Chapter 8

Basic Concepts of Chemical Bonding

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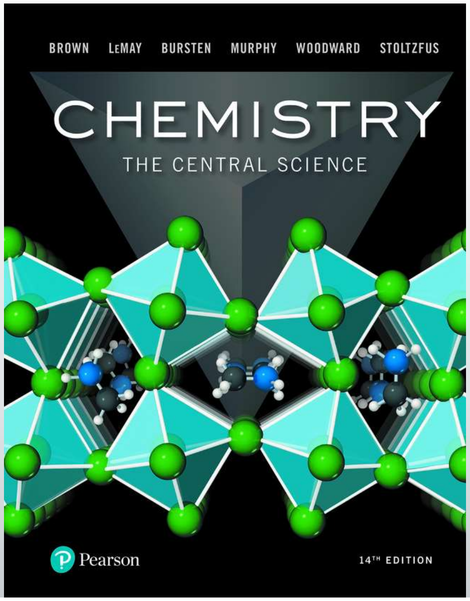
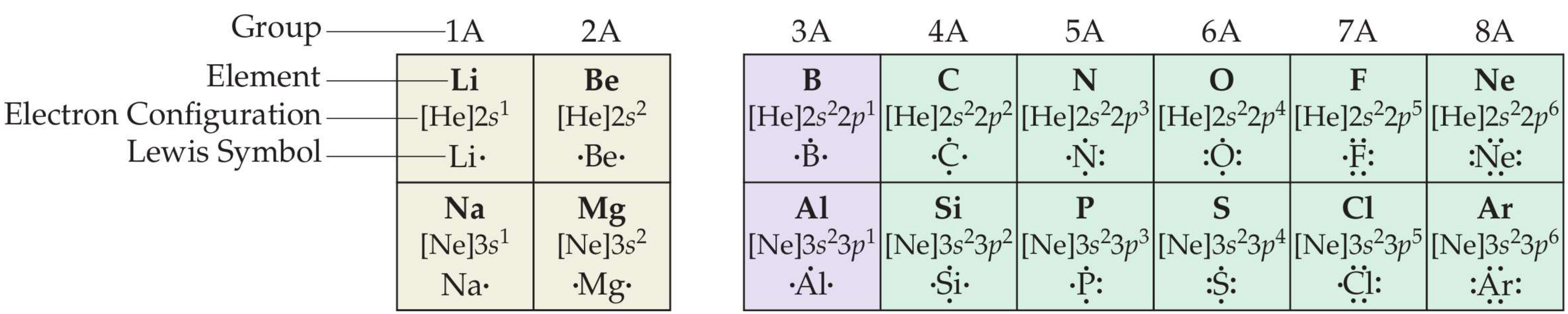


8.1 Lewis Symbols and the Octet Rule

- The Lewis symbol for an element consists of the element's chemical symbol plus a dot for each valence electron.
- The dots are placed on the four sides of the symbol, and each side can accommodate up to two electrons.



8.1 Lewis Symbols and the Octet Rule

The Octet Rule

- Atoms often gain, lose, or share electrons to achieve the same number of electrons as the noble gas closest to them in the periodic table.
- The octet rule: Atoms tend to gain, lose, or share electrons until they are surrounded by eight valence electrons.

8.2 Ionic Bonding

- Consider the following exothermic reaction for forming the ionic compound NaCl:

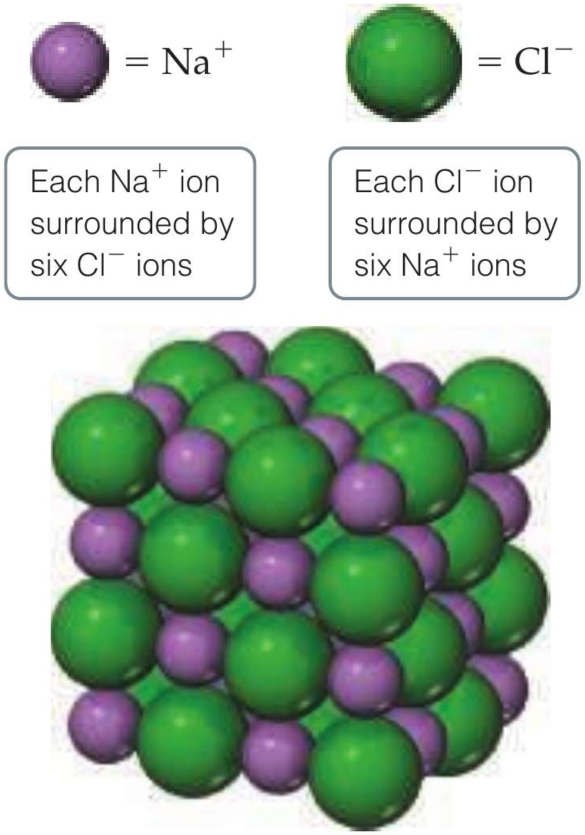
$$\mathrm{Na}(s) + \tfrac{1}{2}\,\mathrm{Cl_2}(g) \longrightarrow \mathrm{NaCl}(s) \qquad \Delta H_f^\circ = -410.9\ \mathrm{kJ}$$

- The formation of Na^+ from Na and Cl^- from Cl_2 indicates that an electron has been lost by a sodium atom and gained by a chlorine atom.
- Using Lewis electron-dot symbols, we can represent this reaction as

$$\mathrm{Na}\cdot + \cdot\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}: \longrightarrow \mathrm{Na}^+ + [:\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}:]^-$$

Energetics of Ionic Bond Formation

- What factors make the formation of ionic compounds so exothermic?
- The principal reason ionic compounds are stable is the attraction between ions of opposite charge.
- This attraction draws the ions together, releasing energy and causing many ions to form a **solid array**, or **lattice**.



▲ Figure 8.4 The crystal structure of sodium chloride.

8.2 Ionic Bonding

- A measure of how much stabilization results from arranging oppositely charged ions in an ionic solid is given by the lattice energy, which is the energy required to completely separate one mole of a solid ionic compound into its gaseous ions.

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

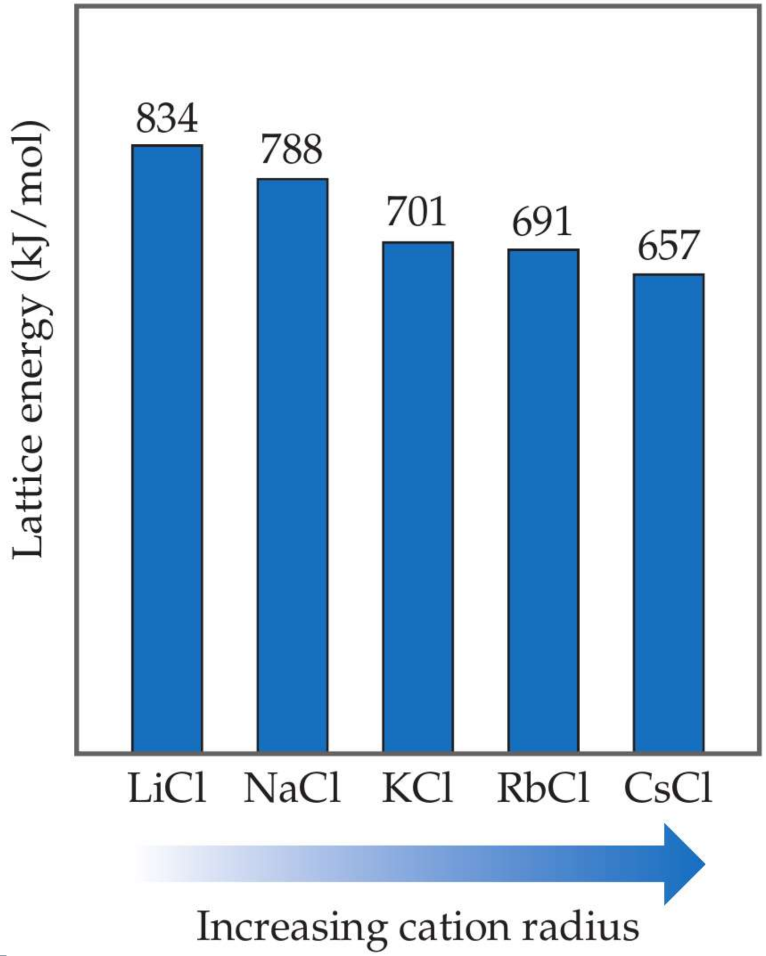
- The reverse process, the coming together of $Na^{+}(g)$ and $Cl^{-}(g)$ to form $NaCl(s)$, is highly exothermic.
- The magnitude of the lattice energy of an ionic solid depends on the charges of the ions, their sizes, and their arrangement in the solid.

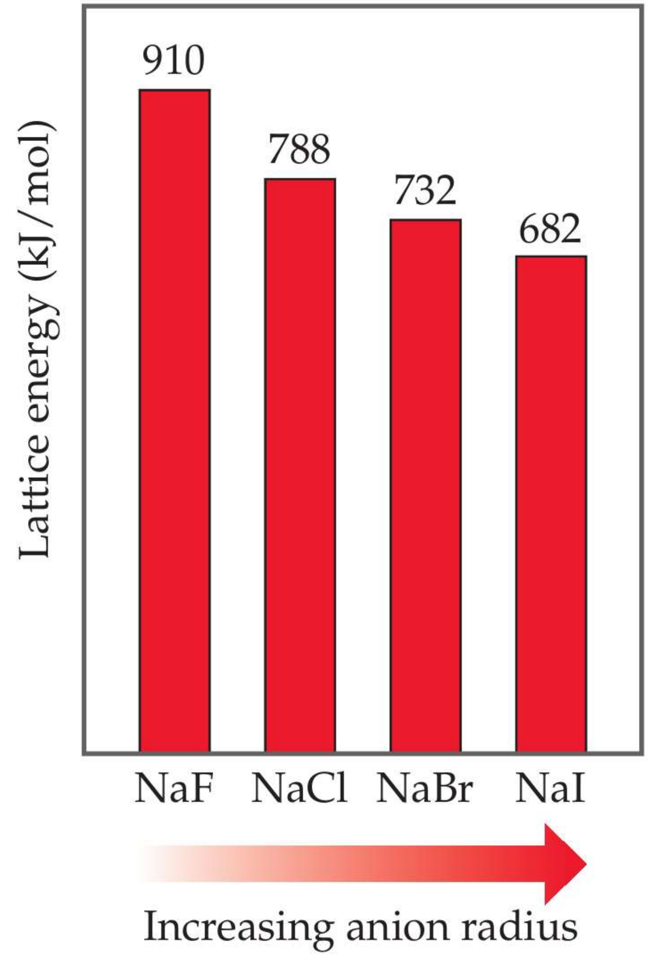
8.2 Ionic Bonding

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

- In this equation, Q_1 and Q_2 are the charges on the particles in Coulombs, with their signs; d is the distance between their centers in meters; and κ is a constant.
- Thus, for a given arrangement of ions, the lattice energy increases as the charges on the ions increase and as their radii decrease.

8.2 Ionic Bonding





Sample Exercise 8.1

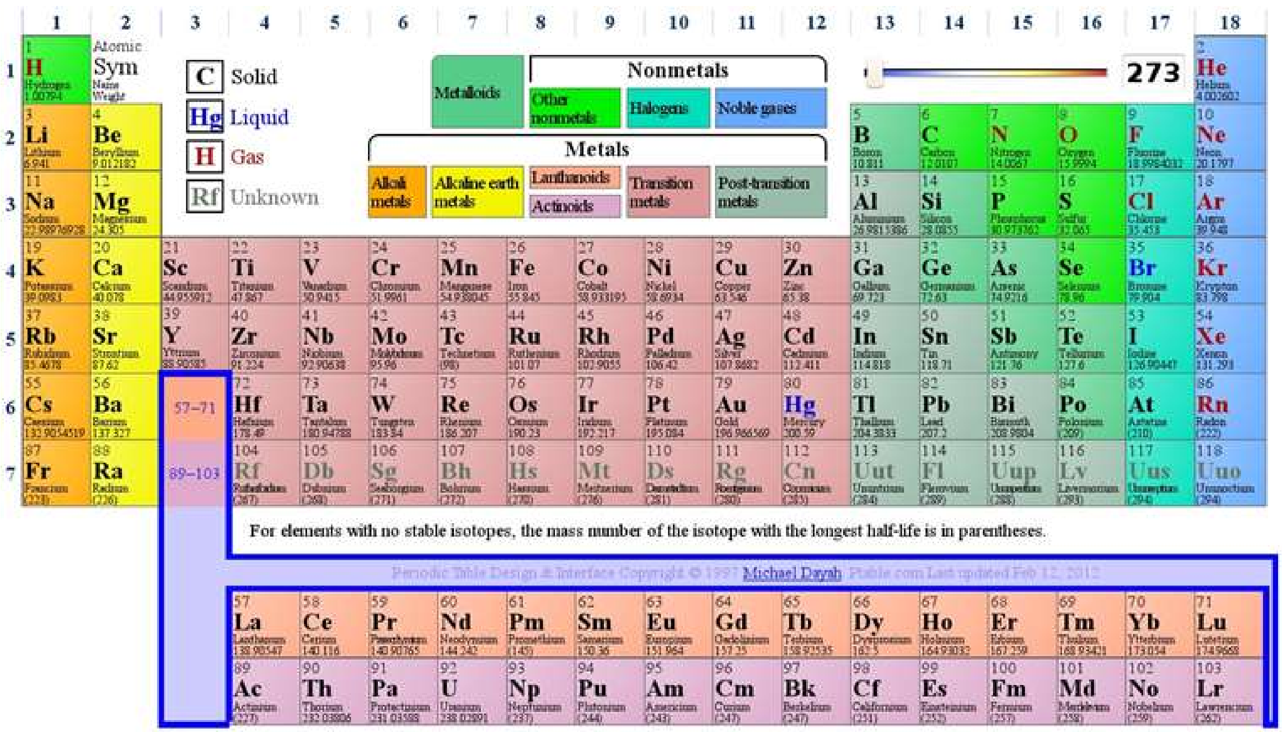
Arrange the ionic compounds NaF, CsI, and CaO in order of increasing lattice energy.

- We expect the lattice energy of CaO, which has 2^+ and 2^- ions, to be the greatest of the three.
- Because ionic size increases as we go down a group in the periodic table, the distance between Na^+ and F^- ions in NaF is less than the distance between the Cs^+ and I^- ions in CsI.
- The lattice energy of NaF should be greater than that of CsI.
- CsI < NaF < CaO

Sample Exercise 8.1: Practice Exercise 1

Arrange the ionic compounds NaCl, MgO, CsI, ScN in order of increasing lattice energy.

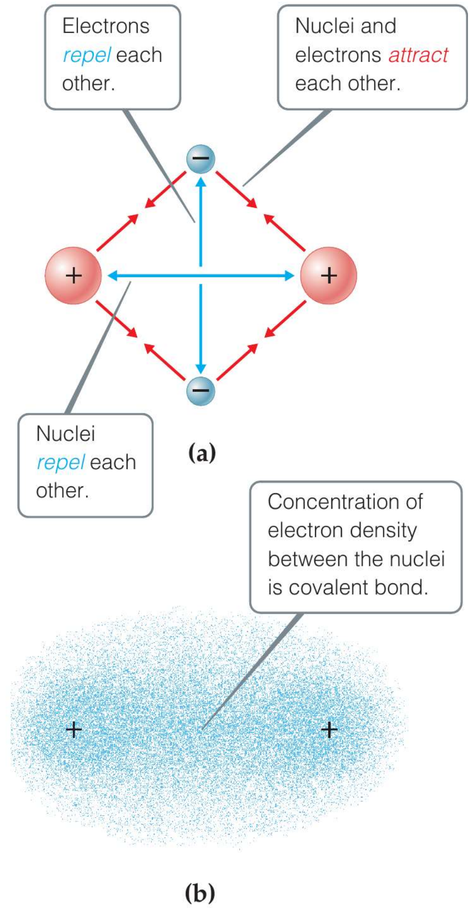
- ➢ CsI < NaCl < MgO < ScN



- A chemical bond formed by sharing a pair of electrons is a covalent bond.
- Because the hydrogen molecule, H_2, is stable, we know that the attractive forces must overcome the repulsive ones.

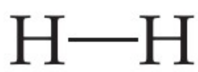
Lewis Structures

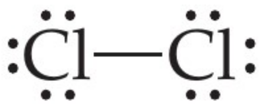
$$H\cdot + \cdot H \longrightarrow H:H$$



▲ Figure 8.7 The covalent bond in H_2.

- The structures shown here for H_2 and Cl_2 are Lewis structures, or Lewis dot structures.





- The more common convention is to show each shared electron pair or bonding pair, as a line and any unshared electron pairs (also called lone pairs or nonbonding pairs) as dots.
- For nonmetals, the number of valence electrons in a neutral atom is the same as the group number.

Sample Exercise 8.3

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

Multiple Bonds

- A shared electron pair constitutes a single covalent bond, generally referred to simply as a single bond.
- When two electron pairs are shared by two atoms, two lines are drawn in the Lewis structure, representing a double bond.

- A triple bond corresponds to the sharing of three pairs of electrons.

8.4 Bond Polarity and Electronegativity

- Bond polarity is a measure of how equally or unequally the electrons in any covalent bond are shared.
- A nonpolar covalent bond is one in which the electrons are shared equally, as in Cl_2 and N_2.
- 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.

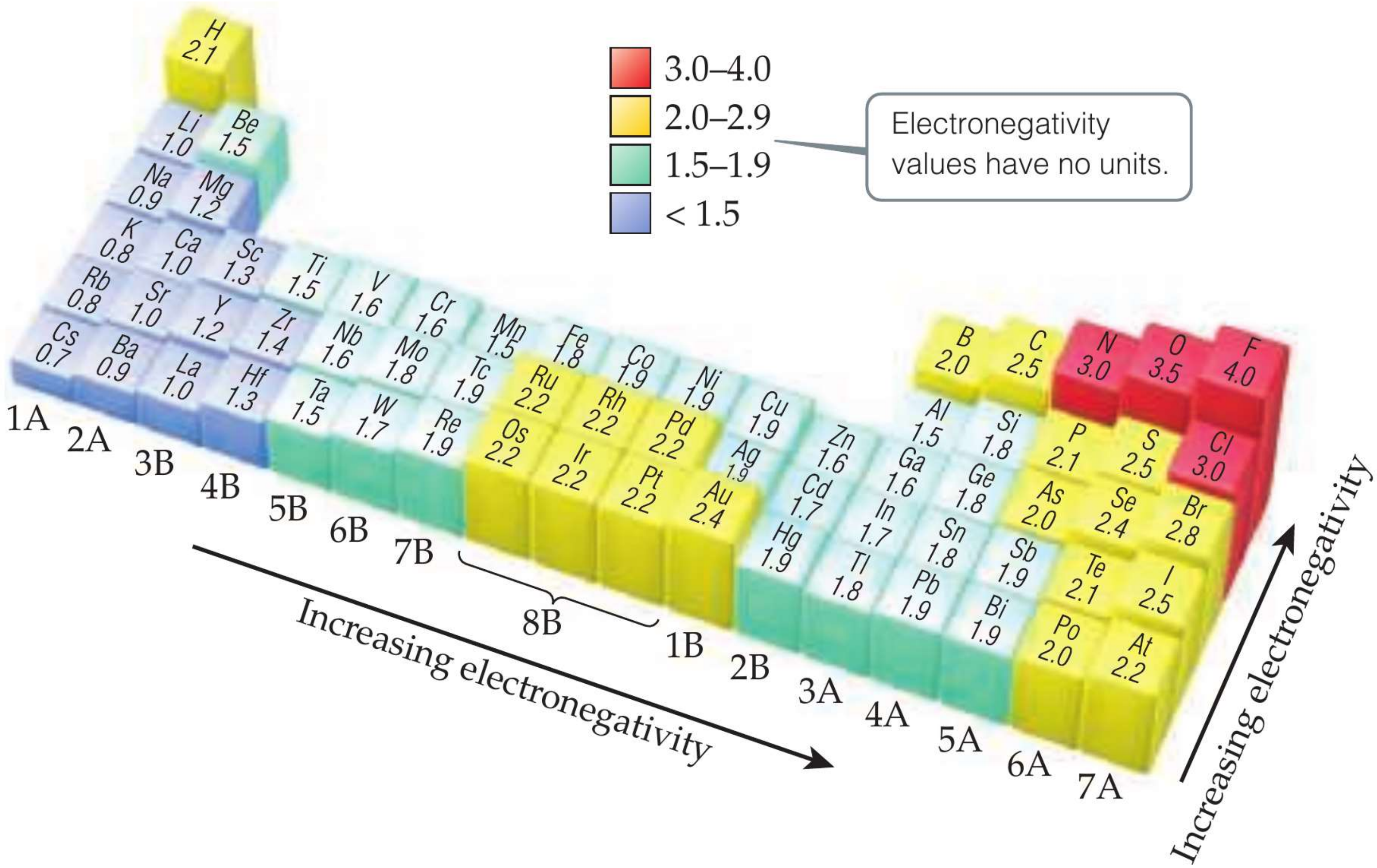
8.4 Bond Polarity and Electronegativity

Electronegativity

- Electronegativity is defined as the ability of an atom in a molecule to attract electrons to itself.
- We use a quantity called electronegativity to estimate whether a given bond is nonpolar covalent, polar covalent, or ionic.
- An atom with a **very negative electron affinity** and a **high ionization energy** both attracts electrons from other atoms and resists having its electrons attracted away; therefore, it is highly electronegative.

8.4 Bond Polarity and Electronegativity

- There is generally an increase in electronegativity from left to right across a period.
- Electronegativity decreases with increasing atomic number in a group.



▲ **Figure 8.8** Electronegativity values based on Pauling's thermochemical data.

8.4 Bond Polarity and Electronegativity

Electronegativity and Bond Polarity

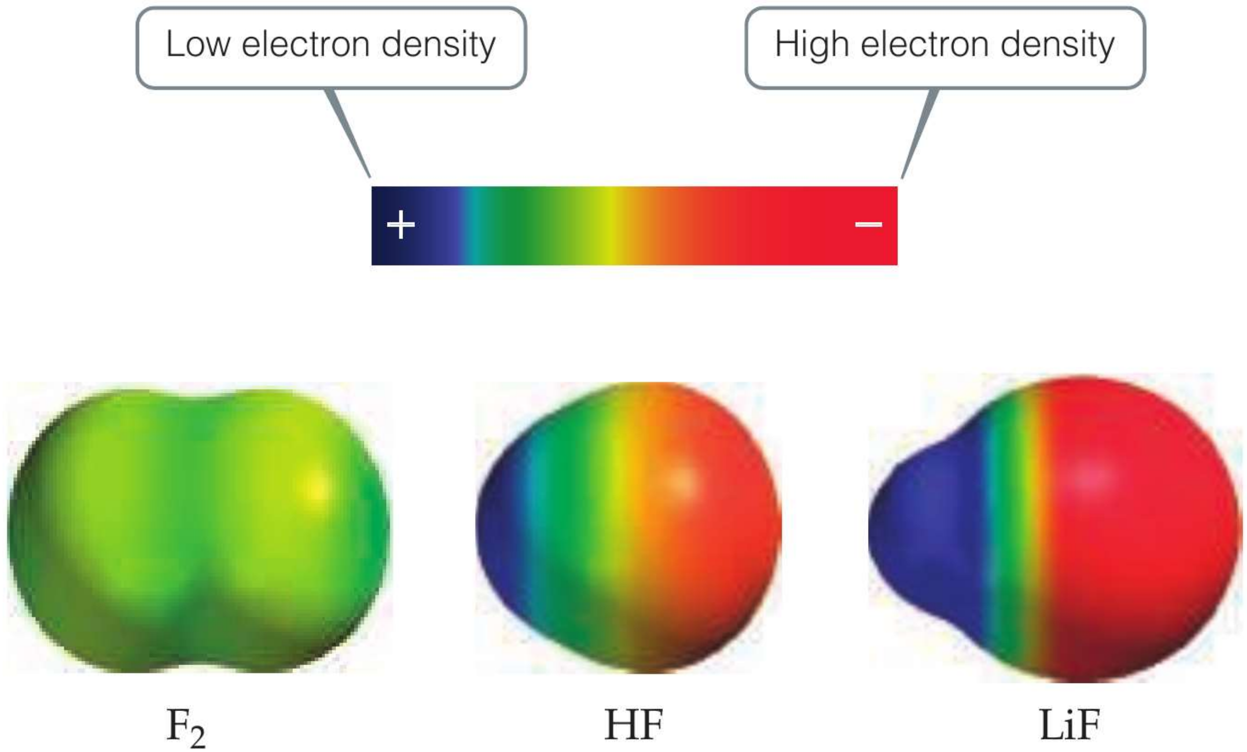
- We can use the difference in electronegativity between two atoms to gauge the polarity of the bond the atoms form.

	F_2	HF	LiF
Electronegativity difference	$4.0 - 4.0 = 0$	$4.0 - 2.1 = 1.9$	$4.0 - 1.0 = 3.0$
Type of bond	Nonpolar covalent	Polar covalent	Ionic

- In HF the more electronegative fluorine atom attracts electron density away from the less electronegative hydrogen atom, leaving a partial positive charge on the hydrogen atom and a partial negative charge on the fluorine atom.

8.4 Bond Polarity and Electronegativity

- If two atoms differ in electronegativity by more than 2.0, many chemists would consider their bond to be an ionic bond.



Sample Exercise 8.4

In each case, which bond is more polar? (a) B—Cl or C—Cl, (b) P—F or P—Cl. Indicate in each case which atom has the partial negative charge.

a. B—Cl bond is more polar; the chlorine atom carries the partial negative charge.
b. P—F bond is more polar; the fluorine atom carries the partial negative charge.

Dipole Moments

- A molecule such as HF, in which the centers of positive and negative charge do not coincide, is a polar molecule.
- We can indicate the polarity of the HF molecule in two ways:

$$\overset{\delta+}{\mathrm{H}}-\overset{\delta-}{\mathrm{F}} \quad \textit{or} \quad \overset{+\!\!\!\longrightarrow}{\mathrm{H}-\mathrm{F}}$$

- Whenever two electrical charges of equal magnitude but opposite sign are separated by a distance, a dipole is established.
- The quantitative measure of the magnitude of a dipole is called its dipole moment (μ).
- The larger the dipole moment, the more polar the bond.

8.4 Bond Polarity and Electronegativity

- If two equal and opposite charges Q+ and Q– are separated by a distance *r*, the magnitude of the dipole moment is

$$\mu = Qr$$

- Dipole moments are usually reported in debyes (D), a unit that equals $3.34 \times 10^{-30}\ \mathrm{C \cdot m}$.
- Notice that as we proceed from HF to HI, the electronegativity difference decreases and the bond length increases.

Sample Exercise 8.5

The bond length in the HCl molecule is 1.27 Å.

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

$$\mu = Qr$$

$$= \left(1.60 \times 10^{-19}\ \mathrm{C}\right)\left(1.27 \times 10^{-10}\ \mathrm{m}\right)\left(\frac{1\ \mathrm{D}}{3.34 \times 10^{-30}\ \mathrm{C \cdot m}}\right)$$

$$= 6.08\ \mathrm{D}$$

Sample Exercise 8.5

b. The experimentally measured dipole moment of HCl(*g*) is 1.08 D. What magnitude of charge, in units of *e*, on the H and Cl atoms leads to this dipole moment?

$$Q = \frac{\mu}{r}$$

$$= \frac{(1.08\ \mathrm{D})\left(\dfrac{3.34 \times 10^{-30}\ \mathrm{C \cdot m}}{1\ \mathrm{D}}\right)}{1.27 \times 10^{-10}\ \mathrm{m}}\left(\frac{1\ e}{1.60 \times 10^{-19}\ \mathrm{C}}\right) = 0.178\ e$$

$$\overset{0.178+}{\mathrm{H}} — \overset{0.178-}{\mathrm{Cl}}$$

8.4 Bond Polarity and Electronegativity

Comparing Ionic and Covalent Bonding

- When covalent bonding is dominant, we expect compounds to exist as molecules, having all the properties we associate with molecular substances, such as relatively low melting and boiling points and nonelectrolyte behavior when dissolved in water.
- When ionic bonding is dominant, we expect the compounds to be brittle, high-melting solids with extended lattice structures, exhibiting strong electrolyte behavior when dissolved in water.

8.5 Drawing Lewis Structures

1. Sum the valence electrons from all atoms, taking into account overall charge. For an anion, add one electron to the total for each negative charge. For a cation, subtract one electron from the total for each positive charge.
2. Write the symbols for the atoms, show which atoms are attached to which, and connect them with a single bond. In many polyatomic molecules and ions, the central atom is usually written first. Remember that the central atom is generally less electronegative than the atoms surrounding it.
3. Complete the octets around all the atoms bonded to the central atom.
4. Place any remaining electrons on the central atom.
5. If there are not enough electrons to give the central atom an octet, try multiple bonds.

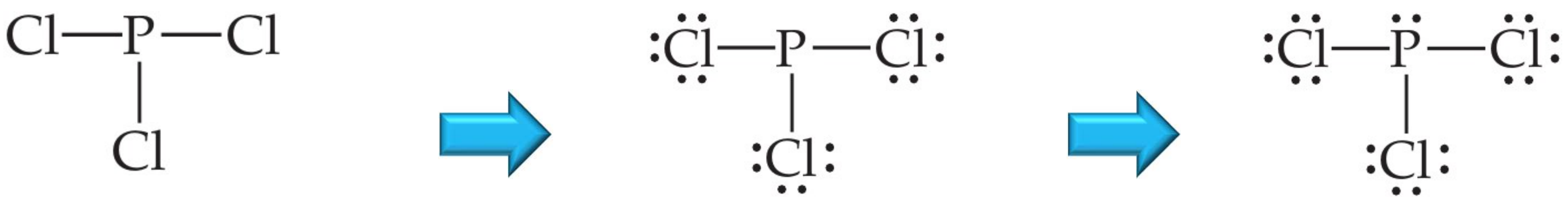
Sample Exercise 8.6

Draw the Lewis structure for phosphorus trichloride, PCl_3.

Number of valence electronson P = 5

Number of valence electronson Cl = 7

The total number of valence electrons = 5 + (3)(7) = 26



Sample Exercise 8.7

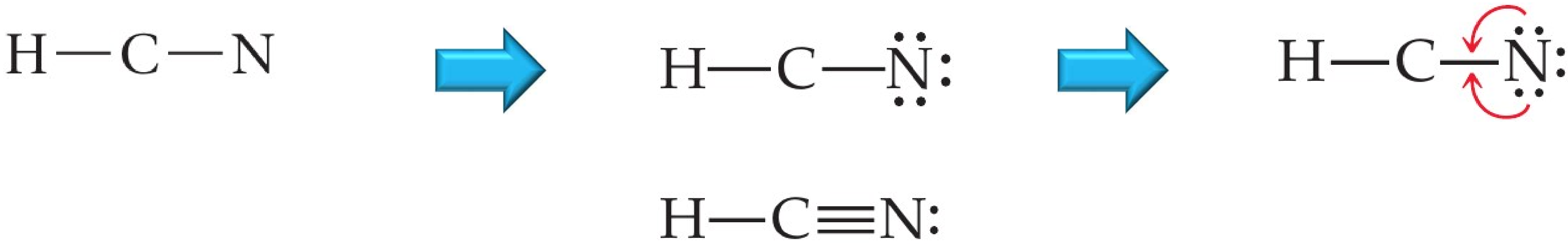
Draw the Lewis structure for HCN.

Number of valence electronson C = 4

Number of valence electronson N = 5

Number of valence electronson H = 1

The total number of valence electrons = 4 + 5 + 1 = 10



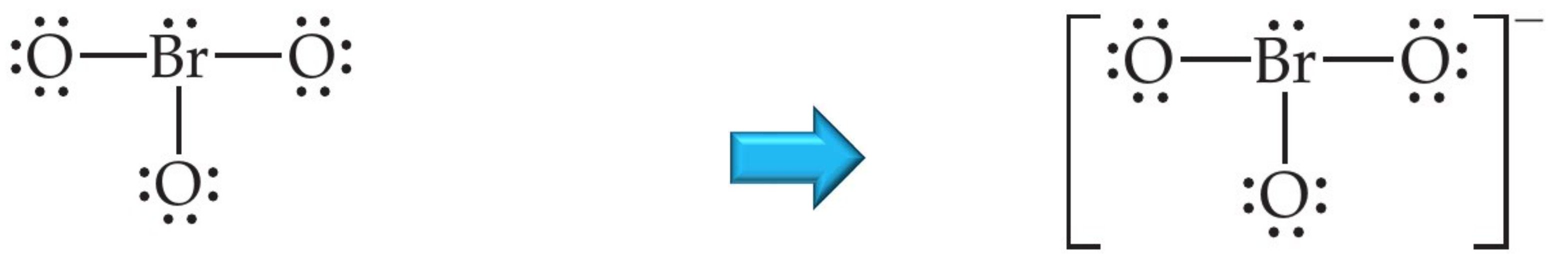
Sample Exercise 8.8

Draw the Lewis structure for the BrO_3^- ion.

Number of valence electronson Br = 7

Number of valence electronson O = 6

The total number of valence electrons = 7 + (3)(6) + 1 = 26



Formal Charge and alternative Lewis Structures

- The formal charge of any atom in a molecule is the charge the atom would have if each bonding electron pair in the molecule were shared equally between its two atoms.

$$\text{Formal charge} = \text{valence electrons} - \frac{1}{2}(\text{bonding electrons}) - \text{nonbonding electrons}$$

- It is important to remember that formal charges do not represent real charges on atoms.

8.5 Drawing Lewis Structures

- Let's practice by calculating the formal charges for the atoms in the cyanide ion, CN^-, which has the Lewis structure

$$[:\mathrm{C}{\equiv}\mathrm{N}:]^-$$

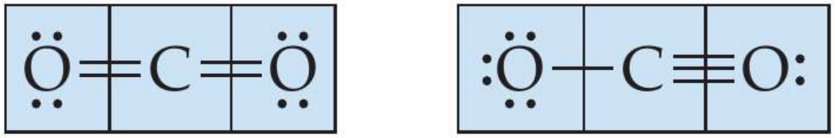
$$\text{Formal charge C} = 4 - \frac{1}{2}(6) - 2 = -1$$

$$\text{Formal charge N} = 5 - \frac{1}{2}(6) - 2 = 0$$

$$[:\overset{-1}{\mathrm{C}}{\equiv}\overset{0}{\mathrm{N}}:]^-$$

8.5 Drawing Lewis Structures

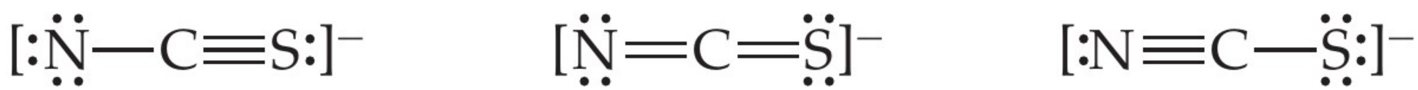
- The dominant Lewis structure is generally the one in which the atoms bear formal charges closest to zero.
- A Lewis structure in which any negative charges reside on the more electronegative atoms is generally more dominant than one that has negative charges on the less electronegative atoms.



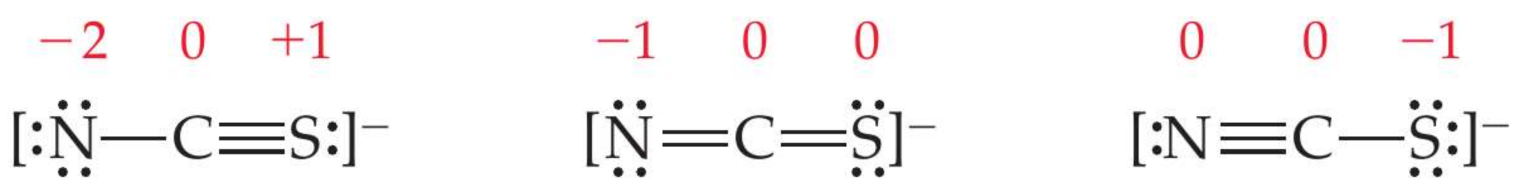
	O	C	O	O	C	O
Valence electrons:	6	4	6	6	4	6
−(Electrons assigned to atom):	6	4	6	7	4	5
Formal charge:	0	0	0	−1	0	+1
		Yes			No	

Sample Exercise 8.9

Three possible Lewis structures for the thiocyanate ion, NCS^-, are



a. Determine the formal charges in each structure.

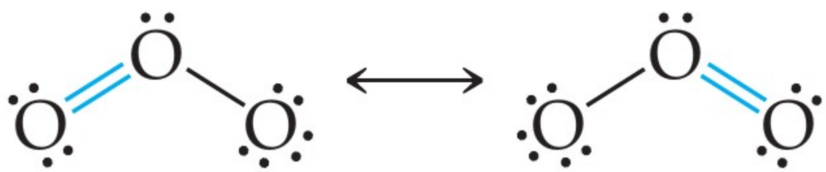


b. Based on the formal charges, which Lewis structure is the dominant one?

➢ N is more electronegative than C or S; therefore, we expect any negative formal charge to reside on the N atom.

8.6 Resonance Structures

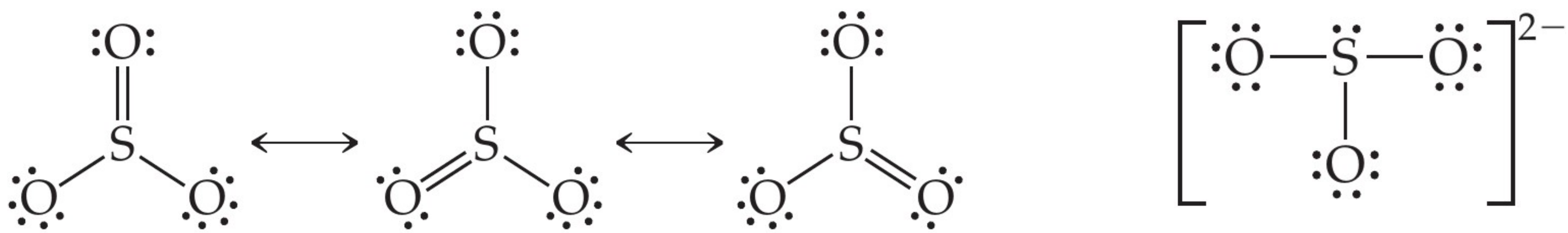
- When the placement of the atoms in alternative but completely equivalent Lewis structures is the same, but the placement of the electrons is different; we call Lewis structures of this sort resonance structures.
- Consider ozone, O_3,



- For some molecules or ions, all possible Lewis structures may not be equivalent; in other words, one or more resonance structures are more dominant than others.

8.6 Resonance Structures

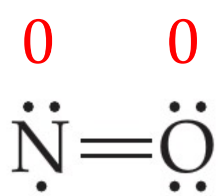
Which is predicted to have the shorter sulfur–oxygen bonds, SO_3 or SO_3^{2-}?



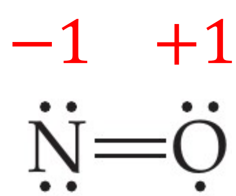
➢ SO_3 should have the shorter S—O bonds and SO_3^{2-} the longer ones.

Odd Number of Electrons

- In a few molecules and polyatomic ions, such as ClO_2, NO, NO_2, and O_2^-, the number of valence electrons is odd.
- **Example**: NO contains 5 + 6 = 11 valence electrons. The two most important Lewis structures for this molecule are



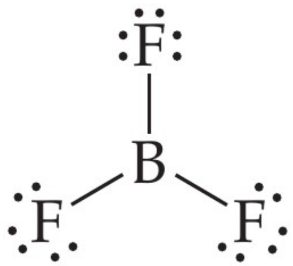
and

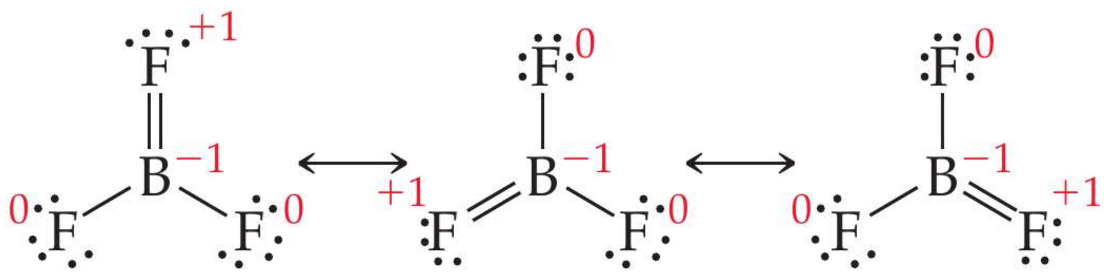


Dominant   Less important

Less than an Octet of Valence Electrons

- This situation is also relatively rare and is most often encountered in compounds of boron and beryllium.

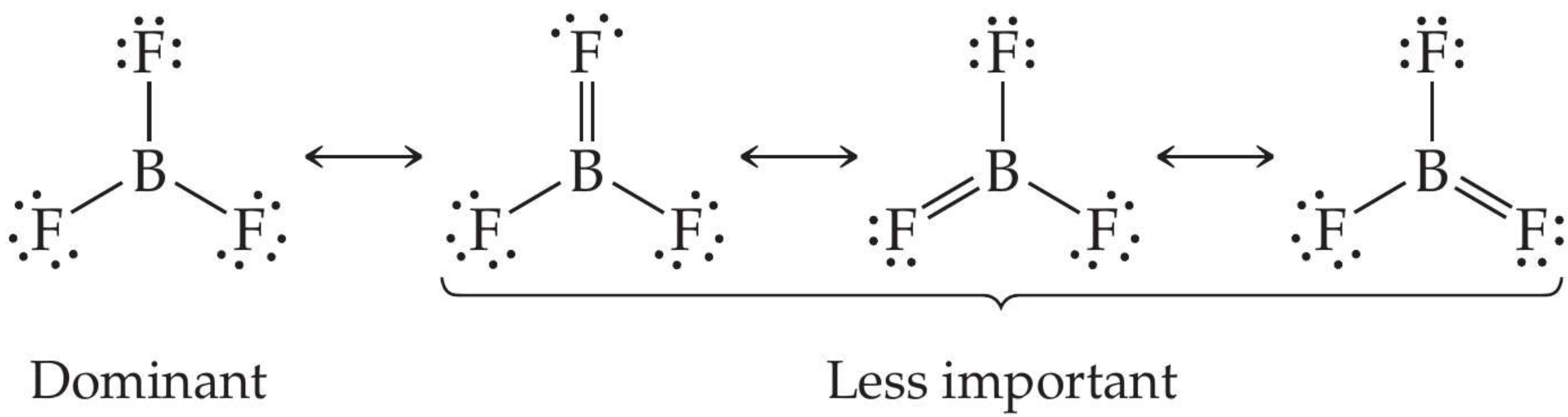




- Each of these structures forces a fluorine atom to share additional electrons with the boron atom, which is inconsistent with the high electronegativity of fluorine.

8.7 Exceptions to the Octet Rule

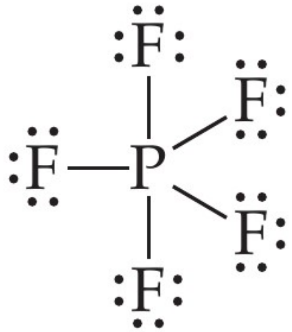
- In fact, the formal charges tell us that this is an unfavorable situation.



8.7 Exceptions to the Octet Rule

More than an Octet of Valence Electrons

- Molecules and ions with more than an octet of electrons around the central atom are often called hypervalent.
- Hypervalent molecules are formed only for central atoms from period 3 and below in the periodic table.
- The principal reason for their formation is the relatively larger size of the central atom.
- **Example**: the Lewis structure for PF_5 is



8.7 Exceptions to the Octet Rule

- Because size is a factor, hypervalent molecules occur most often when the central atom is bonded to the smallest and most electronegative atoms; F, Cl, and O.
- The notion that a valence shell can contain more than eight electrons is also consistent with the presence of unfilled *nd* orbitals in atoms from period 3 and below.
- Most chemists now believe that the larger size of the atoms from periods 3 through 6 is more important to explain hypervalency than is the presence of unfilled d orbitals.

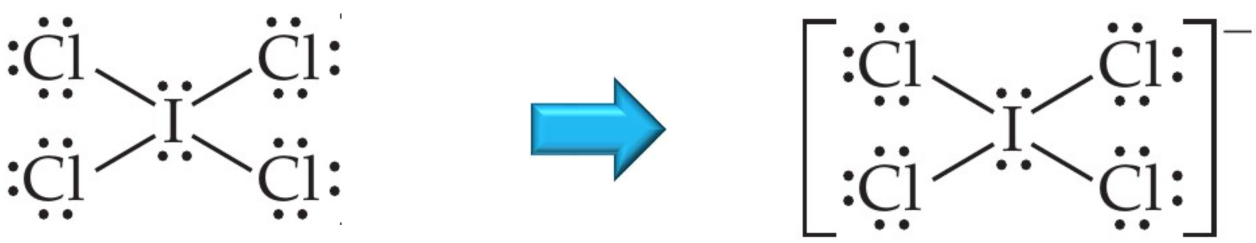
Sample Exercise 8.11

Draw the Lewis structure for ICl_4^-.

Number of valence electronson I $= 7$

Number of valence electronson Cl $= 7$

The total number of valence electrons $= 7 + (4)(7) + 1 = 36$



8.8 Strengths and Lengths of Covalent Bonds

- In general, as the number of bonds between two atoms increases, the bond grows shorter and stronger.

C—C	C=C	C≡C
1.54 Å	1.34 Å	1.20 Å
348 kJ/mol	614 kJ/mol	839 kJ/mol