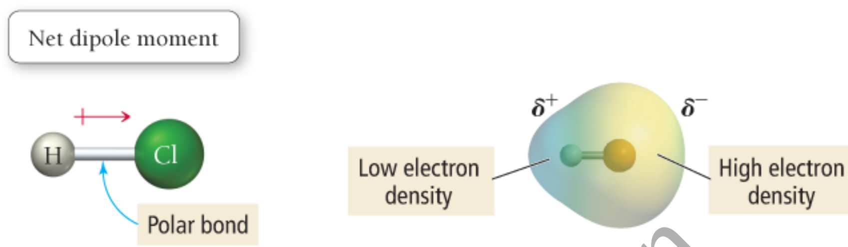
Pearson

5.10: Molecular Shape and Polarity

In Section 5.2, we discussed polar bonds. Entire molecules can also be polar, depending on their shape and the nature of their bonds.

Polarity in Diatomic Molecules

If a diatomic molecule has a polar bond, the molecule as a whole is polar.



In the figure shown here, the image to the right is an electrostatic potential map of HCl. In these maps, yellow/red areas indicate electron-rich regions in the molecule and the blue areas indicate electron-poor regions. Yellow indicates moderate electron density. Notice that the region around the more electronegative atom (chlorine) is more electron rich than the region around the hydrogen atom. Thus the molecule itself is polar. If the bond in a diatomic molecule is *nonpolar*, the molecule as a whole will be *nonpolar*.

Polarity in Polyatomic Molecules

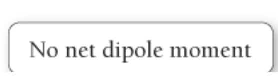
In polyatomic molecules, the presence of polar bonds may or may not result in a polar molecule, depending on the molecular geometry. If the molecular geometry is such that the dipole moments of individual polar bonds sum together to a net dipole moment, then the molecule is polar. But if the molecular geometry is such that the dipole moments of the individual polar bonds cancel each other (that is, sum to zero), then the molecule is nonpolar. It all depends on the geometry of the molecule.

Consider carbon dioxide:

$$:\ddot{O}=C=\ddot{O}:$$

Each C═O bond in CO_2 is polar because oxygen and carbon have significantly different electronegativities (3.5 and 2.5, respectively). However, since CO_2 is a linear molecule, the polar bonds directly oppose one another and the dipole moment of one bond exactly opposes the dipole moment of the other. The two dipole moments sum to zero, and the *molecule* is nonpolar.

Dipole moments cancel each other because they are *vector quantities*; they have both a magnitude and a direction. Think of each polar bond as a vector, pointing in the direction of the more electronegative atom. The length of the vector is proportional to the electronegativity difference between the bonding atoms. In CO_2, we have two identical vectors pointing in exactly opposite directions—the vectors sum to zero, much as +1 and −1 sum to zero:



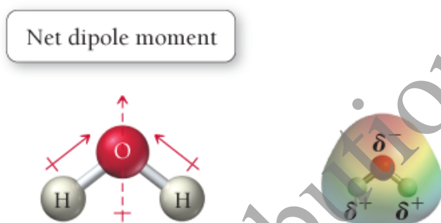
See the next section, titled Vector Addition, for instructions about adding vectors.

Notice that the electrostatic potential map of CO_2 shows regions of moderately high electron density (yellow with slight red) positioned symmetrically on either end of the molecule with a region of low electron density (blue) located in the middle.

In contrast, consider water:

$$\mathrm{H{-}\ddot{\underset{\cdot\cdot}{O}}{-}H}$$

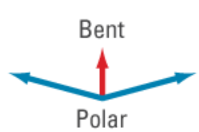
The O–H bonds in water are also polar; oxygen and hydrogen have electronegativities of 3.5 and 2.1, respectively. However, the water molecule is not linear but bent. Therefore the two dipole moments do not sum to zero. If we imagine each bond as a vector pointing toward oxygen (the more electronegative atom), we see that, because of the angle between the vectors, they do not cancel, but sum to an overall vector or a net dipole moment (shown by the dashed arrow):



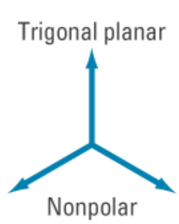
Water's electrostatic potential map shows an electron-rich region at the oxygen end of the molecule. Consequently, water is a polar molecule. Table 5.6 summarizes common geometries and molecular polarity.

Table 5.6 Common Cases of Adding Dipole Moments to Determine whether a Molecule Is Polar

The dipole moments of two identical polar bonds pointing in opposite directions will cancel. The molecule is nonpolar.



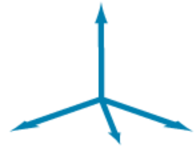
The dipole moments of two polar bonds with an angle of less than 180° between them will not cancel. The resulting dipole moment vector is shown in red. The molecule is polar.



The dipole moments of three identical polar bonds at 120° from each other will

polar bonds at 120° from each other will
cancel. The molecule is nonpolar.

Tetrahedral



Nonpolar

The dipole moments of four identical polar bonds in a tetrahedral arrangement (109.5° from each other) will cancel. The molecule is nonpolar.

Trigonal pyramidal

Polar

The dipole moments of three polar bonds in a trigonal pyramidal arrangement (109.5° from each other) will not cancel. The resulting dipole moment vector is shown in red. The molecule is polar.

Note: In all cases in which the dipoles of two or more polar bonds cancel, the bonds are assumed to be identical. If one or more of the bonds are different from the other(s), the dipoles will not cancel and the molecule will be polar.

Summarizing Determining Molecular Shape and Polarity:

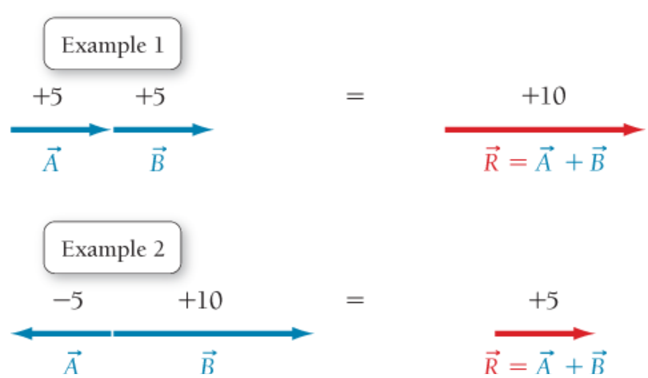
- ***Draw the Lewis structure for the molecule and determine its molecular geometry.***
- ***Determine if the molecule contains polar bonds.*** A bond is polar if the two bonding atoms have sufficiently different electronegativities (see Figure 5.4). If the molecule contains polar bonds, superimpose a vector, pointing toward the more electronegative atom, on each bond. Make the length of the vector proportional to the electronegativity difference between the bonding atoms.
- ***Determine if the polar bonds add together to form a net dipole moment.*** Sum the vectors corresponding to the polar bonds together. If the vectors sum to zero, the molecule is nonpolar. If the vectors sum to a net vector, the molecule is polar.

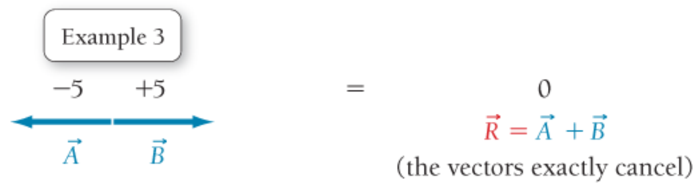
Vector Addition

As discussed previously, we can determine whether a molecule is polar by summing the vectors associated with the dipole moments of all the polar bonds in the molecule. If the vectors sum to zero, the molecule will be nonpolar. If they sum to a net vector, the molecule will be polar. Here, we demonstrate how to add vectors together in one dimension and in two or more dimensions.

One Dimension

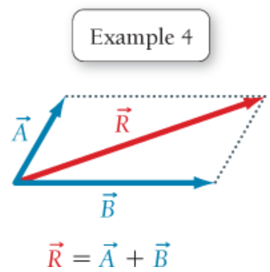
To add two vectors that lie on the same line, assign one direction as positive. Vectors pointing in that direction have positive magnitudes. Vectors pointing in the opposite direction have negative magnitudes. Sum the vectors (always remembering to include their signs), as shown in Examples 1–3.

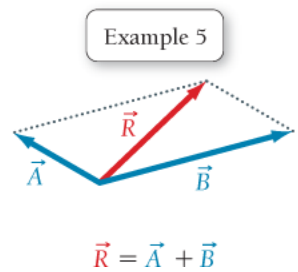




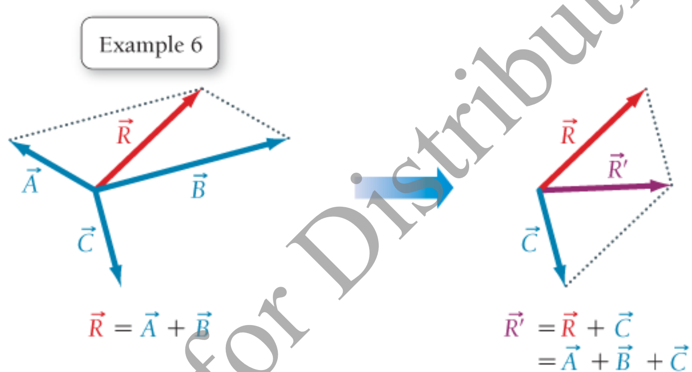
Two or More Dimensions

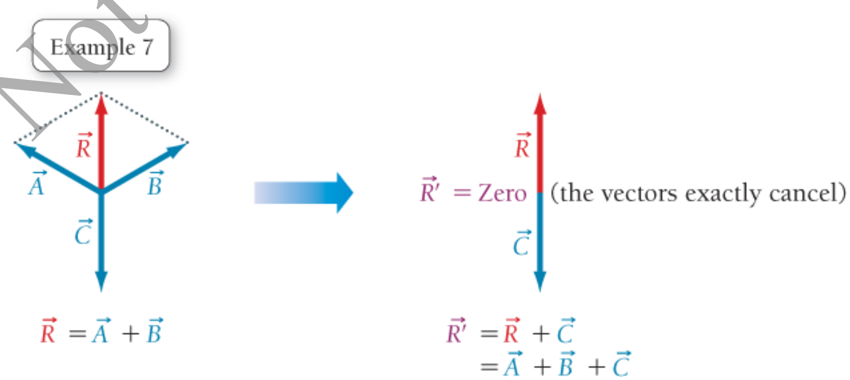
To add two vectors, draw a parallelogram in which the two vectors form two adjacent sides. Draw the other two sides of the parallelogram parallel to and the same length as the two original vectors. Draw the resultant vector beginning at the origin and extending to the far corner of the parallelogram as shown in Examples 4 and 5.



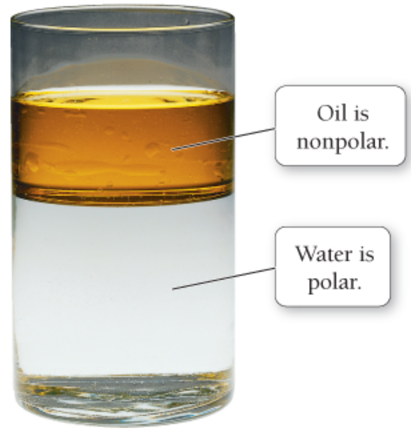


To add three or more vectors, add two of them together first, and then add the third vector to the result as shown in Examples 6 and 7.





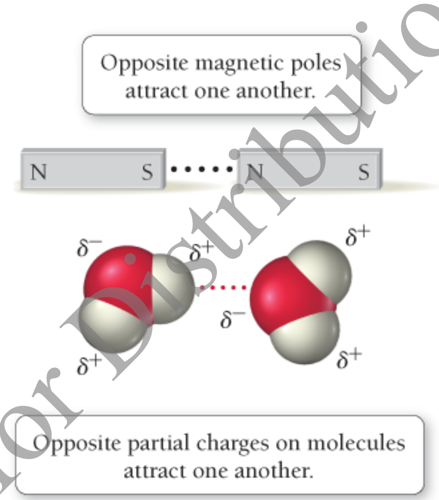
The ability to predict and examine a molecule's polarity is a key connection between the structure of a molecule and its properties, the theme of this book. Water and oil do not mix, for example, because water molecules are polar and the molecules that compose oil are generally nonpolar. Polar molecules interact strongly with other polar molecules because the positive end of one molecule is attracted to the negative end of another, just as the south pole of a magnet is attracted to the north pole of another magnet (Figure 5.11). A mixture of polar and nonpolar molecules is similar to a mixture of small magnetic particles and nonmagnetic ones. The magnetic particles (which are like polar molecules) clump together, excluding the nonmagnetic particles (which are like nonpolar molecules) and separating into distinct regions.



Oil and water do not mix because water molecules are polar and the molecules that compose oil are nonpolar.

Figure 5.11 **Interaction of Polar Molecules**

The north pole of one magnet attracts the south pole of another magnet. In an analogous way, the positively charged end of one molecule attracts the negatively charged end of another (although the forces involved are different). As a result of this electrical attraction, polar molecules interact strongly with one another.



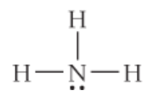
A mixture of polar and nonpolar molecules is analogous to a mixture of magnetic marbles (opaque) and nonmagnetic marbles (transparent). As with the magnetic marbles, mutual attraction causes polar molecules to clump together, excluding the nonpolar molecules.

Example 5.13 Determining if a Molecule Is Polar

Determine if NH_3 is polar.

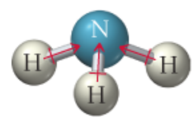
SOLUTION

Draw the Lewis structure for the molecule and determine its molecular geometry.



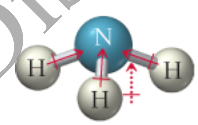
The Lewis structure has three bonding groups and one lone pair about the central atom. Therefore, the molecular geometry is trigonal pyramidal.

Determine if the molecule contains polar bonds. Sketch the molecule and superimpose a vector for each polar bond. Make the relative length of each vector proportional to the electronegativity difference between the atoms forming each bond. Point the vector in the direction of the more electronegative atom. The electronegativities of nitrogen and hydrogen are 3.0 and 2.1, respectively. Therefore, the bonds are polar.



Determine if the polar bonds add together to form a net dipole moment. Examine the symmetry of the vectors (representing dipole moments) and determine if they cancel each other or sum to a net dipole moment.

The three dipole moments sum to a net dipole moment. The molecule is polar.



FOR PRACTICE 5.13 Determine if CF_4 is polar.

Interactive Worked Example 5.13 **Determining Whether a Molecule Is Polar**