

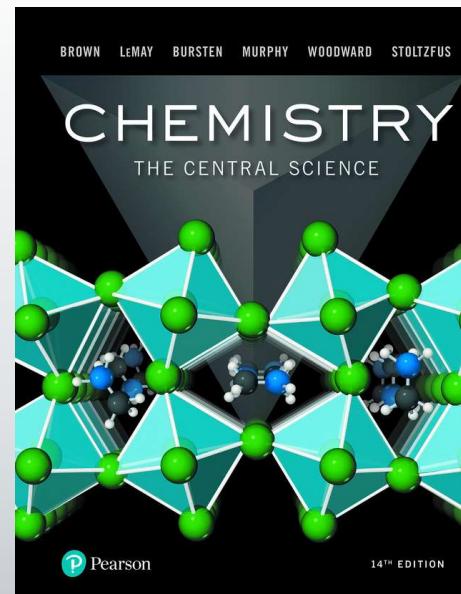
Chapter 8

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.

Group	1A	2A	3A	4A	5A	6A	7A	8A
Element	Li	Be	B	C	N	O	F	Ne
Electron Configuration	[He]2s ¹	[He]2s ²	[He]2s ² 2p ¹	[He]2s ² 2p ²	[He]2s ² 2p ³	[He]2s ² 2p ⁴	[He]2s ² 2p ⁵	[He]2s ² 2p ⁶
Lewis Symbol	Li·	·Be·	·B·	·C·	·N·	·O·	·F·	·Ne·
	Na	Mg	Al	Si	P	S	Cl	Ar
	[Ne]3s ¹	[Ne]3s ²	[Ne]3s ² 3p ¹	[Ne]3s ² 3p ²	[Ne]3s ² 3p ³	[Ne]3s ² 3p ⁴	[Ne]3s ² 3p ⁵	[Ne]3s ² 3p ⁶
	Na·	·Mg·	·Al·	·Si·	·P·	·S·	·Cl·	·Ar·

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:



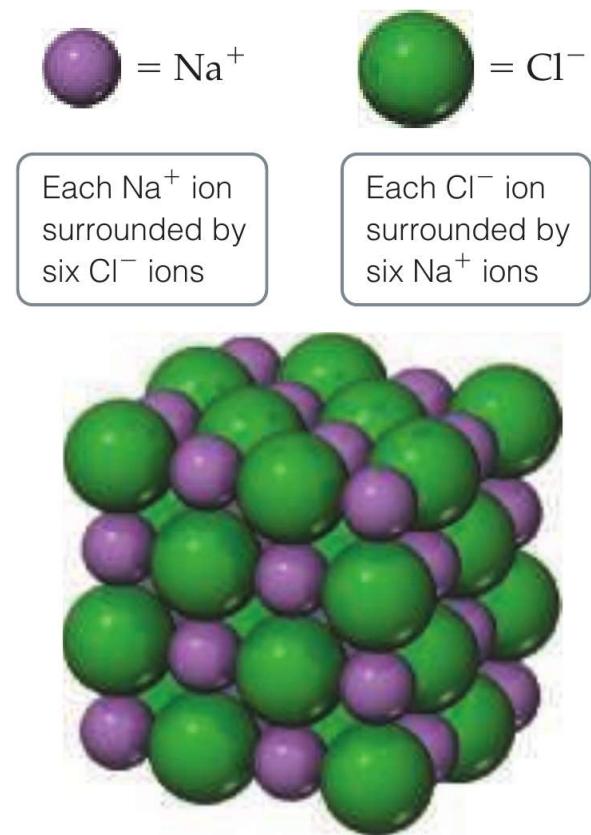
- ❖ The formation of Na^+ from Na and Cl^- from Cl_2 indicates that an electron has been lost by a sodium atom and gained by a chlorine atom.
- ❖ Using Lewis electron-dot symbols, we can represent this reaction as



8.2 Ionic Bonding

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.



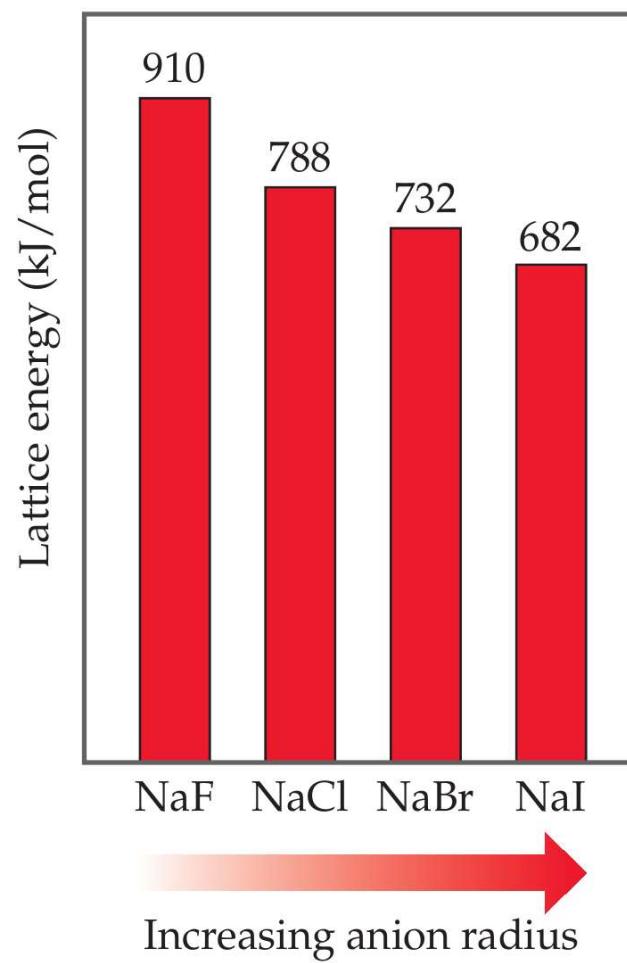
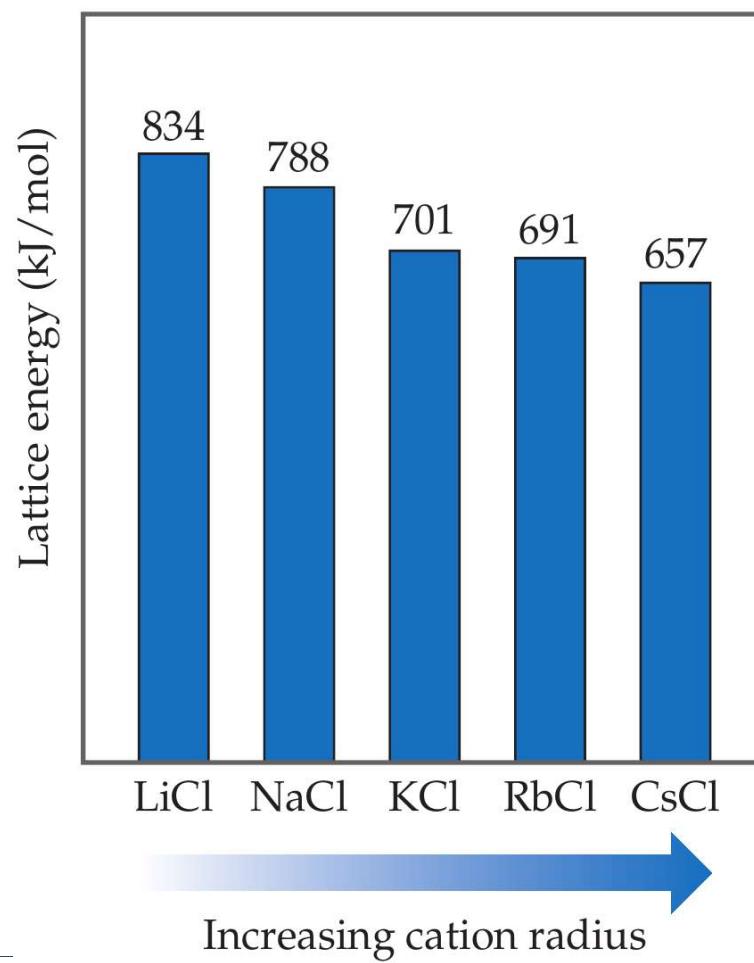
- ❖ The reverse process, the coming together of $\text{Na}^+(g)$ and $\text{Cl}^-(g)$ to form $\text{NaCl}(s)$, is highly exothermic.
- ❖ The magnitude of the lattice energy of an ionic solid depends on the charges of the ions, their sizes, and their arrangement in the solid.

8.2 Ionic Bonding

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

- ❖ 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.
- $\text{CsI} < \text{NaF} < \text{CaO}$

Sample Exercise 8.1: Practice Exercise 1

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

➤ $\text{CsI} < \text{NaCl} < \text{MgO} < \text{ScN}$

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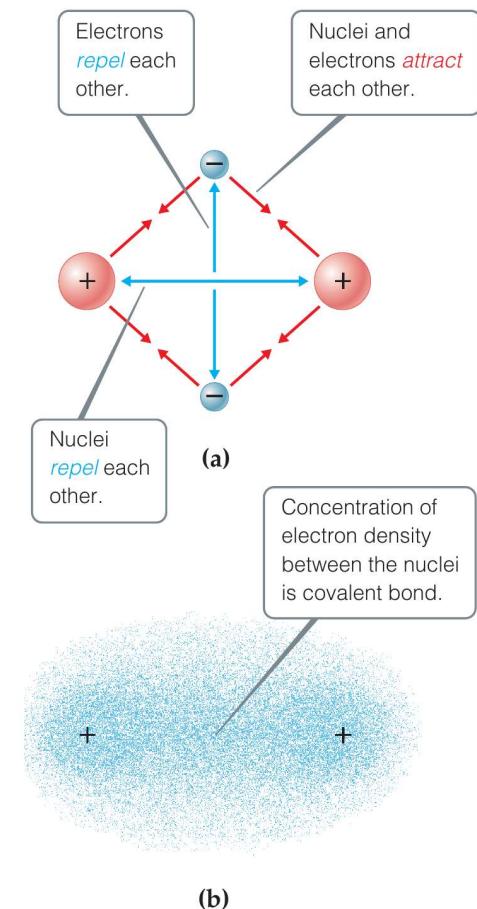
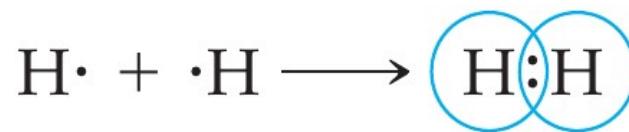
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
1 H Hydrogen 1.00794	2 He Helium 4.002602	3 Li Lithium 6.941	4 Be Beryllium 9.01182	5 C Solid	6 Hg Liquid	7 Al Unknown	8 Metalloids Other nonmetals	9 Nonmetals Halogens	10 Nonmetals Noble gases	11 Metals Alkali metals	12 Metals Alkaline earth metals	13 Metals Lanthanoids	14 Metals Transition metals	15 Metals Post-transition metals	16 He Helium 4.002602	17 He Helium 4.002602		
2 Li Lithium 6.941	3 Be Beryllium 9.01182	4 C Solid	5 Hg Liquid	6 Al Unknown	7 Si Silicon 28.0353	8 B Boron 10.831	9 C Carbon 12.0107	10 N Nitrogen 14.0067	11 O Oxygen 15.9994	12 F Fluorine 18.998403	13 Ne Neon 20.1791	14 Na Sodium 22.98976928	15 Mg Magnesium 24.305	16 Al Aluminum 26.98113865	17 Si Silicon 28.0353	18 Cl Chlorine 35.453	19 Ar Argon 39.948	
3 Na Sodium 22.98976928	4 Mg Magnesium 24.305	5 Sc Scandium 44.95912	6 Ti Titanium 47.867	7 V Vanadium 50.9415	8 Cr Chromium 51.9861	9 Mn Manganese 54.938045	10 Fe Iron 55.845	11 Co Cobalt 58.933195	12 Ni Nickel 58.6934	13 Cu Copper 63.546	14 Zn Zinc 65.38	15 Ga Gallium 69.723	16 Ge Germanium 72.63	17 As Arsenic 74.9516	18 Se Selenium 78.96	19 Br Bromine 79.904	20 Kr Krypton 83.798	
4 K Potassium 39.0983	5 Ca Calcium 40.078	6 Sc Scandium 44.95912	7 Ti Titanium 47.867	8 V Vanadium 50.9415	9 Cr Chromium 51.9861	10 Mn Manganese 54.938045	11 Fe Iron 55.845	12 Co Cobalt 58.933195	13 Ni Nickel 58.6934	14 Cu Copper 63.546	15 Zn Zinc 65.38	16 Ga Gallium 69.723	17 Ge Germanium 72.63	18 As Arsenic 74.9516	19 Se Selenium 78.96	20 Br Bromine 79.904	21 Ar Argon 39.948	
5 Rb Rubidium 35.4078	6 Sr Strontium 87.62	7 Y Yttrium 87.224	8 Zr Zirconium 92.90638	9 Nb Niobium 91.924	10 Mo Molybdenum 95.96	11 Tc Technetium (98)	12 Ru Ruthenium 101.07	13 Rh Rhodium 102.9035	14 Pd Rhodium 106.42	15 Ag Silver 107.8682	16 Cd Cadmium 112.411	17 In Indium 114.818	18 Sn Tin 118.71	19 Sb Antimony 121.76	20 Te Tellurium 127.6	21 I Iodine 126.95447	22 Xe Xenon 131.291	23 Rn Radon (222)
6 Cs Cesium 131.9054519	7 Ba Barium 137.327	8 Hf Hafnium 178.49733	9 Ta Tantalum 180.94733	10 W Tungsten 183.207	11 Re Rhenium 186.207	12 Os Osmium 190.23	13 Ir Iridium 192.217	14 Pt Platinum 195.084	15 Au Gold 196.986569	16 Hg Mercury 200.59	17 Tl Thallium 204.3833	18 Pb Lead 207.2	19 Bi Bismuth 209.9904	20 Po Polonium (209)	21 At Astatine (210)	22 Rn Radon (222)	23 Lu Lutetium (174.9668)	
7 Fr Francium (223)	8 Ra Radium (226)	9 Fr Rutherfordium (267)	10 Db Dubnium (268)	11 Sg Sesquium (270)	12 Bh Bohrium (270)	13 Hs Hassium (270)	14 Mt Meitnerium (281)	15 Ds Darmstadtium (280)	16 Rg Roentgenium (283)	17 Cn Copernicium (285)	18 Uut Ununtrium (284)	19 Fl Flame (289)	20 Uup Ununpentium (289)	21 Lv Livermorium (293)	22 Uus Ununseptium (294)	23 Uuo Ununoctium (294)	24 Lu Lutetium (174.9668)	

For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.

8.3 Covalent Bonding

- ❖ 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



▲ Figure 8.7 The covalent bond in H_2 .

8.3 Covalent Bonding

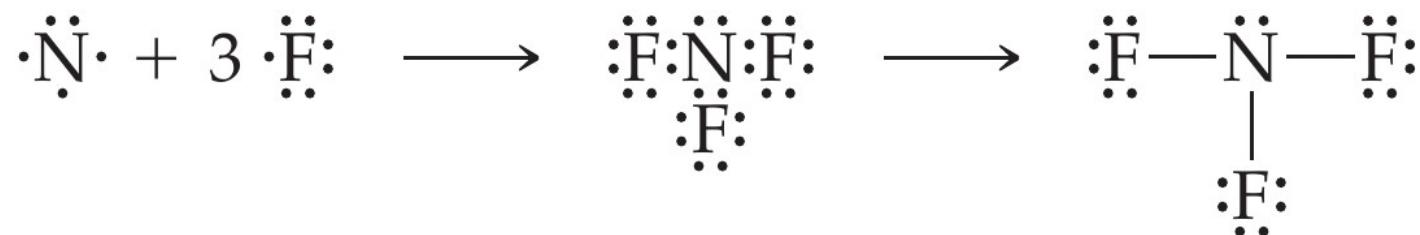
- ❖ The structures shown here for H_2 and Cl_2 are **Lewis structures**, or **Lewis dot structures**.



- ❖ 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.



8.3 Covalent Bonding

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.

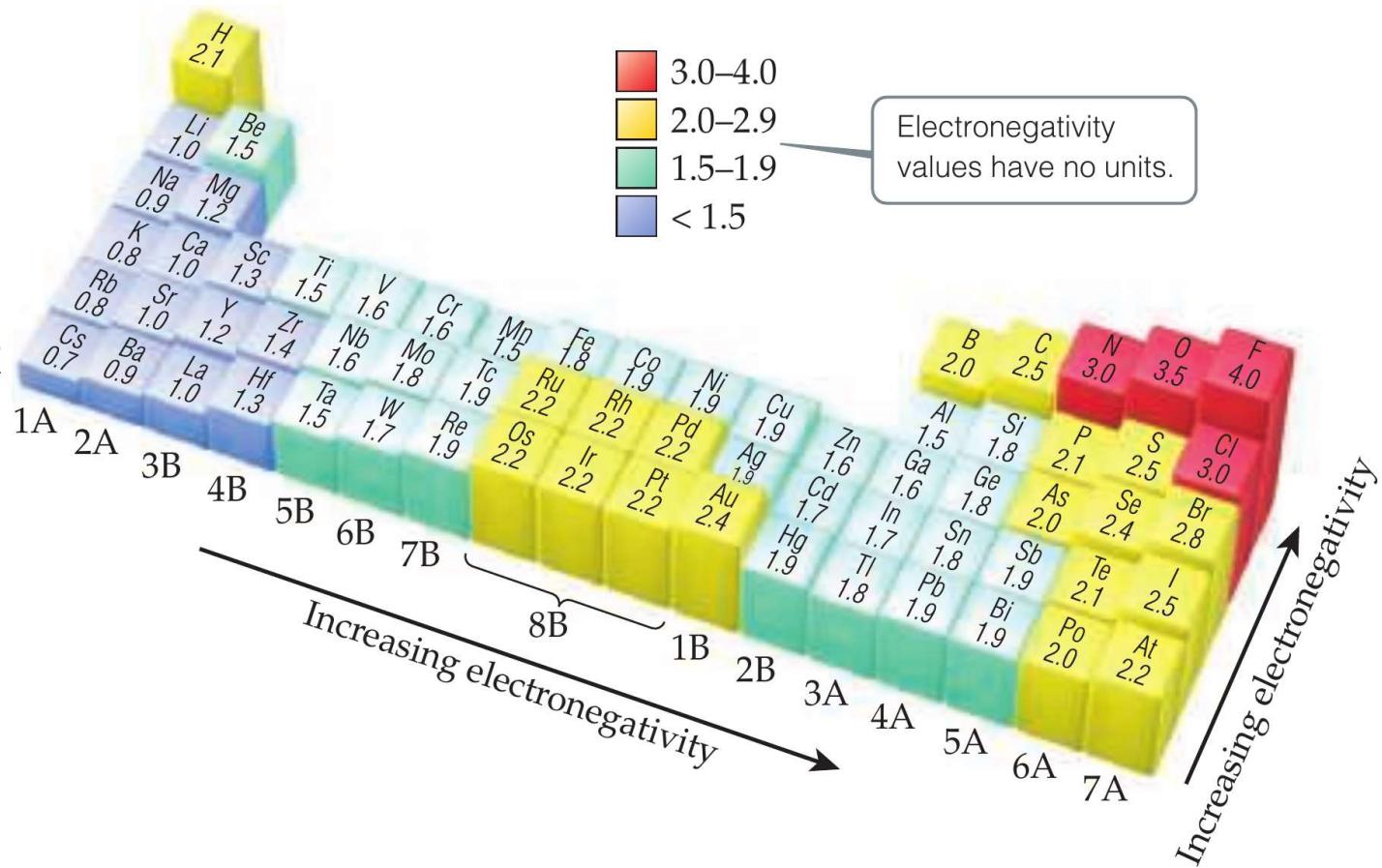
8.4 Bond Polarity and Electronegativity

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 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

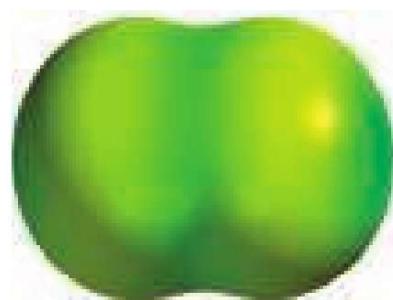
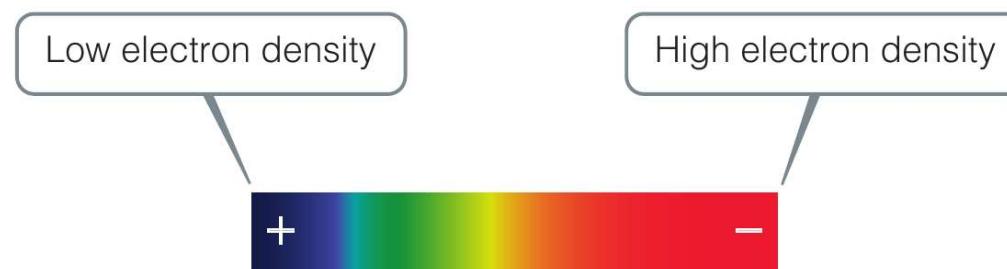
- ❖ We can use the difference in electronegativity between two atoms to gauge the polarity of the bond the atoms form.

	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

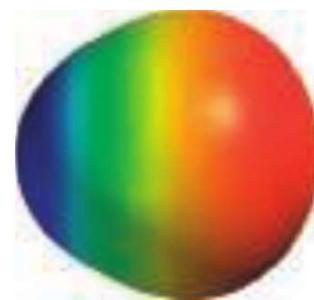
- ❖ In HF the more electronegative fluorine atom attracts electron density away from the less electronegative hydrogen atom, leaving a partial positive charge on the hydrogen atom and a partial negative charge on the fluorine atom.

8.4 Bond Polarity and Electronegativity

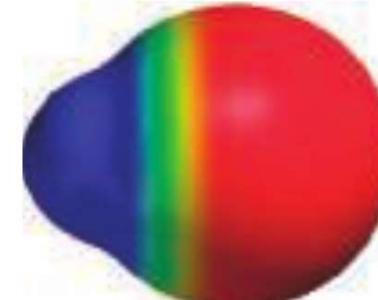
- ❖ If two atoms differ in electronegativity by more than 2.0, many chemists would consider their bond to be an ionic bond.



F_2



HF



LiF

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.

8.4 Bond Polarity and Electronegativity

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:



- ❖ 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 $3.34 \times 10^{-30} \text{ C} \cdot \text{m}$.
- ❖ 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.

$$\mu = Qr$$

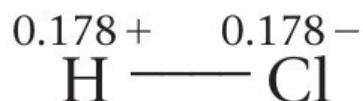
$$= (1.60 \times 10^{-19} \text{ C})(1.27 \times 10^{-10} \text{ m}) \left(\frac{1 \text{ D}}{3.34 \times 10^{-30} \text{ C} \cdot \text{m}} \right)$$

$$= 6.08 \text{ D}$$

Sample Exercise 8.5

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

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



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.

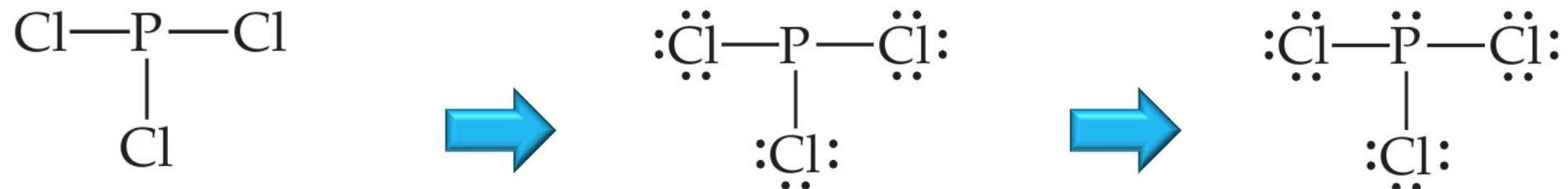
Sample Exercise 8.6

Draw the Lewis structure for phosphorus trichloride, PCl_3 .

Number of valence electrons on P = 5

Number of valence electrons on Cl = 7

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



Sample Exercise 8.7

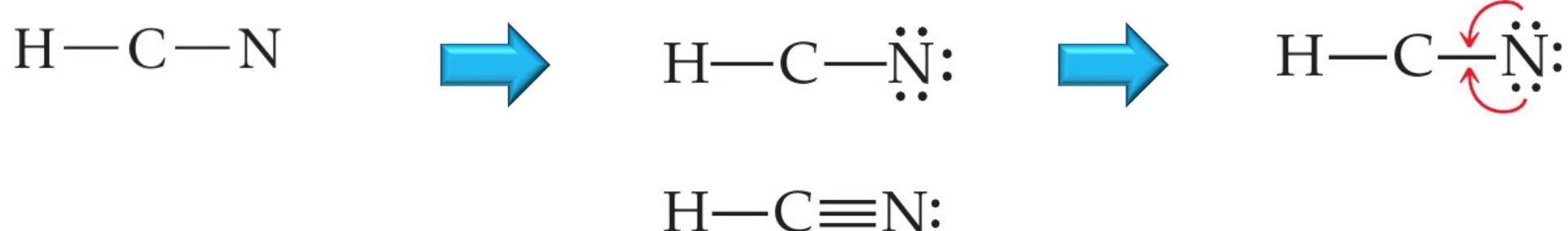
Draw the Lewis structure for HCN.

Number of valence electrons on C = 4

Number of valence electrons on N = 5

Number of valence electrons on H = 1

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



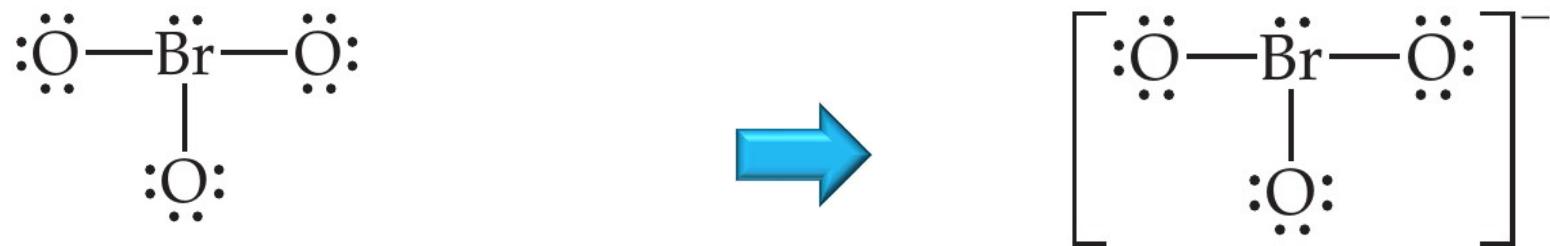
Sample Exercise 8.8

Draw the Lewis structure for the BrO_3^- ion.

Number of valence electrons on Br = 7

Number of valence electrons on O = 6

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



8.5 Drawing Lewis Structures

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



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

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

-1 0



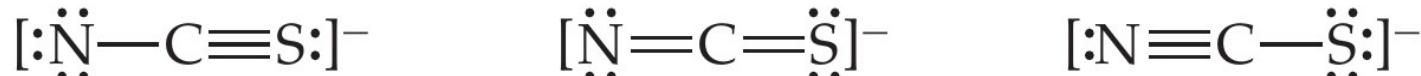
8.5 Drawing Lewis Structures

- ❖ 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.

	$\ddot{\text{O}}=\text{C}=\ddot{\text{O}}$			$:\ddot{\text{O}}-\text{C}\equiv\text{O}:$		
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		

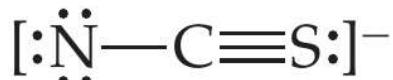
Sample Exercise 8.9

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

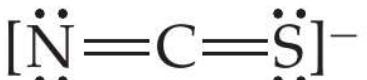


a. Determine the formal charges in each structure.

$-2 \quad 0 \quad +1$



$-1 \quad 0 \quad 0$



$0 \quad 0 \quad -1$

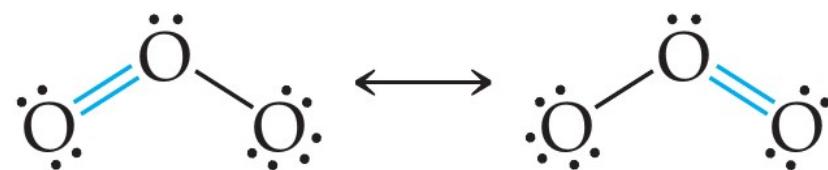


b. Based on the formal charges, which Lewis structure is the dominant one?

➤ 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

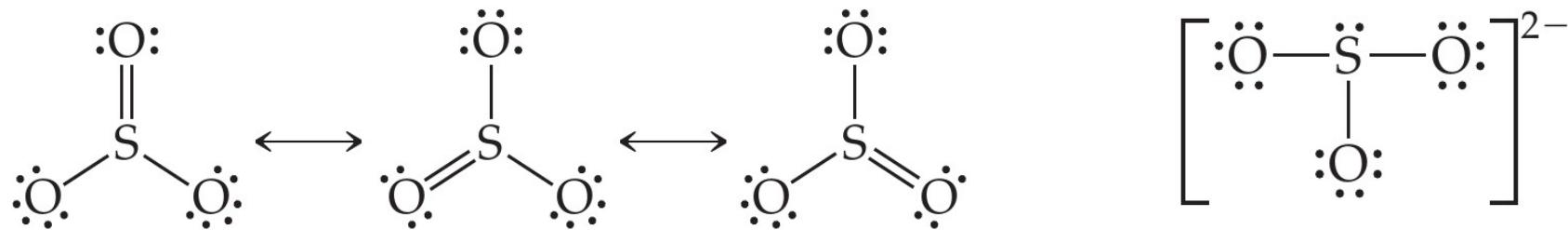
- ❖ When the placement of the atoms in alternative but completely equivalent Lewis structures is the same, but the placement of the electrons is different; we call Lewis structures of this sort **resonance structures**.
- ❖ Consider ozone, O_3 ,



- ❖ 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-} ?

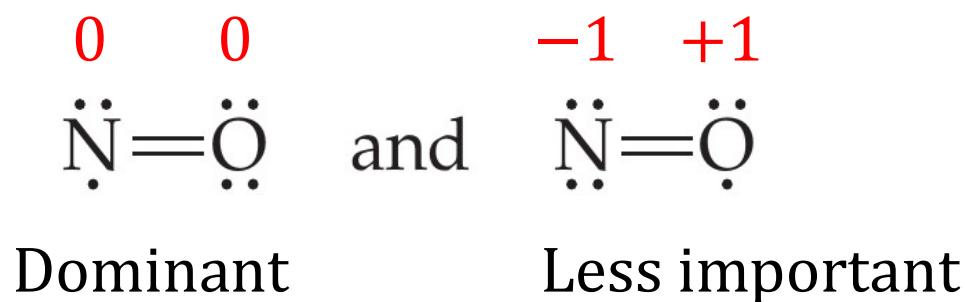


➤ SO_3 should have the shorter S–O bonds and SO_3^{2-} the longer ones.

8.7 Exceptions to the Octet Rule

Odd Number of Electrons

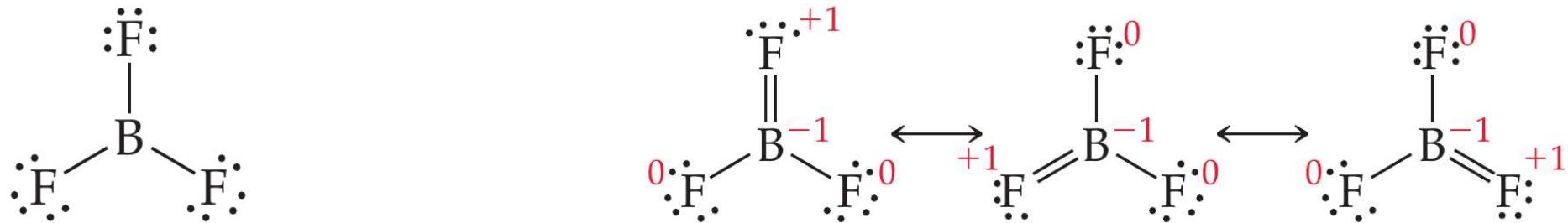
- ❖ In a few molecules and polyatomic ions, such as ClO_2 , NO , NO_2 , and O_2^- , the number of valence electrons is odd.
- ❖ **Example:** NO contains $5 + 6 = 11$ valence electrons. The two most important Lewis structures for this molecule are



8.7 Exceptions to the Octet Rule

Less than an Octet of Valence Electrons

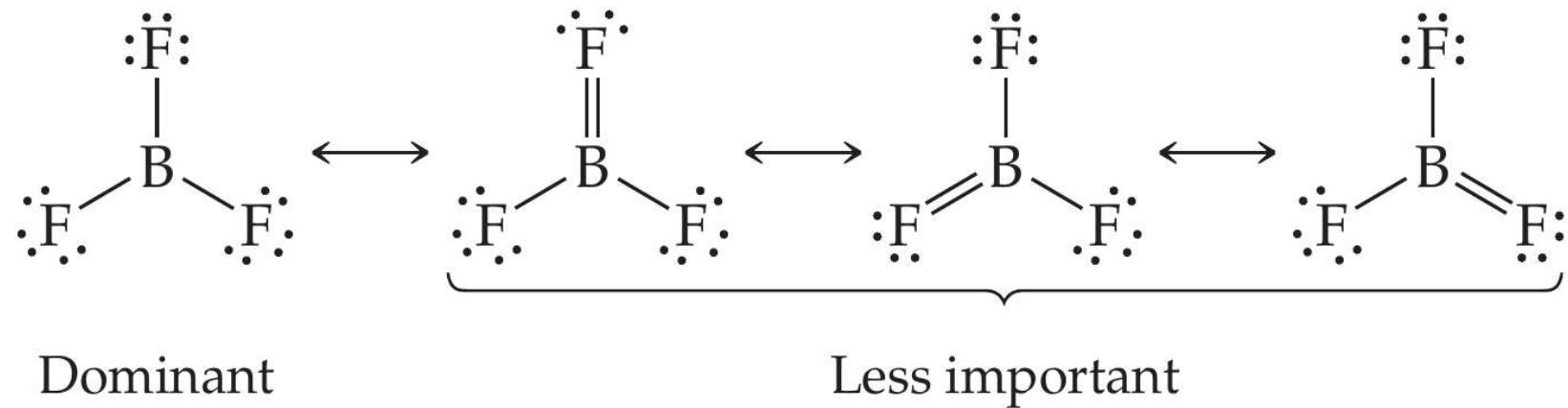
- ❖ This situation is also relatively rare and is most often encountered in compounds of boron and beryllium.



- ❖ 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

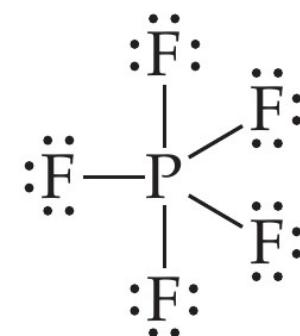
- ❖ In fact, the formal charges tell us that this is an unfavorable situation.



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.

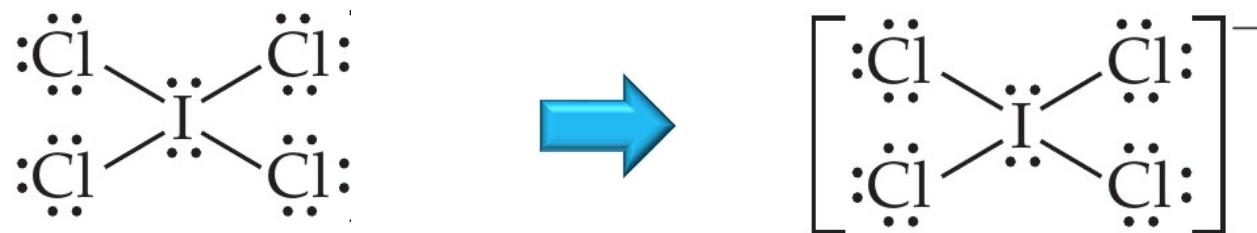
Sample Exercise 8.11

Draw the Lewis structure for ICl_4^- .

Number of valence electrons on I = 7

Number of valence electrons on Cl = 7

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



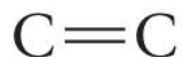
8.8 Strengths and Lengths of Covalent Bonds

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



1.54 Å

348 kJ/mol



1.34 Å

614 kJ/mol



1.20 Å

839 kJ/mol