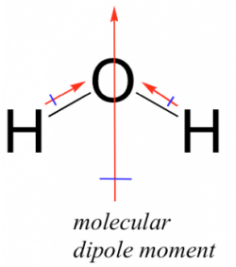
4.5: Molecular Shapes, Polarity, and Molecular Interactions



Now we really have to begin to use our 3D thinking and consider several additional factors: the shape of the molecules and how they interact. Much of this thinking is best done hands on with molecular models but we will outline the logic involved here. The HF molecule has a simple shape; it is linear with (partially) positively and (partially) negatively charged ends. In contrast, the H_2O molecule has a more complex shape; it has two polar $O-H$ bonds. To understand how this affects the polarity of the molecule we have to take into account the number of bonds, their polarization, and the overall shape of the molecule. Bond polarity is a vector quantity, which means it has both a magnitude and a direction. This is where an understanding of the 3D structure of the molecule becomes critical. Each $O-H$ bond is polarized and the overall polarity of the molecule is determined by the vector sum of these bond polarities (that is you have to take into account both the magnitude and the direction of the bond dipoles). This may sound a bit complicated but in practice it is relatively easy to predict qualitatively what the overall polarity of the molecule is as long as you keep in mind its 3D structure. In water the two $O-H$ bonds are at an angle of about 107° to each other ($\rightarrow$). If we add the bond dipole moments up you can see that the overall direction of the dipole for the molecule bisects that angle, as shown in the figure. Now you might think that this exercise is a bit of a waste of time—surely it would make sense that if a molecule has polar bonds, then the molecule itself should be polar. However, as we will see shortly this is not always the case.

If we apply a similar analysis to ammonia (CH_4) we see that the $N-H$ bond is polar with a $\delta+$s on the hydrogen atoms and a $\delta-$ on the nitrogen atom. Remembering that the actual shape of NH_3 is a triangular based pyramid, with an $H-N-H$ bond angle of $\sim 105^{\circ}$, we can see that there is an overall dipole moment in ammonia. Therefore ammonia is a polar molecule.

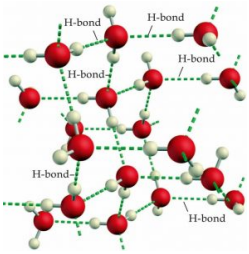
If we contrast this with methane, however, we see two differences. The first is that carbon is not nearly as electronegative as nitrogen, oxygen, or fluorine, so the $C-H$ bond is not as polar. That said, there is an electronegativity difference and so the electron density in the $C-H$ bond is distorted towards the carbon atom (because it is a little more electronegative than the hydrogen atom.) At the same time, CH_4 is symmetrical (tetrahedral.) If we add up all the bond dipoles they cancel each other out giving a molecular dipole moment of zero. Even if we were to replace the hydrogen atoms in methane with fluorine atoms to give CF_4 (carbon tetrafluoride) the resulting molecule would still be non-polar, despite the fact that the electronegativity difference between carbon and fluorine is greater than that between hydrogen and oxygen! This is another example of something counterintuitive: something made up of polar parts that is not polar.

The Famous Hydrogen “Bond”

Now that we have a better idea of how the shape and types of bonds in a molecule can affect its polarity, let us look a little more closely at how molecules interact with each other. The first thing to note is that globally non-polar molecules interact solely via London dispersion forces just like atoms of neon or helium. The boiling point of neon is $-246^{\circ}C$ while the boiling point of CH_4 is $-161^{\circ}C$. This means that methane molecules are more strongly attracted to each other than are neon atoms. We can explain this based on the fact that a methane molecule is larger than a neon atom. Because the electrons in methane molecules are dispersed over a larger area and their distribution (in space) is easier to distort, we say methane molecules are more polarizable. At the same time because methane molecules are non-polar, the boiling point of methane is much lower than that of substances made of polar molecules of similar size.[11]

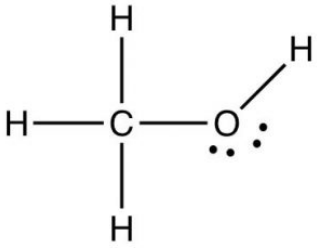
Let us consider three such molecules: HF (bp $19.5^{\circ}C$), H_2O (bp $100^{\circ}C$), and NH_3 (bp $-33^{\circ}C$). All three are polar so they stick together but why are there such large differences in their boiling points? The answer lies in the fact that the molecules interact with one another in multiple ways. They all interact via London dispersion forces and dipole–dipole interactions. In addition, a new type of interaction, known as a hydrogen bond (or H-bond) is also possible. The term H-bond is somewhat misleading because these are much weaker than covalent bonds and do not involve shared electrons; the energy required to break a typical hydrogen bond is between 5 and $\boxed{30 \mathrm{~kJ/mole}}$, whereas it requires over $\boxed{400 \mathrm{~kJ/mole}}$ to break a $C-C$ bond.[12] In biological

systems and in liquid water, H-bonds are continuously breaking and reforming. Hydrogen bonds are formed between two separate molecules.[13] In contrast to London dispersion forces, but like covalent bonds, H-bonds have a direction; they form when the hydrogen of one molecule, which is covalently bonded to an O, N or F, is attracted by the lone pair on an O, N of F of a neighboring molecule.

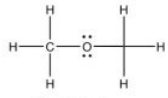


H-bonds are a special case of an electrostatic interaction involving a hydrogen atom that is bonded to a very electronegative atom (typically oxygen or fluorine) and an electronegative atom that has lone pairs of electrons. When a hydrogen is bonded in this way most of the electron density moves toward the electronegative atom, leaving a relatively large $\delta+$ on the hydrogen. Water is a particularly important example of a molecule able to engage in hydrogen bonding, because each molecule of water has the possibility of forming four H-bonds ($\rightarrow$). Each of the hydrogen atoms within a water molecule can bond to another water molecule, while each oxygen atom has two lone pairs that can interact with the electron-deficient hydrogen atoms of two different neighboring water molecules, shown in the figure. The ability to form large numbers and networks of hydrogen bonds is responsible for many of the unique properties of water including its relatively high melting point, boiling point, heat capacity, viscosity, and low vapor pressure. In contrast, HF and NH_3 can form, on average, only two H-bonds per molecule. Can you figure out why this is so? Because there are fewer H-bonds to break, they have lower boiling points. HF has a higher boiling point than NH_3 because the H-bonds in HF are stronger than those in NH_3. (Can you figure out why?) In addition to their role in the bulk properties of substances like water, we will see that H-bonds play a critical role in the organization of biological systems, from the structure of DNA and proteins, to the organization of lipid membranes and catalytic mechanisms (but more about that later).

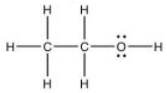
Other Polar Bonds



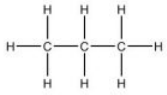
We have seen that when hydrogen is covalently bonded to oxygen, nitrogen, or fluorine, the result is that the covalent bond is highly polarized and the majority of the electron density is located on the most electronegative atom. This means that the hydrogen atom has very little electron density remaining around it. Because hydrogen is such a small atom, the resulting positive charge density on the hydrogen atom is high. This leads to unusually strong attractions (H-bonds) with atoms that have lone pairs with which the positively charged hydrogen atom can interact. H-bonding is unique to molecules in which a hydrogen atom is covalently bonded to an oxygen, nitrogen, or fluorine atom. However, there are uneven charge distributions possible whenever two atoms with different electronegativities form a bond. Consider, for example, methanol (CH_3OH). It has several different types of bonds with different distributions of charge in them. The familiar $O-H$ bond in methanol is very much like the $O-H$ bond found in water. That is, it is highly polarized and the hydrogen atom is a small, dense region of highly positive charge that can attract and will be attracted to regions of high electron density such as the lone pairs on oxygen. The methanol molecule also has a $C-O$ bond and three $C-H$ bonds. If we consider the differences in electronegativity we can predict the polarization of these bonds. Remember that carbon and hydrogen have quite similar electronegativities, and so the $C-H$ bond is not very polarized. Carbon and oxygen, in contrast, are quite different in their electronegativities and the result is that the $C-O$ bond is strongly polarized, with the $\delta+$ located on the carbon atom and the negative end of the bond dipole on the oxygen atom. As we will see later this has implications for how methanol (and all $C-O$ containing compounds) interact (and react) with other substances.



Dimethyl ether



Ethanol



Propane

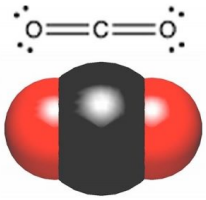
An inspection of the Lewis structure can reveal (to the trained mind!) a huge amount about the structure and polarity of a molecule and taking that one step further we can make predictions about the properties of the compound. For example if we compare the relative boiling points of methanol (CH_3OH, bp $65^\circ C$) and ethane (CH_3CH_3, bp $-88.6^\circ C$) we see (just as you already predicted no doubt) that methanol has a much higher boiling point because it takes more energy to separate molecules of methanol. The question arises: is this because methanol can form an H-bond with itself? Can you draw a picture of how this happens? Or is it because of the $C-O$ dipole? We can look at this idea a little more closely by comparing the boiling points of three compounds that have similar molecular weights (so that they experience similar London dispersion forces), but different types of bonds in them.

If we classify the kinds of bonds as before we see that dimethyl ether has non-polar $C-H$ bonds and polar $C-O$ bonds. The $C-O-C$ bond angle is about 104°. Because each atom (except for H) is surrounded by four centers of electron density, the molecule is not linear as pictured. (Why not?) The molecule as whole is polar but cannot form hydrogen bonds with itself because none of the hydrogen atoms have a significant $\delta+$ as they would if they were bonded to an oxygen atom. We call the type of forces between dimethyl ether molecules, dipole–dipole forces. On the other hand, an ethanol molecule—which has exactly the same molecular weight and formula—can form hydrogen bonds with itself because it has an $O-H$ bond, and so has a small partially positively charged hydrogen atom. This minor difference has a huge effect on boiling point: ethanol boils at $78^\circ C$ whereas dimethyl ether boils at $-23^\circ C$. Both of them are considerably higher than propane at $-44^\circ C$ (remembering that absolute zero is $-273.15^\circ C$). From comparing these three similar compounds we can see that a simple dipole–dipole attraction increases the boiling point by $21^\circ C$, and on top of that the H-bonding attraction in ethanol is worth another $99^\circ C$, bringing the boiling point of ethanol to $78^\circ C$.

Intermolecular Forces

Taken together, London dispersion forces, dipole-dipole interactions, and hydrogen bonds comprise a set of attractive forces that make separate molecules stick together. These are collectively named intermolecular forces, IMFs. These forces are caused by either permanent or temporary distortions of the electron cloud in a molecule – which leads to electrostatic attractions between separate molecules. For small molecules, the typical order for strengths of IMFs is:
H-bonding (where available) > dipole–dipole interactions > London dispersion forces. At the same time, because London dispersion forces increase with molecular size and the extent of surface-surface interactions, they are often the predominant intermolecular force between large biological macromolecules.

The Importance of Shape



While we are on the subject of carbon and oxygen containing compounds, let us take a look at one of the most common compounds of carbon and oxygen, carbon dioxide. You can draw the structure of CO_2 with the carbon atom in the middle, double bonded to each of the oxygen atoms. That is, CO_2 has two quite polar bonds in it, and so we might reasonably predict that its boiling point might lie somewhere between dimethyl ether and ethanol. But, as you probably already know, this is not the case. CO_2 exists as a

gas at room temperature. In fact CO_2 does not have a liquid phase at standard atmospheric pressure; it changes directly from a solid to a gas, a process called sublimation, at $-78^\circ C$. How is such behavior to be understood, particularly given that CO_2 has about the same molar mass as ethanol (CH_3CH_2OH), which is a liquid at room temperature? Once again we have to make sure we have considered all the factors that affect molecular polarity including bond polarity and shape. If you reflect back to the ideas about bond polarity and structure you will see that we have another case here of a molecule with polar bonds, but no overall polarity. CO_2 has a linear structure so the bond polarities cancel each other out (they are at 180° from each other) ($\rightarrow$). CO_2 has no overall molecular polarity, even though it has polar bonds. Therefore the molecules do not stick together very well and it is a gas at room temperature.

? Questions

Questions to Answer

- What is the direction of the molecular dipole moment in ammonia? Draw out a picture showing how you came up with the answer. Does it matter which way you draw the molecule? What if you draw it upside down? Will that affect the direction of the dipole (in the real world)?
- Why are the interactions between H_2O molecules stronger than those between HF molecules even though the polarity of the HF bond is larger than the polarity of the OH bond?
- Why don't more than four water molecules interact with a central water molecule?
- What would you predict would be the relative boiling points of methanol (CH_3OH) and ethane (CH_3CH_3), which have similar molecular weights?
- What would you predict would be the relative boiling points of methanol (CH_3OH) and ethanol (CH_3CH_2OH)?
- What kind of compound (or what structural feature) would you expect might be attracted to the $\delta+$ located on the carbon atom in methanol?

Questions to Ponder

- What would be the consequences (for life, the universe, and everything) if water molecules were linear?