionic bonding.

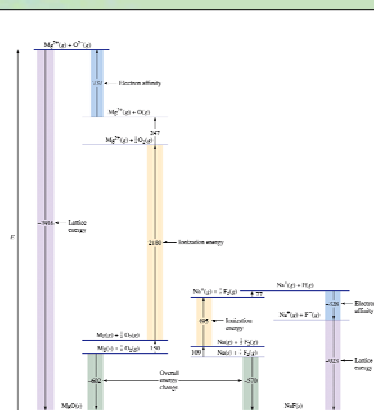


Calculation of NaCl Lattice energy



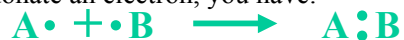
- $\text{Na}^+(\text{g}) + \text{e}^- \rightarrow \text{Na}(\text{g})$ -495 kJ - I.E.
 - $\text{Na}(\text{g}) \rightarrow \text{Na}(\text{s})$ -109 kJ heat of condensation
 - $\text{Na}(\text{s}) + 1/2 \text{Cl}_2(\text{g}) \rightarrow \text{NaCl}(\text{s})$ -411 kJ heat of formation
 - $\text{Cl}(\text{g}) \rightarrow 1/2 \text{Cl}_2(\text{g})$ -119.5 kJ $1/2$ bond energy
 - $\text{Cl}^-(\text{g}) \rightarrow \text{Cl}(\text{g}) + \text{e}^-$ + 349 kJ - electron affinity
- $$\text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) \rightarrow \text{NaCl}(\text{s}) \quad - 786 \text{ kJ}$$

Figure 8.10: Comparison of the energy changes involved in the formation of solid sodium fluoride and solid magnesium oxide.



Coordinate Covalent Bonds

- When bonds form between atoms that both donate an electron, you have:



- It is, however, possible that both electrons are donated by one of the atoms. This is called a **coordinate covalent bond**.



Bond Length and Bond Order

- Bond length** (or **bond distance**) is the distance between the nuclei in a bond.
 - Knowing the bond length in a molecule can sometimes give clues as to the type of bonding present.
 - Covalent radii** are values assigned to atoms such that the sum of the radii of atoms "A" and "B" approximate the A-B bond length.

Bond Length and Bond Order

- Table 9.4 lists some covalent radii for nonmetals.
 - For example, to predict the bond length of C-Cl, you add the covalent radii of the two atoms.

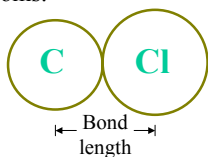


Table 9.4
Single-Bond Covalent Radii for Nonmetallic Elements (in pm)

				H
				37
B	C	N	O	F
88	77	70	66	64
	Si	P	S	Cl
	117	110	104	99
		As	Se	Br
		121	117	114
			Te	I
			137	133

Bond Length and Bond Order

- The **bond order**, determined by the Lewis structure, is the number of pairs of electrons in a bond.
 - Bond length depends on bond order.
 - As the bond order increases, the bond gets shorter and stronger.

	Bond length	Bond energy
C—C	154 pm	346 kJ/mol
C=C	134 pm	602 kJ/mol
C≡C	120 pm	835 kJ/mol

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

Bond Energies

- Bond **breaking** requires energy (endothermic).
- Bond formation releases energy (exothermic).

$$\square \Delta H = \underbrace{\sum D(\text{bonds broken})}_{\text{energy required}} - \underbrace{\sum D(\text{bonds formed})}_{\text{energy released}}$$

Bond Energy

- We define the A-B **bond energy** (denoted BE) as the average enthalpy change for the breaking of an A-B bond in a molecule in its gas phase.
 - The enthalpy, ΔH , of a reaction is approximately equal to the **sum of the bond energies of the reactants minus the sum of the bond energies of the products**.
 - Table 9.5 lists values of some bond energies.

Table 9.5
Bond Energies (in kJ/mol)*

Single Bonds									
	H	C	N	O	S	F	Cl	Br	I
H	432								
C	411	346							
N	386	305	167						
O	459	358	201	142					
S	363	272	—	—	226				
F	565	485	283	190	284	155			
Cl	428	327	313	218	255	249	240		
Br	362	285	—	201	217	249	216	190	
I	295	213	—	201	—	278	208	175	149

Multiple Bonds									
C=C	602	C=N	615	C=O	745 (799 in CO ₂)				
C≡C	835	C≡N	887	C=O	1072				
N=N	418	N=O	607	S=O (in SO ₂)	532				
N≡N	942	O=O	494	S=O (in SO ₃)	469				

*Data are taken from J. E. Huheey, Keiter, and Keiter, *Inorganic Chemistry*, 4th ed. (New York: HarperCollins, 1993), pp. A21–A34.

Bond Energy

- To illustrate, let's estimate the ΔH for the following reaction.



- In this reaction, one C-H bond and one Cl-Cl bond must be broken.
- In turn, one C-Cl bond and one H-Cl bond are formed.

Figure 9.19: Reaction of methane with chlorine.



Bond Energy

- Referring to Table 9.5 for the bond energies, a little simple arithmetic yields ΔH .



$$\Delta H = \text{BE}(\text{C}-\text{H}) + \text{BE}(\text{Cl}-\text{Cl}) - \text{BE}(\text{C}-\text{Cl}) - \text{BE}(\text{H}-\text{Cl})$$

$$\Delta H = (411 + 240 - 327 - 428) \text{ kJ}$$

$$\Delta H = -104 \text{ kJ}$$