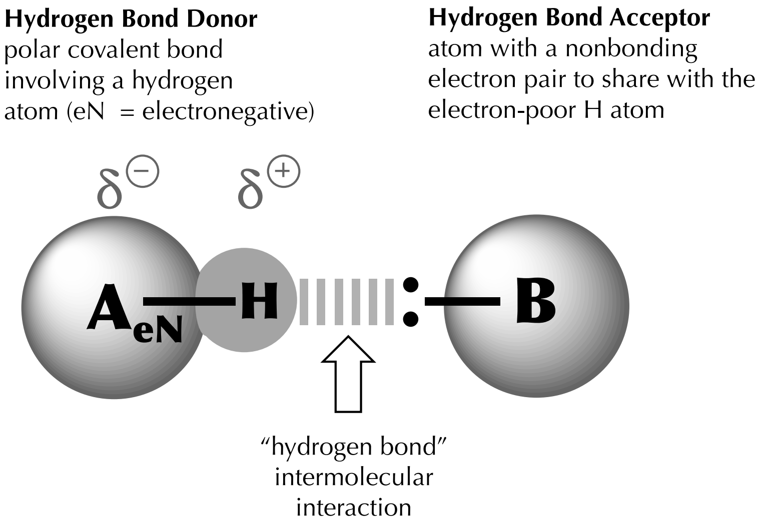
Figure 0250

General picture of a hydrogen bond and its defining partners.



Water is the molecule typically used in general chemistry to illustrate both hydrogen bonding and dipole-dipole attraction as intermolecular forces. The comparison between methane (CH_4), ammonia (NH_3), and water (H_2O) is particularly informative. A property called the kinetic volume of a molecule can be measured; this value gives the effective surface area of the molecule when they are undergoing collisions. The kinetic volumes for these three molecules are 29 Å^3 (methane), 11 Å^3 (ammonia), and 10 Å^3 (water). Although the masses of these three compounds are comparable, methane has more atoms and is more naturally larger, and it should accordingly have higher London dispersion forces than either ammonia or water. In contrast, ammonia and water are about the same size, so the difference in boiling points between these three can give an idea of whether size alone is making a difference. And indeed, these three molecules have distinctively different boiling points (methane: 112 K; ammonia: 240 K; water: 371 K), so intermolecular attractive forces above and beyond London dispersion forces are needed to explain these differences.

Methane (CH_4, molecular weight 16 g/mol) and ammonia (NH_3, 17 g/mol) have nearly the same mass as water (H_20, 18 g/mol). Methane is made up of nonpolar CH bonds and it is a perfectly symmetrical tetrahedron with a molecular dipole moment of 0 Debye; its boiling point is –161.5˚ (111.7 Kelvin, temperature above absolute zero, which exemplifies the importance of London dispersion forces, as described earlier, even in such a small and symmetrical molecule). Ammonia has an asymmetrical trigonal pyramidal structure that creates a permanent dipole moment, which is observed to be 1.46 Debye. The boiling point of ammonia (-33.4 ˚C, 239.8 K) is over 100 degrees higher than methane, which is evidence for needing to overcome the intermolecular dipole-dipole interactions.

The OH bonds in water are more polar than either CH or NH bonds because of the higher electronegativity of oxygen, and the bent geometry results in a molecular dipole moment of 1.85 Debye, larger but ultimately comparable to that of ammonia. The magnitude of the boiling point of water (100 ˚C, 371.2 K), relative to ammonia, is difficult to explain on the basis of only the dipole-dipole attraction. The added interaction of hydrogen bonding between the molecules of water is used to explain this relatively high boiling point (Figure 0251).

Liquid water is a perfect storm of hydrogen bonding: each molecule of water has two hydrogen bond donor sites and two hydrogen bond acceptor sites, and this aggregate collection of intermolecular interactions needs to be overcome to get water from the liquid phase into the gas phase. By the middle of the 20th century, direct experimental evidence emerged for the arrangement of the atoms in solid water (ice). As the x-ray crystallographer, William H. Zachariasen, wrote in 1935, "[between two water molecules, we observe that] every hydrogen atom is thus linked to two oxygen atoms; undoubtedly it is linked more