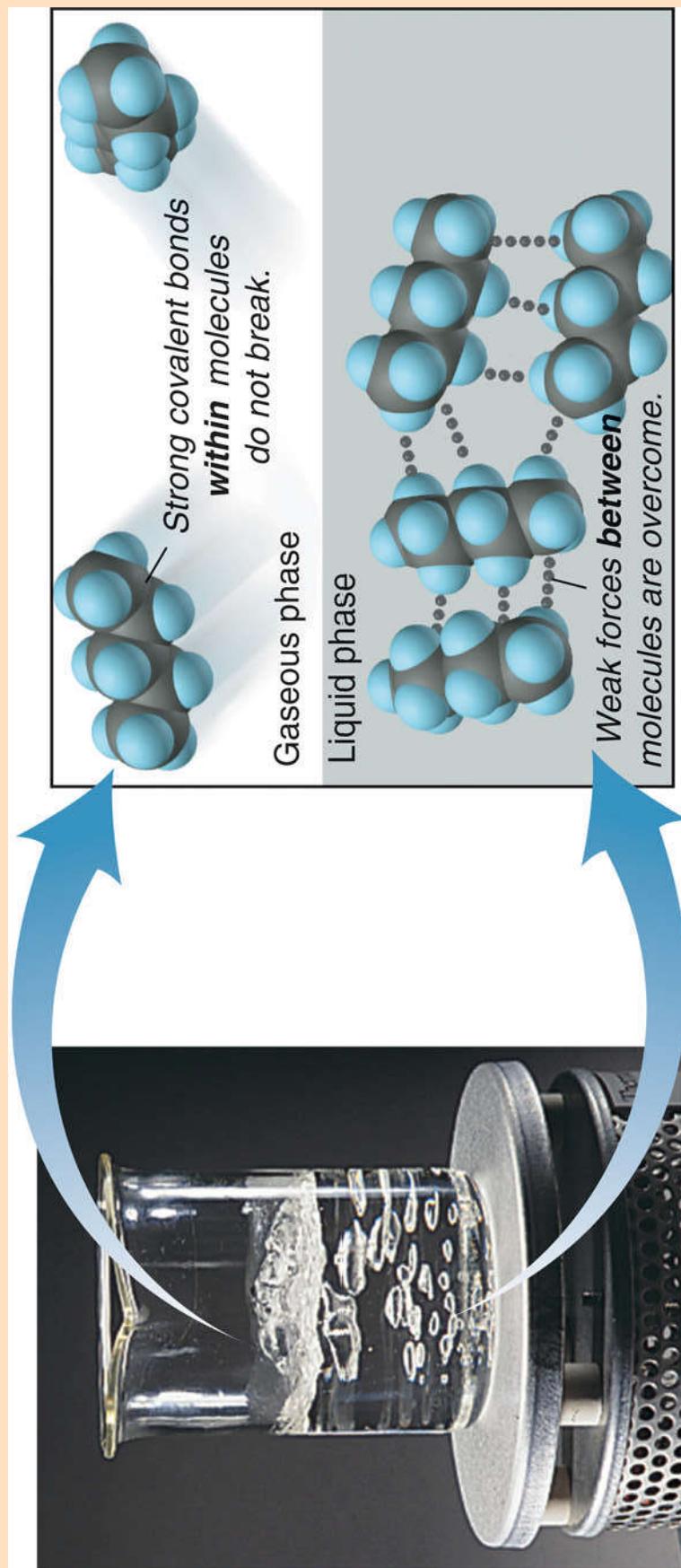
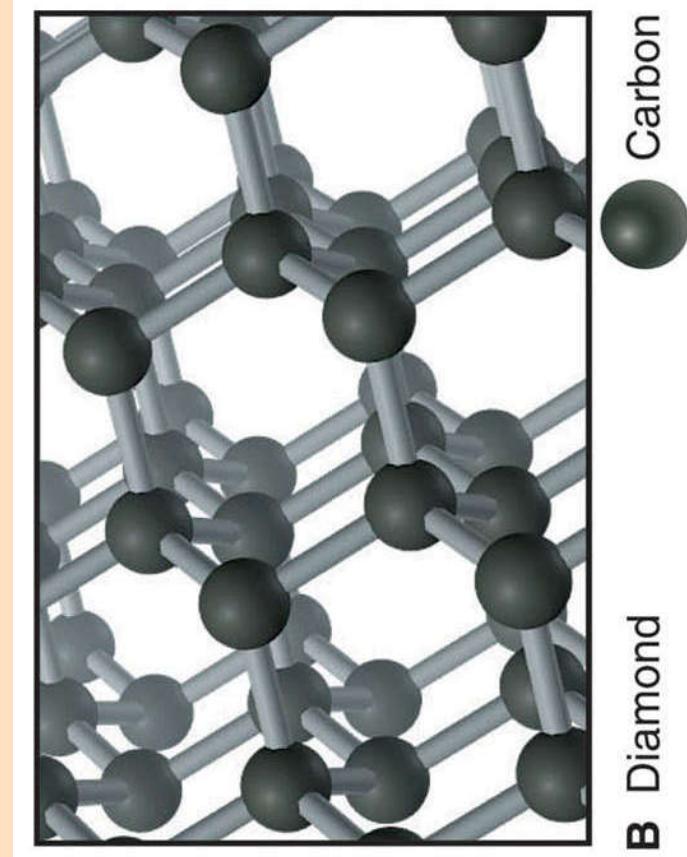
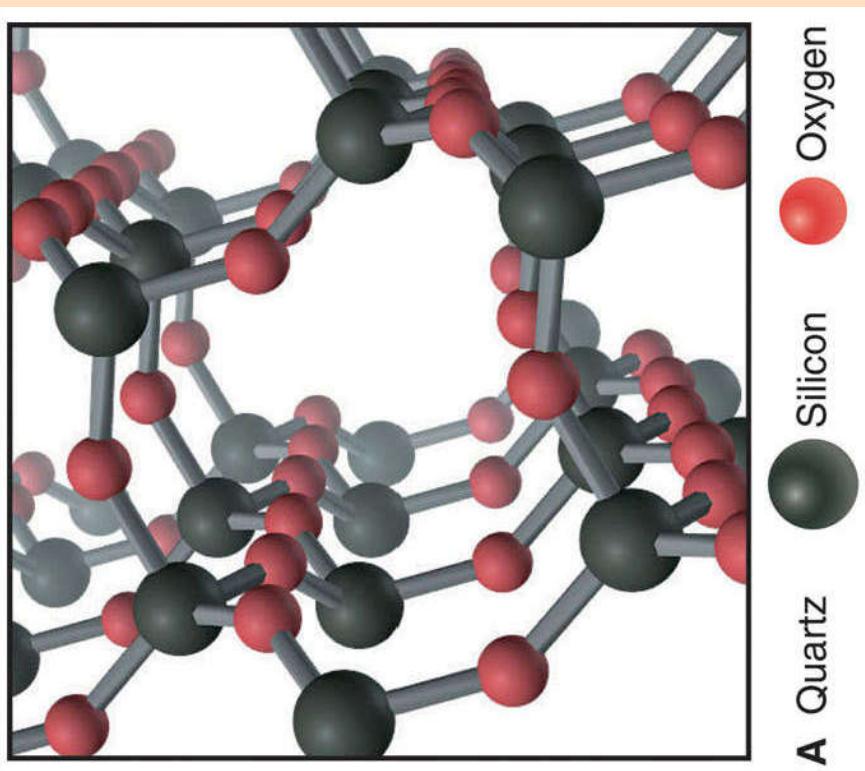


# Strong forces within molecules and weak forces between them.



# Covalent bonds of network covalent solids: quartz and diamond.



## DIPOLE MOMENTS

Because atoms have different electronegativities, pairs of electrons that are shared in covalent bonds are not necessarily shared equally. The result is that the bond has a polarity with the center of negative charge generally residing on the atom having the higher electronegativity. For a covalent bond between two atoms, the dipole moment,  $\mu$ , is expressed

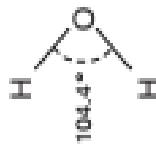
$$\mu = q r$$

where  $q$  is the quantity of charge separated and  $r$  is the distance of separation. Several properties of molecules are related to their polarity, and it is a useful parameter for understanding molecular structure, so it is appropriate to explore this topic in greater detail. Before doing so, a comment on units is appropriate. The charge on an electron is  $1.6022 \times 10^{-19}$  coulomb, and internuclear distances can be expressed in meters. As a result, the units on dipole moments are coulomb-meter ( $C\ m$ ). A unit of polarity is defined as the *debye*, which is named after Peter Debye, who did pioneering work on polar molecules. The relationship in SI units is

$$1 \text{ debye} = 1 \text{ D} = 3.33564 \times 10^{-30} \text{ C m}$$

$$1 \text{ debye}^2 = 1 \text{ D}^2 = 10^{-18} \text{ esu cm}$$

For molecules that have several polar bonds, a rough approximation of the overall dipole moment can be made by considering the *bond moments* as vectors and finding the vector sum. Consider the water molecule, which has the structure



and for which the overall dipole moment is 1.85 D. If we consider that value to be the vector sum of the two O–H bond moments, we find that

$$1.85 \text{ D} = 2 \cos 52.25 \times \mu_{\text{O}-\text{H}}$$

Solving for  $\mu_{\text{O}-\text{H}}$ , we find a value of 1.51 D. We have another way to estimate the dipole moment of the O–H bond by making use of the equation

$$\% \text{ Ionic character} = 16 |\chi_A - \chi_B| + 3.5 |\chi_A - \chi_B|^2$$

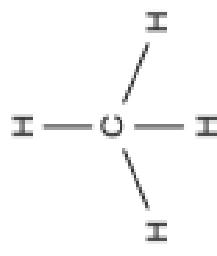
where  $\chi_A$  and  $\chi_B$  are the electronegativities of the atoms. By calculating the percent ionic character, we can determine the charge on the atoms. For an O–H bond,

$$\% \text{ Ionic character} = 16 |3.5 - 2.1| + 3.5 |3.5 - 2.1|^2 = 29.4\%$$

Therefore, because the length of the O–H bond is  $1.10 \times 10^{-8}$  cm (110 pm),

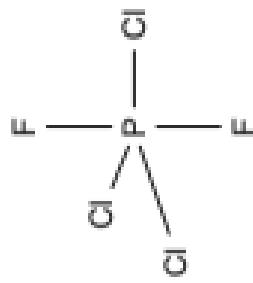
$$\mu_{\text{O}-\text{H}} = 0.294 \times 4.8 \times 10^{-10} \text{ esu} \times 1.10 \times 10^{-8} \text{ cm} = 1.58 \times 10^{-18} \text{ esu cm} = 1.58 \text{ D}$$

The effect of molecular geometry can often be evaluated in a straightforward manner. Consider the tetrahedral  $\text{CH}_4$  molecule, which will be shown as having one C–H bond pointing “up” and the other three forming a tripod-like base:



The bond pointing “up” constitutes one C–H bond in that direction while the other three must exactly equal the effect of one C–H pointing “down.” The “down” component of each of the three bonds can be obtained from  $\cos(180 - 109^\circ 28') = 1/3$ . Therefore, the three bonds exactly equal the effect of the one bond pointing in the “up” direction. This would be true for any regular tetrahedral molecule, so the dipole moment would be zero.

In Chapter 4, it was discussed that peripheral atoms of high electronegativity tend to bond to hybrid orbitals having a low degree of *s* character. In that connection, the molecule  $\text{PCl}_3\text{F}_2$  is nonpolar indicating that the structure of the molecule is



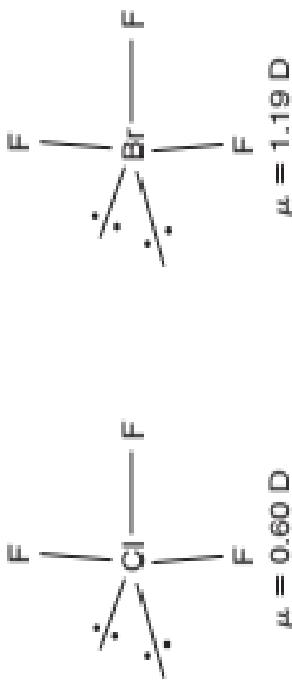
The axial orbitals used by phosphorus in this molecule can be considered as *dp* in character (see Chapter 4), which means they have no *s* character, whereas the orbitals in equatorial positions are  $sp^2$  hybrids. As expected, the fluorine atoms are found in axial positions and the molecule is nonpolar. This illustration shows the value of dipole moments in predicting the details of molecular structure.

One of the interesting aspects of dipole moments for molecules is seen when the molecules  $\text{NH}_3$  and  $\text{NF}_3$  are considered:



Bond angle:  $107^\circ$   
Dipole moment:  $1.47 \text{ D}$

The dipole moments of  $\text{ClF}_3$  and  $\text{BrF}_3$  provide another interesting illustration of the effects of unshared pairs of electrons. The molecules can be shown as follows:



Owing to the difference in electronegativities, the Br-F bonds are more polar than are the Cl-F bonds. However, the unshared pairs in  $\text{ClF}_3$  are held closer to the Cl atom and the polarity of the Cl-F bond is in the opposite direction as the resultant of the two unshared pairs of electrons. In  $\text{BrF}_3$ , the equatorial Br-F bond is slightly more polar than a Cl-F bond, but the unshared pairs reside farther away from the Br atom. Therefore, there is a greater effect produced by the two unshared pairs of electrons in  $\text{BrF}_3$  that dominates the polarity of the equatorial Br-F bond. The result is that the dipole moment of  $\text{BrF}_3$  is about twice as large as that of  $\text{ClF}_3$ .

# Electronegativity and Bond Polarity

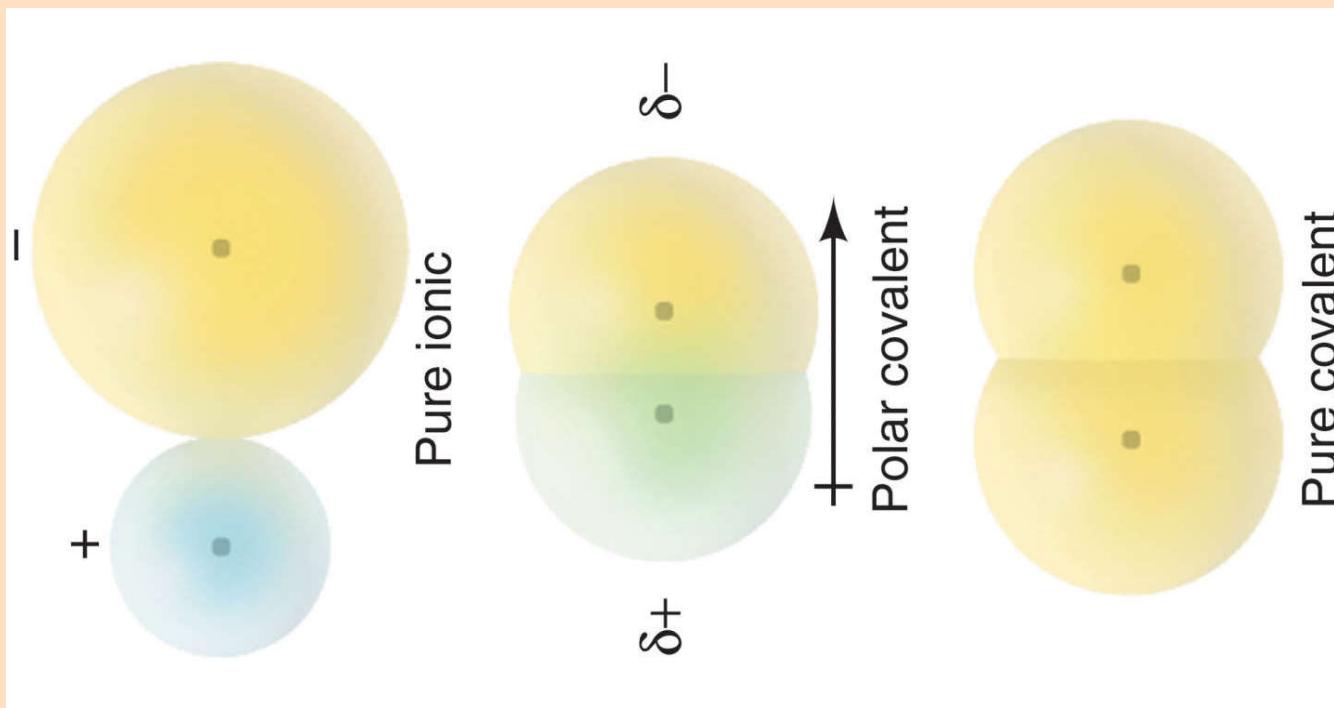
A covalent bond in which the shared electron pair is not shared equally, but remains closer to one atom than the other, is a *polar covalent bond*.

The ability of an atom in a covalent bond to attract the shared electron pair is called its *electronegativity*.

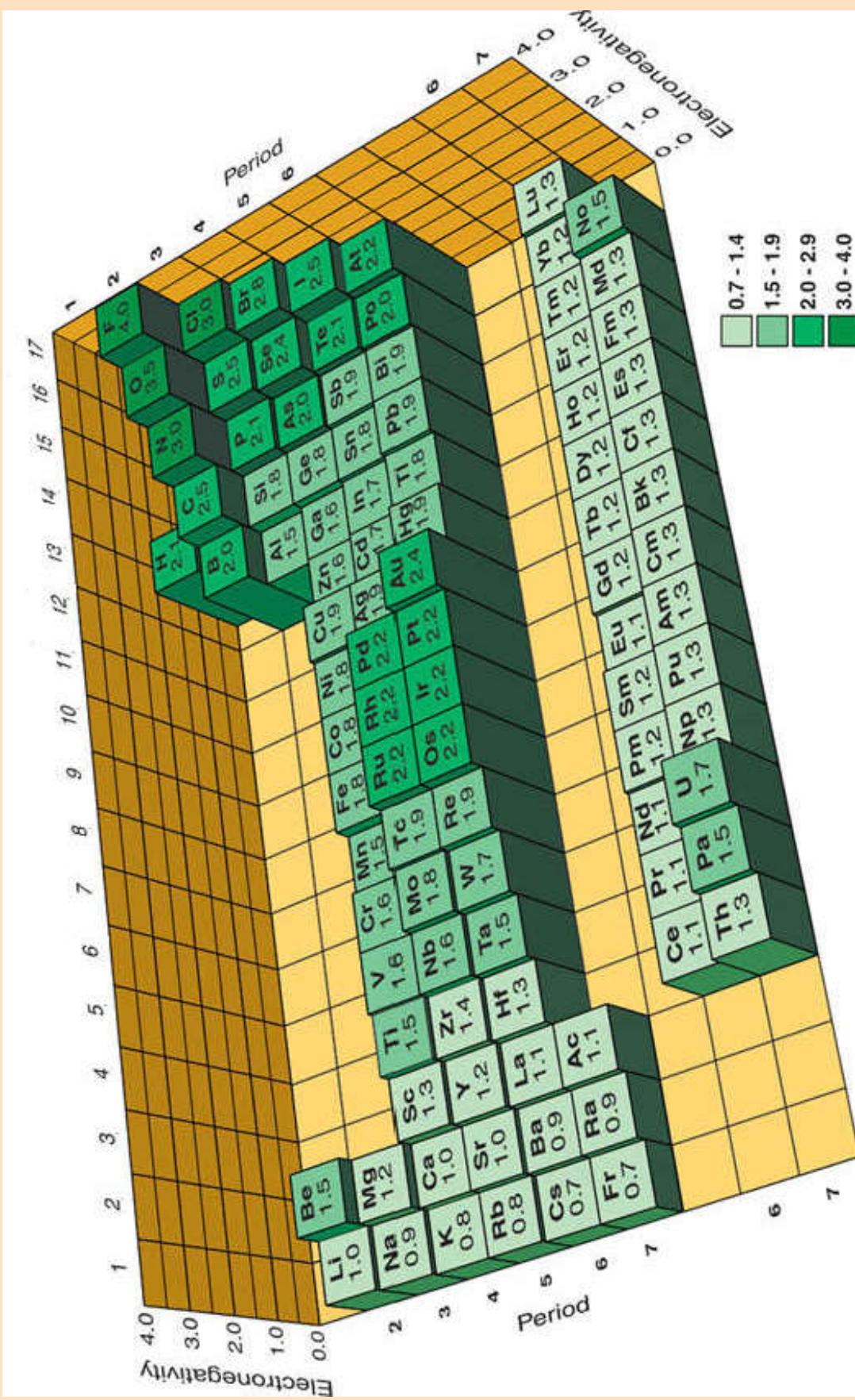
Unequal sharing of electrons causes the more electronegative atom of the bond to be *partially negative* and the less electronegative atom to be *partially positive*.

# Bonding between the models.

Polar covalent bonds are much more common than either pure ionic or pure covalent bonds.



The Pauling electronegativity (EN) scale.



# Trends in Electronegativity

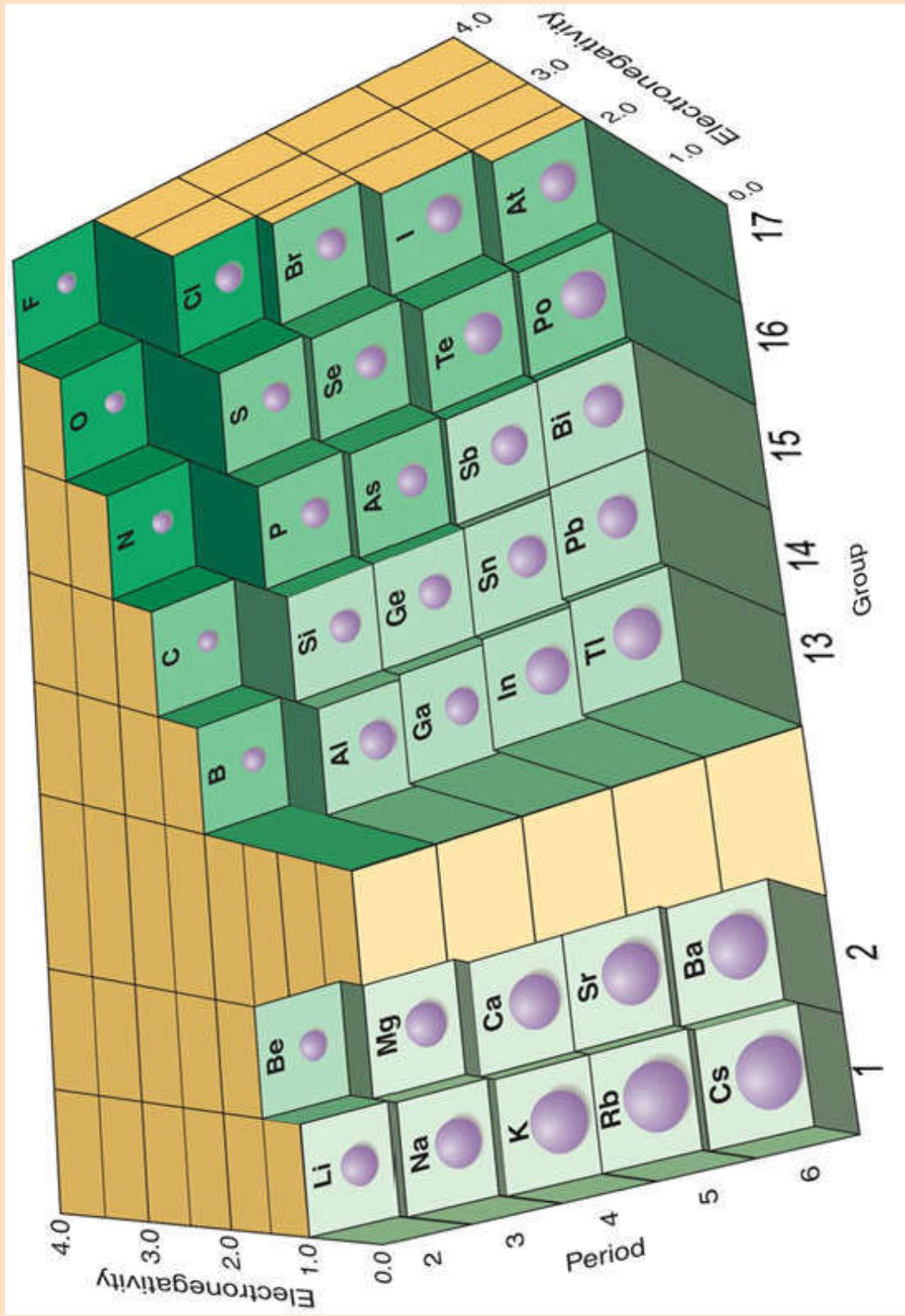
The most electronegative element is *fluorine*.

In general electronegativity *decreases* down a group as atomic size *increases*.

In general electronegativity *increases* across a period as atomic size *decreases*.

Nonmetals are *more* electronegative than metals.

# Electronegativity and atomic size.



# Electronegativity and Oxidation Number

Electronegativities can be used to assign oxidation numbers:

- The more electronegative atom is assigned *all* the **shared** electrons.
- The less electronegative atom is assigned *none* of the shared electrons.
- Each atom in a bond is assigned *all* of its *unshared* electrons.
- O.N. = # of valence e<sup>-</sup> (# of shared e<sup>-</sup> + # of unshared e<sup>-</sup>)

Example:



Cl is more electronegative than H, so for Cl:

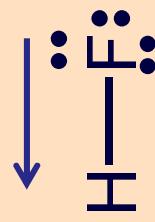
$$\begin{aligned}\text{valence e}^- &= 7 \\ \text{shared e}^- &= 2 \\ \text{unshared e}^- &= 6 \\ \text{O.N.} &= 7 - (2 + 6) = -1\end{aligned}$$

H is less electronegative than Cl, so for H:

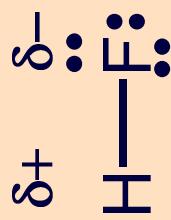
$$\begin{aligned}\text{valence e}^- &= 1 \\ \text{shared e}^- &= 0 \text{ (all shared e}^- \text{ assigned to Cl)} \\ \text{unshared e}^- &= 0 \\ \text{O.N.} &= 1 - (0 + 0) = +1\end{aligned}$$

# Depicting Polar Bonds

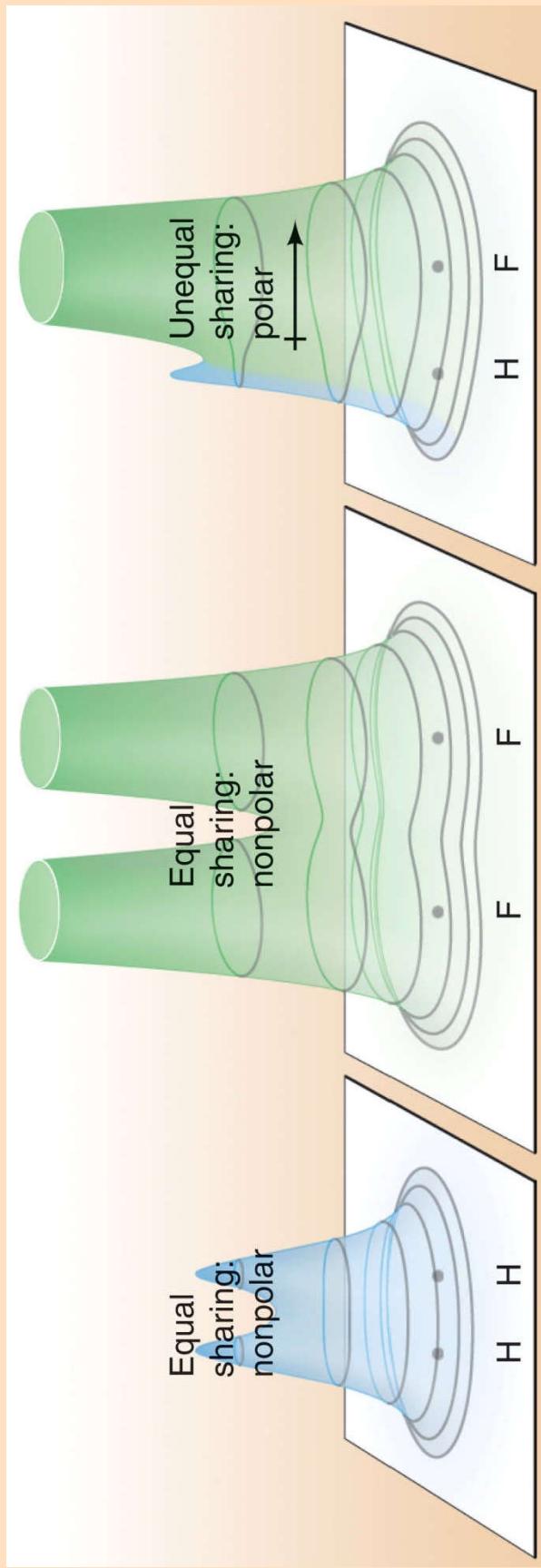
The unequal sharing of electrons can be depicted by a vector. The head of the arrow points to the ***from the more negative to the more positive element.***



A polar bond can also be marked using  $\delta+$  and  $\delta-$  symbols.



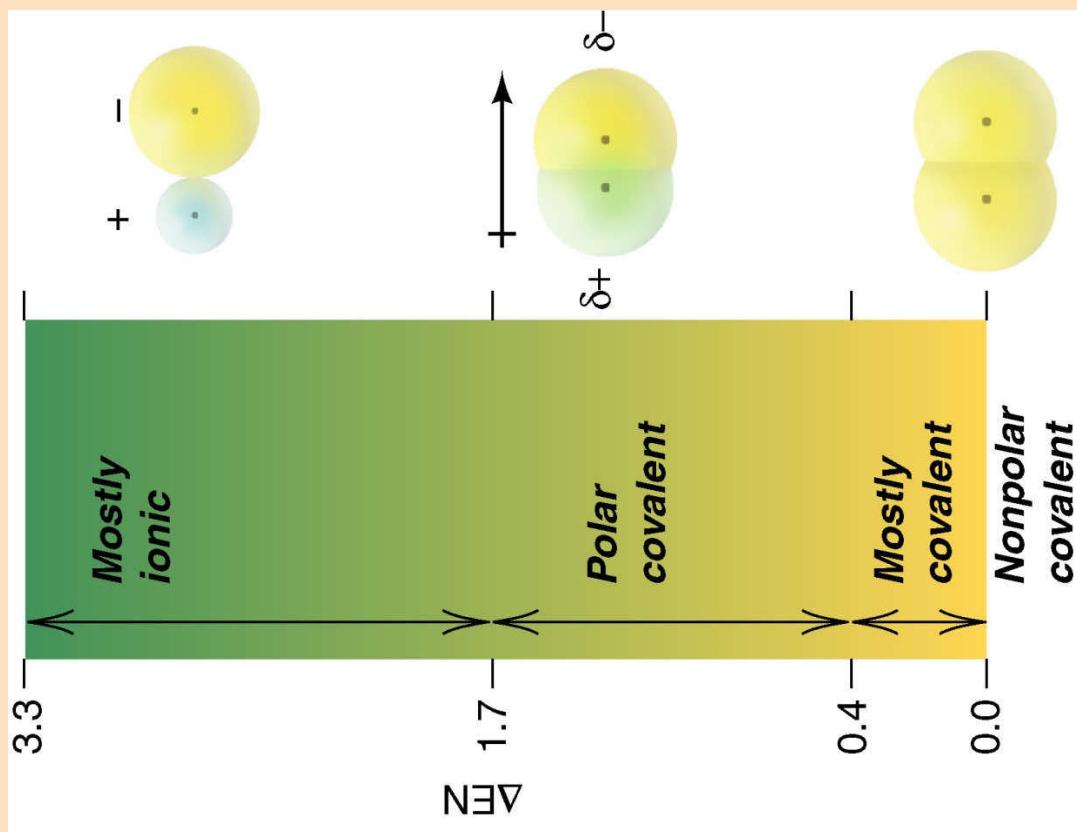
# Electron density distributions in $\text{H}_2$ , $\text{F}_2$ , and $\text{HF}$ .



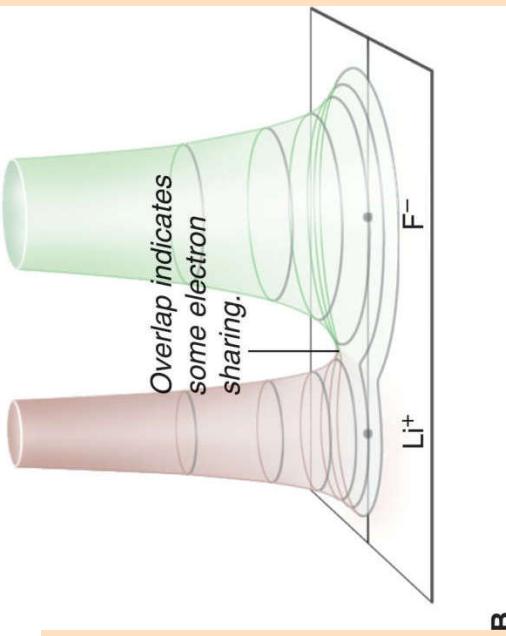
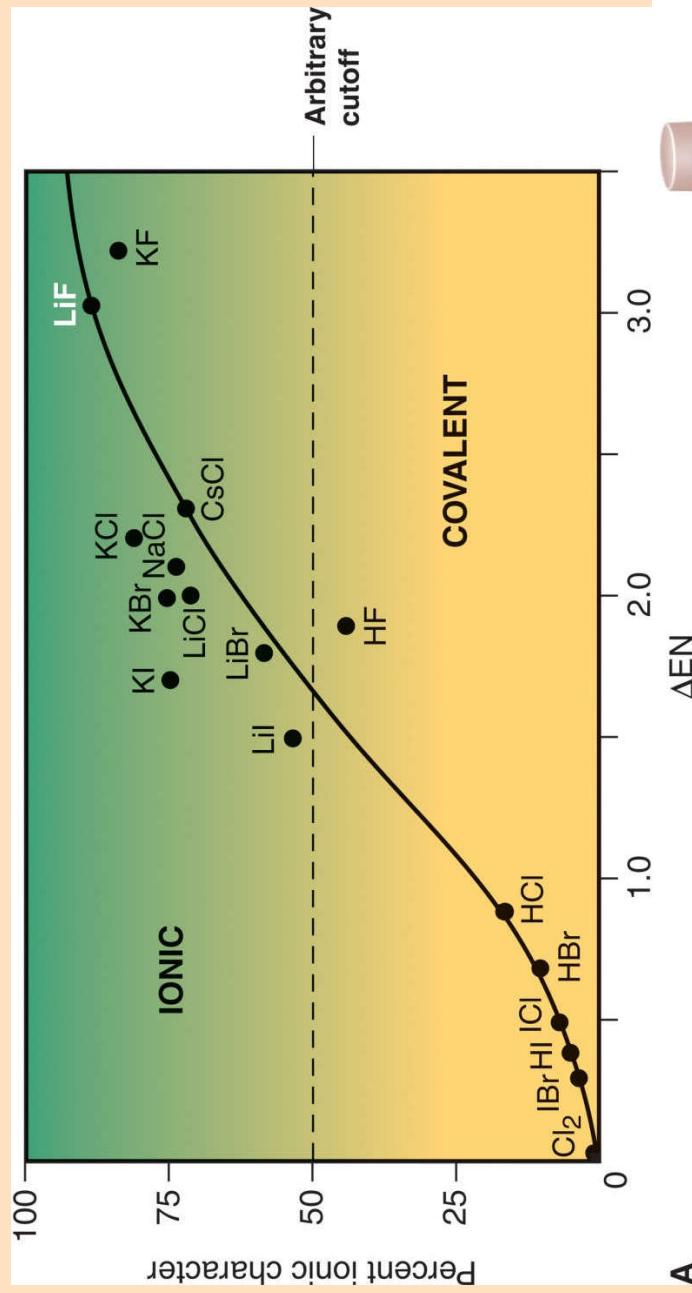
In  $\text{HF}$ , the electron density shifts from  $\text{H}$  to  $\text{F}$ .

The  $\text{H}-\text{F}$  bond has partial ionic character.

# $\Delta\text{EN}$ ranges for classifying the partial ionic character of bonds.



# Percent ionic character as a function of $\Delta\text{EN}$ .



### Sample Problem 9.4

### Determining Bond Polarity from EN Values

**PROBLEM:** (a) Use a polar arrow to indicate the polarity of each bond: N–H, F–N, I–Cl.

(b) Rank the following bonds in order of increasing polarity: H–N, H–O, H–C.

**PLAN:** (a) We use Figure 9.21 to find the EN values for each element. The polar arrow points toward the more electronegative element.

(b) The greater the  $\Delta\text{EN}$  between the atoms, the more polar the bond.

**SOLUTION:** (a) The EN values are:

$$\text{N} = 3.0, \text{H} = 2.1; \text{F} = 4.0; \text{I} = 2.5, \text{Cl} = 3.0$$



### **Sample Problem 9.4**

**(b)** The EN values are:

$$N = 3.0, H = 2.1; O = 3.5; C = 2.5$$

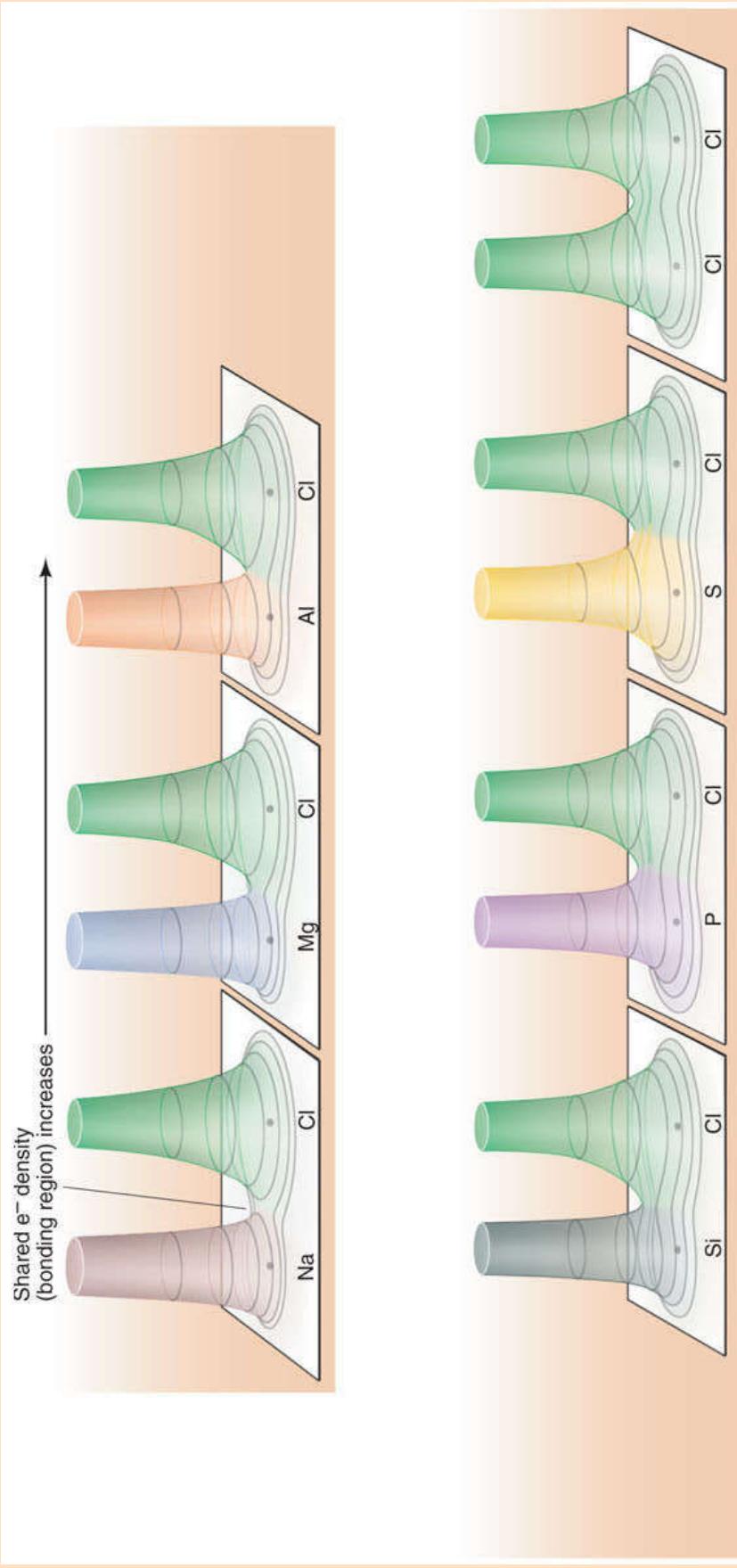
$$\Delta EN \text{ for } H-N = 3.0 - 2.1 = 0.9$$

$$\Delta EN \text{ for } H-O = 3.5 - 2.1 = 1.4$$

$$\Delta EN \text{ for } H-C = 2.5 - 2.1 = 0.4$$

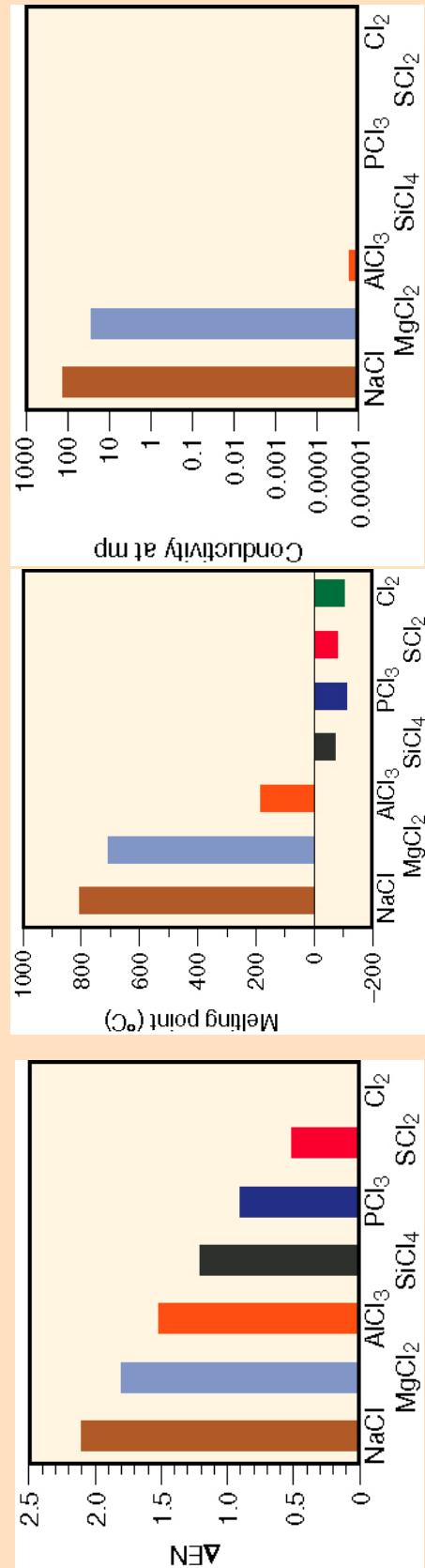
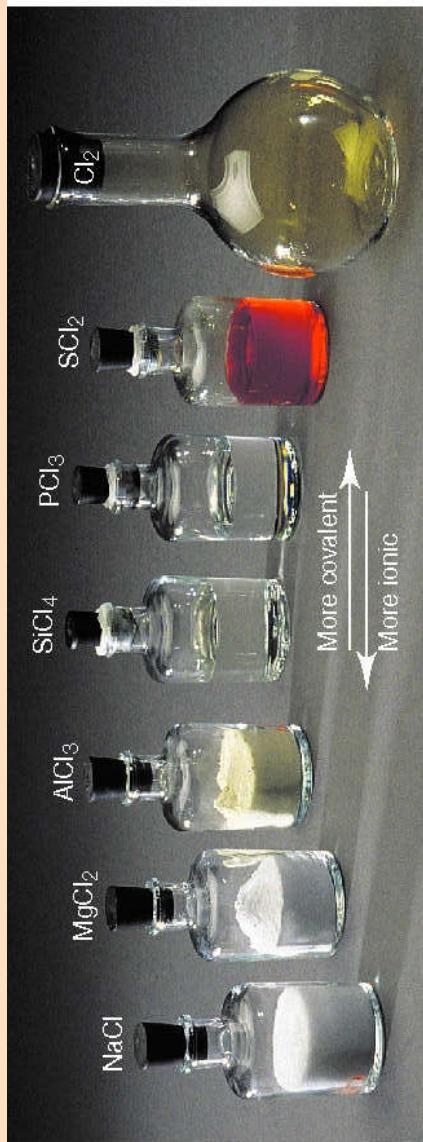
$$\boxed{H-C < H-N < H-O}$$

# Electron density distributions in bonds of the Period 3 chlorides.



There is a steady increase in electron sharing from left to right.

# Properties of the Period 3 chlorides.



As  $\Delta EN$  decreases, melting point and electrical conductivity decrease because the bond type changes from ionic to polar covalent to nonpolar covalent.

# Metallic Bonding

The *electron sea* model of metallic bonding proposes that:

- All metal atoms in the sample contribute their valence electrons to form a delocalized electron “sea”.
- The metal “ions” (nuclei with core electrons) lie in an orderly array within this mobile sea.
- All the atoms in the sample share the electrons.
- The metal is held together by the attraction between the metal “cations” and the “sea” of valence electrons.

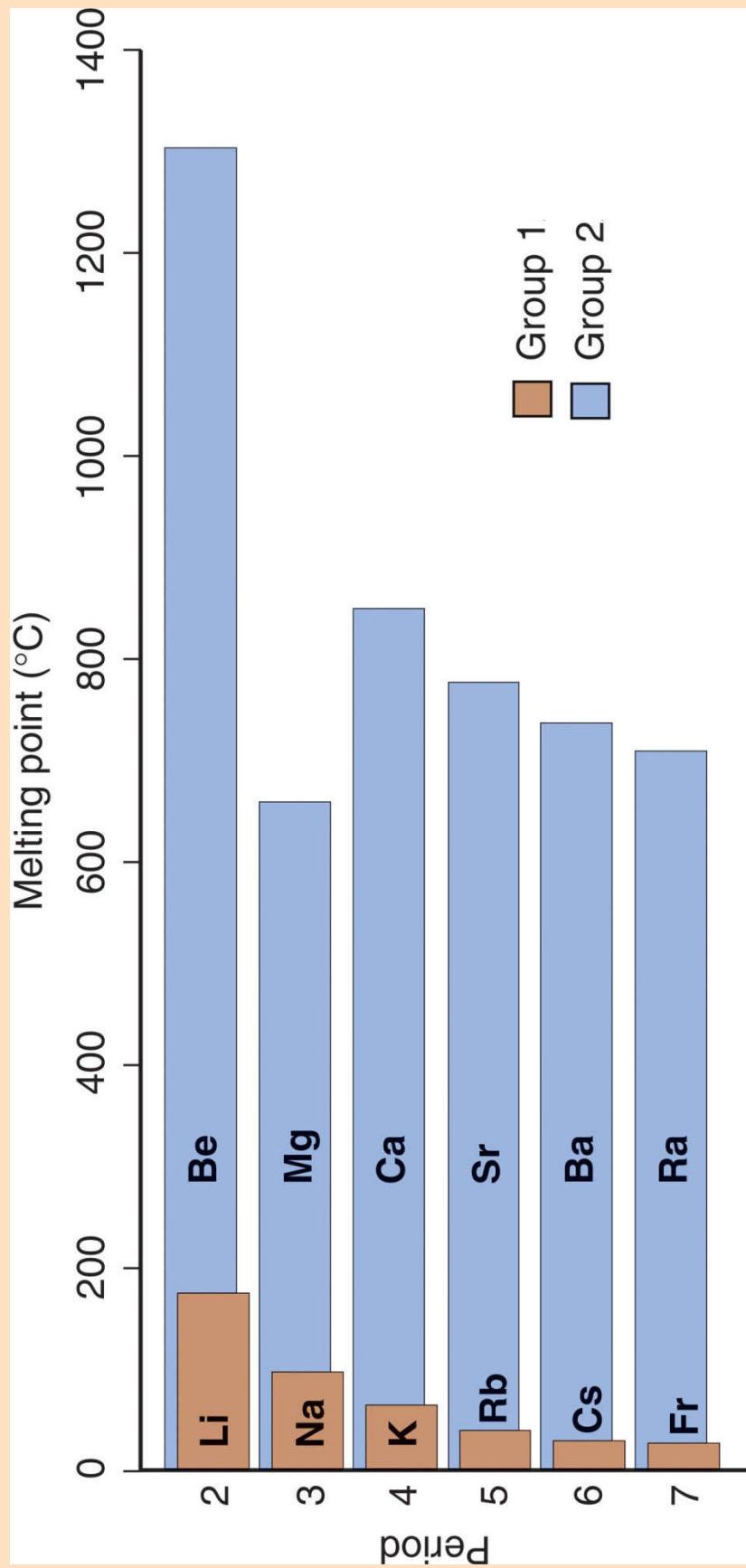
# Properties of Metals

- Metals are generally solids with moderate to high melting points and much higher boiling points.
  - Melting points decrease down a group and increase across a period.
- Metals can be shaped without breaking.
  - The electron sea allows the metal ions to slide past each other.
- Metals are good conductors of electricity in both the solid and liquid states.
  - The electron sea is mobile in both phases.
- Metals are good conductors of heat.

**Table 9.5 Melting and Boiling Points of Some Metals**

<b>Element</b>	<b>mp (°C)</b>	<b>bp (°C)</b>
Lithium (Li)	180	1347
Tin (Sn)	232	2623
Aluminum (Al)	660	2467
Barium (Ba)	727	1850
Silver (Ag)	961	2155
Copper (Cu)	1083	2570
Uranium (U)	1130	3930

# Melting points of the Group 1 and Group 2 metals.



# Why metals dent and bend rather than crack.

