

The formal charge on an atom in a Lewis structure is the number of valence electrons in the free (uncombined) atom minus the number of electrons assigned to that atom in the Lewis structure, with the electrons assigned in the following way.

- Count *lone-pair electrons* as belonging entirely to the atom on which they are found.
- Divide *bond-pair electrons* equally between the bonded atoms.

Assigning electrons (e^-) in this way is equivalent to writing that e^- assigned to a bonded atom in a Lewis structure

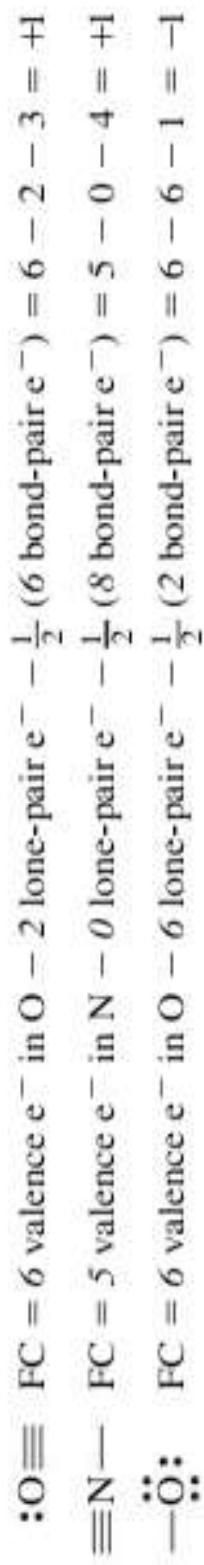
$$= \text{number lone-pair } e^- + \frac{1}{2} \text{ number bond-pair } e^-$$

Because formal charge is the difference between the assignment of valence electrons to a free (uncombined) atom and to the atom in a Lewis structure, it can be expressed as

$$\text{FC} = \text{number valence } e^- \text{ in free atom} - \text{number lone-pair } e^- - \frac{1}{2} \text{ number bond-pair } e^- \quad (10.16)$$

The formal charge gives an indication of the extent to which atoms have gained or lost electrons in the process of covalent bond formation; atom arrangements and Lewis structures with lowest formal charges are likely to have the lowest energy.

Now, let us assign formal charges to the atoms in structure (10.15), proceeding from left to right.



Formal charges in a Lewis structure can be shown by using small, encircled numbers.



The following are general rules that can help to determine the plausibility of a Lewis structure based on its formal charges.

- The sum of the formal charges in a Lewis structure must equal *zero* for a neutral molecule and must equal the magnitude of the charge for a polyatomic ion. [Thus for structure (10.17), this sum is $+1 + 1 - 1 = +1$.]
- Where formal charges are required, they should be as small as possible.
- Negative formal charges usually appear on the most electronegative atoms; positive formal charges, on the least electronegative atoms.
- Structures having formal charges of the same sign on adjacent atoms are unlikely.

Write the most plausible Lewis structure of nitrosyl chloride, NOCl , one of the oxidizing agents present in *aqua regia*, a mixture of concentrated nitric and hydrochloric acids capable of dissolving gold.

Although the formula is written as NOCl , we can reject the skeletal structure $\text{N}—\text{O}—\text{Cl}$ because it places the most electronegative atom as the central atom. (We are asked to consider $\text{N}—\text{O}—\text{Cl}$ in Practice Example A.) Having ruled out $\text{N}—\text{O}—\text{Cl}$ as a possible skeletal structure, we are left with the following as possibilities:



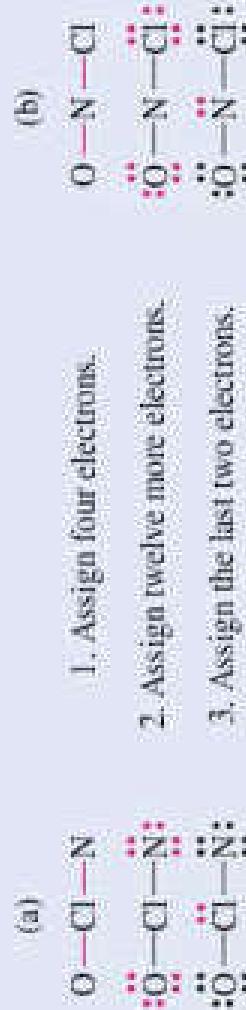
To determine the best structure, we must first complete the skeletal structures and then assign formal charges. The best structure will have the fewest and smallest formal charges.

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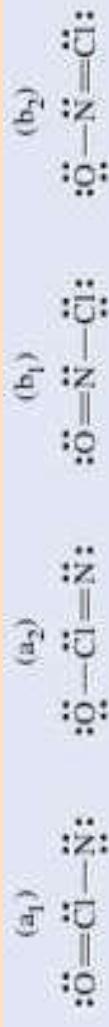
Regardless of the skeletal structure chosen, the number of valence electrons (dots) that must appear in the final Lewis structure is

55/mm N + 6 (mm O) = 7 (mm Cl) ≡ 18

When we apply the four steps listed below to the two possible skeletal structures, we obtain a total of four Lewis structures—two for each skeletal structure. This doubling occurs because in step 4, there are two ways to complete the octets of the central atoms. The final Lewis structures obtained are labeled (a*i*), (a*j*), (b*i*), and (b*j*).



4. Complete the octet on the central atom.



Evaluate formal charges by using equation (10.16). In structure (a₁), for the N atom,

$$\text{FC} = 5 - 6 - \frac{1}{2}(2) = -2$$

for the O atom,

$$\text{FC} = 6 - 4 - \frac{1}{2}(4) = 0$$

for the Cl atom,

$$\text{FC} = 7 - 2 - \frac{1}{2}(6) = +2$$

Proceed in a similar manner for the other three structures. Summarize the formal charges for the four structures.

	(a ₁)	(a ₂)	(b ₁)	(b ₂)
N:	-2	-1	0	0
O:	0	-1	0	-1
Cl:	+2	+2	0	+1

Select the best Lewis structure in terms of the formal-charge rules. First, note that all four structures obey the requirement that formal charges of a neutral molecule add up to zero. In structure (a₁), the formal charges are large (+2 on Cl and -2 on N) and the negative formal charge is not on the most electronegative atom. Structure (a₂) has formal charges on all atoms, one of them large (+2 on Cl). Structure (b₁) is the ideal we seek—no formal charges. In structure (b₂), we again have formal charges. The best Lewis structure of nitrosyl chloride is



Resonance

An important consequence of resonance is that it stabilizes a molecule by lowering its total energy. This stabilization makes benzene less reactive than expected for a molecule with three carbon–carbon double bonds. Resonance results in the greatest lowering of energy when the contributing structures have equal energies, as for the two Kekulé structures of benzene. However, in general, a molecule is a blend of all reasonable Lewis structures, including those with different energies. In these cases, the lowest energy structures contribute most strongly to the overall structure.

Resonance occurs only between structures with the same arrangement of atoms. For example, although we might be able to write two hypothetical structures for the dinitrogen oxide (nitrous oxide) molecule, NNO and NON, there is no resonance between them, because the atoms lie in different locations.

Resonance is a blending of structures with the same arrangement of atoms but different arrangements of electrons. It spreads multiple bond character over a molecule and results in a lower energy.

Count the valence electrons.

Oxygen is a member of Group 16/VI; so each atom has six valence electrons:
 $6 + 6 + 6 = 18$ electrons.



Draw a second Lewis structure by rearranging the bonds and lone pairs.

Draw the resonance hybrid.

Because all three bonds are identical, a better model of the nitrate ion is a *blend* of all three Lewis structures with each bond intermediate in properties between a single and a double bond. This blending of structures, which is called resonance, is depicted in (9) by double-headed arrows. The blended structure is a resonance hybrid of the contributing Lewis structures. A molecule does not flicker between different structures: a resonance hybrid is a blend of structures, just as a mule is a blend of a horse and a donkey, not a creature that flickers between the two.

Electrons that are shown in different positions in a set of resonance structures are said to be **delocalized**. Delocalization means that a shared electron pair is distributed over several pairs of atoms and cannot be identified with just one pair of atoms.



9 Nitrate ion, NO_3^-

EXCEPTIONS TO THE OCTET RULE

The octet rule accounts for the valences of many of the elements and the structures of many compounds. Carbon, nitrogen, oxygen, and fluorine obey the octet rule rigorously, provided there are enough electrons to go around. However, some compounds have an odd number of electrons. In addition, an atom of phosphorus, sulfur, chlorine, or another nonmetal in Period 3 and subsequent periods can accommodate more than eight electrons in its valence shell. The following two sections show how to recognize exceptions to the octet rule.

Odd-Electron Species

The molecule NO has 11 valence electrons, an odd number. If the number of valence electrons in a Lewis structure is odd, there must be an unpaired electron somewhere in the structure. Lewis theory deals with electron pairs and does not tell us where to put the unpaired electron; it could be on either the N or the O atom. To obtain a structure free of formal charges, however, we will put the unpaired electron on the N atom.



The presence of unpaired electrons causes odd-electron species to be paramagnetic. NO is paramagnetic. Molecules with an even number of electrons are expected to have all electrons paired and to be diamagnetic. An important exception is seen in the case of O_2 , which is paramagnetic despite having 12 valence electrons. Lewis theory does not provide a good electronic structure for O_2 , but the molecular orbital theory that we will consider in the next chapter is much more successful.

The number of stable odd-electron molecules is quite limited. More common are **free radicals**, or simply *radicals*, highly reactive molecular fragments with one or more unpaired electrons. The formulas of free radicals are usually written with a dot to emphasize the presence of an unpaired electron, such as in the *methyl radical*, $\cdot\text{CH}_3$, and the *hydroxyl radical*, $\cdot\text{OH}$. The Lewis structures of these two free radicals are

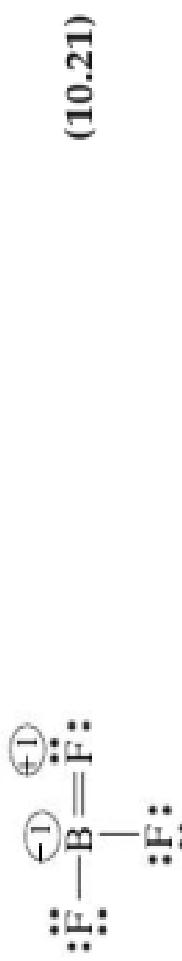


Incomplete Octets

Our initial attempt to write the Lewis structure of boron trifluoride leads to a structure in which the B atom has only six electrons in its valence shell—an *incomplete octet*.



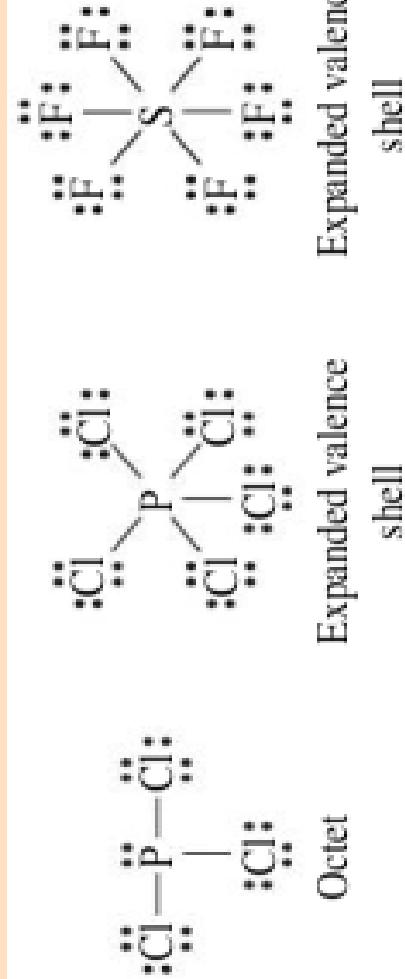
We have learned to complete the octets of central atoms by shifting lone-pair electrons from terminal atoms to form multiple bonds. One of three equivalent structures with a boron-to-fluorine double bond is shown below.



Expanded Valence Shells

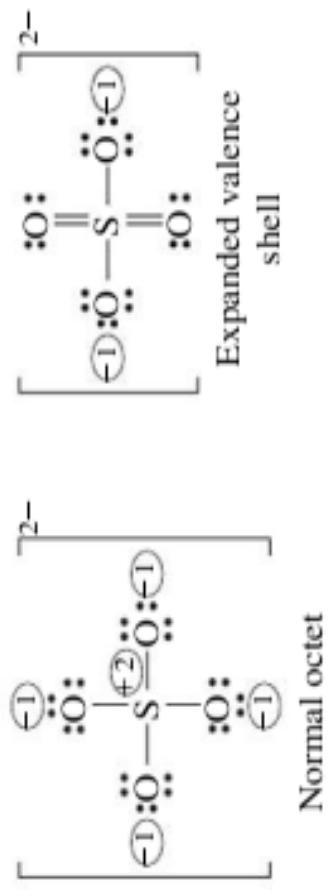
We have consistently tried to write Lewis structures in which all atoms except H have a complete octet, that is, in which each atom has eight valence electrons. There are a few Lewis structures that break this rule by having 10 or even 12 valence electrons around the central atom, creating what is called an **expanded valence shell**. Describing bonding in these structures is an area of active interest among chemists.

Molecules with expanded valence shells typically involve nonmetal atoms of the third period and beyond that are bonded to highly electronegative atoms. For example, phosphorus forms two chlorides, PCl_3 and PCl_5 . We can write a Lewis structure for PCl_3 with the octet rule. In PCl_5 , with five Cl atoms bonded directly to the central P atom, the outer shell of the P atom appears to have ten electrons. We might say that the valence shell has expanded to ten electrons. In the SF_6 molecule, the valence shell appears to expand to 12.

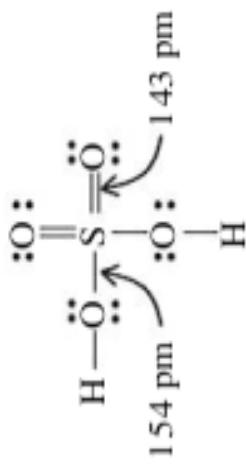
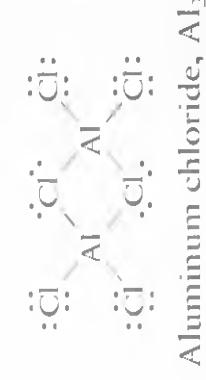


SHELL

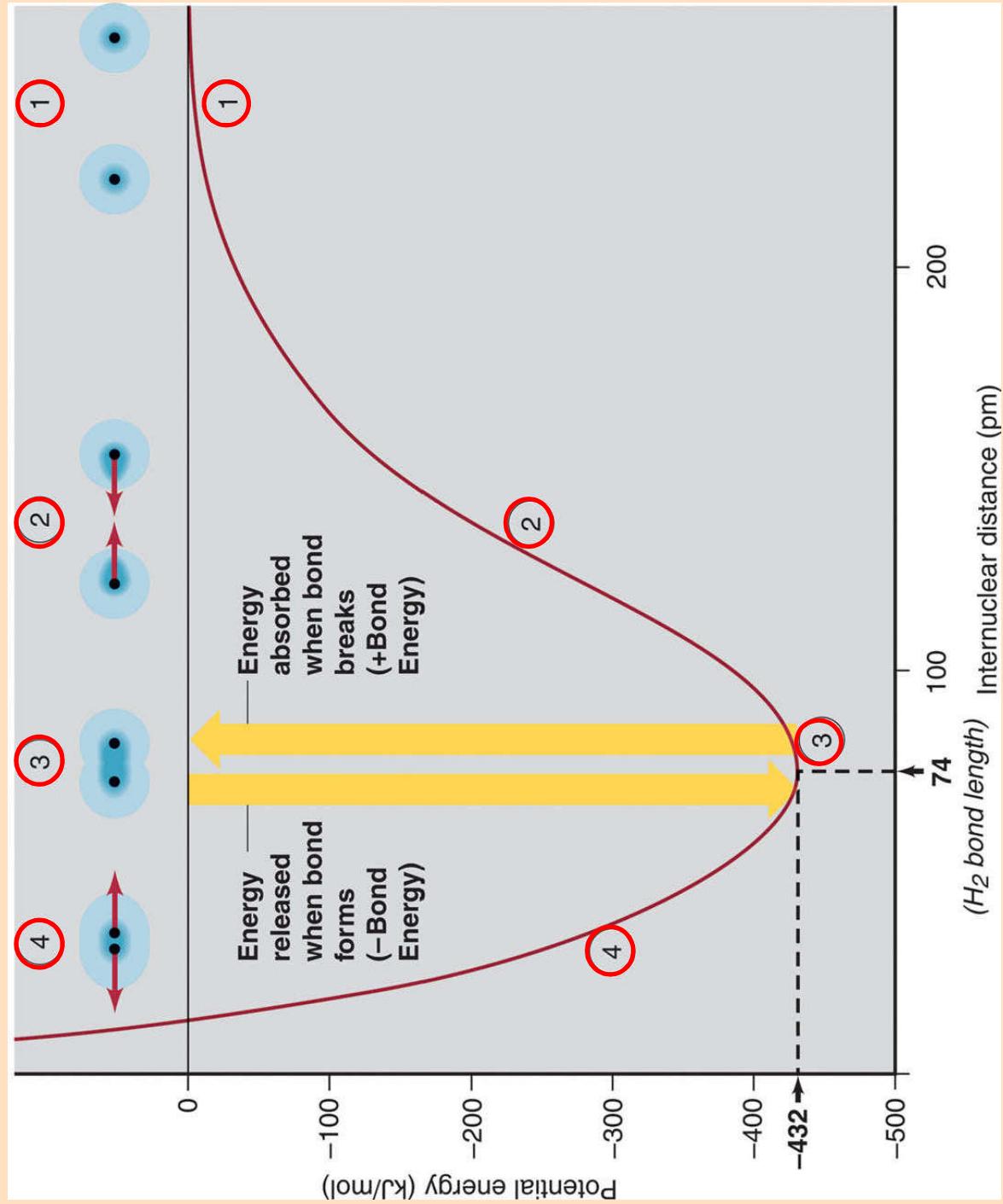
Expanded valence shells have also been used in cases where they appear to give a better Lewis structure than strict adherence to the octet rule, as suggested by the two Lewis structures for the sulfate ion that follow.



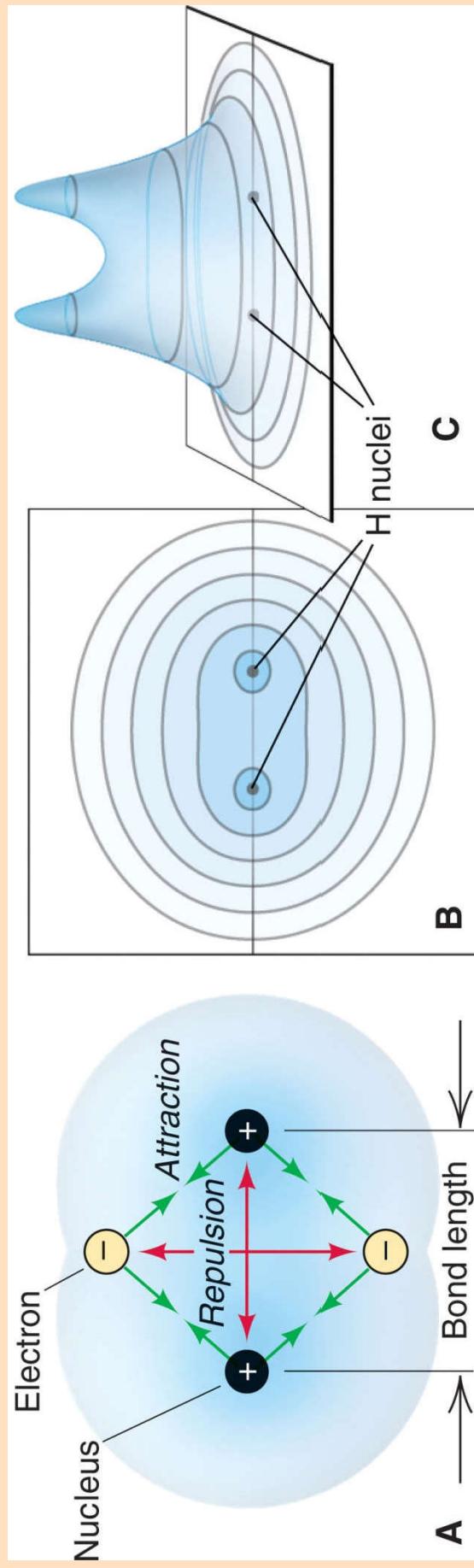
The argument for including the expanded valence-shell structure is that it reduces formal charges. Also, the experimentally determined sulfur-to-oxygen bond lengths in SO_4^{2-} and H_2SO_4 are in agreement with this idea. The experimental results for H_2SO_4 , summarized in structure (10.23), indicate that the S—O bond with O as a central atom and with an attached H atom is longer than the S—O bond with O as a terminal atom.



Covalent bond formation in H_2 .



Distribution of electron density in H_2 .



At some distance (bond length), attractions balance repulsions.

Electron density is high around and between the nuclei.

Bonding Pairs and Lone Pairs

Atoms share electrons to achieve a full outer level of electrons. The shared electrons are called a **shared pair** or **bonding pair**.

The shared pair is represented as a pair of dots or a line:



An outer-level electron pair that is not involved in bonding is called a **lone pair**, or **unshared pair**.



Properties of a Covalent Bond

The **bond order** is the number of electron pairs being shared by a given pair of atoms.

A single bond consists of one bonding pair and has a bond order of 1.

The **bond energy** (BE) is the energy needed to overcome the attraction between the nuclei and the shared electrons. The **stronger** the bond the **higher** the bond energy.

The **bond length** is the distance between the nuclei of the bonded atoms.

Trends in bond order, energy, and length

For a given pair of atoms, a *higher bond order* results in a **shorter bond length** and **higher bond energy**.

For a given pair of atoms, a shorter bond is a stronger bond.

Bond length *increases* down a group in the periodic table and *decreases* across the period.

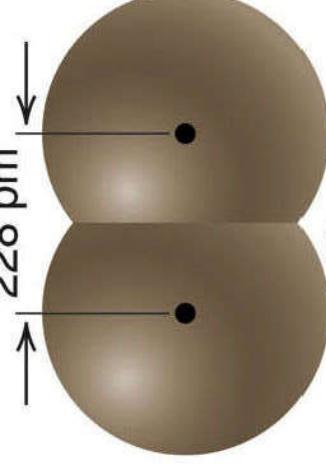
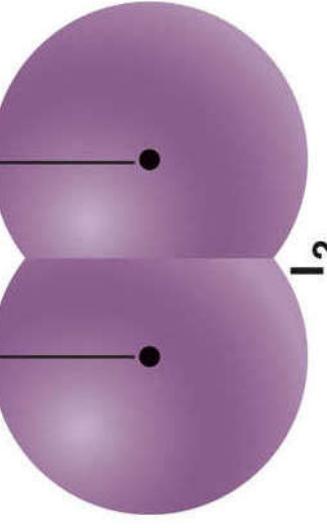
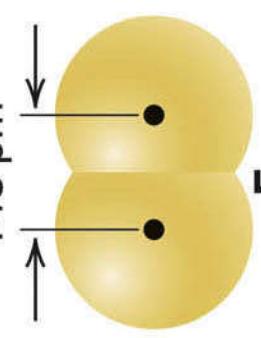
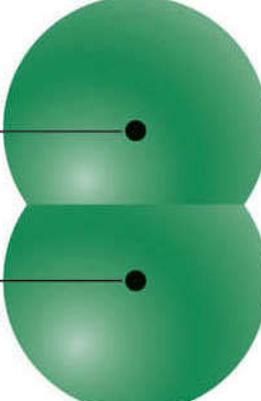
Bond energy shows the opposite trend.

Table 9.2 Average Bond Energies (kJ/mol) and Bond Lengths (pm)

Table 9.3 The Relation of Bond Order, Bond Length, and Bond Energy

Bond	Bond Order	Average Bond Length (pm)	Average Bond Energy (kJ/mol)
C—O	1	143	358
C=O	2	123	745
C≡O	3	113	1070
C—C	1	154	347
C=C	2	134	614
C≡C	3	121	839
N—N	1	146	160
N=N	2	122	418
N≡N	3	110	945

Bond length and covalent radius.

Internuclear distance (bond length)	Covalent radius	Internuclear distance (bond length)	Covalent radius
143 pm	72 pm	228 pm	114 pm
			
		Br_2	I_2
Internuclear distance (bond length)	Covalent radius	Internuclear distance (bond length)	Covalent radius
199 pm	100 pm	266 pm	133 pm
			
		F_2	Cl_2

Sample Problem 9.2

Comparing Bond Length and Bond Strength

PROBLEM: Using the periodic table, but not Tables 9.2 or 9.3, rank the bonds in each set in order of *decreasing* bond length and decreasing bond strength:



PLAN: (a) S is singly bonded to three different halogen atoms, so the bond order is the same. Bond length increases and bond strength decreases as the atomic radius of the halogen increases.

(b) The same two atoms are bonded in each case, but the bond orders differ. Bond strength increases and bond length decreases as bond order increases.

Sample Problem 9.2

SOLUTION:

- (a) Atomic size increases going down a group, so F < Cl < Br.

Bond length: S–Br > S–Cl > S–F

Bond strength: S–F > S–Cl > S–Br

- (b) By ranking the bond orders, we get

Bond length: C–O > C=O > C \equiv O

Bond strength: C \equiv O > C=O > C–O