

Section 5: Observation 3: Dipole Moments in Polyatomic Molecules

We might reasonably expect from our analysis to observe a dipole moment in any molecule formed from atoms with different electronegativities. Although this must be the case for a diatomic molecule, this is not necessarily true for a polyatomic molecule, i.e. one with more than two atoms. For example, carbon is more electronegative than hydrogen. However, the simplest molecule formed from carbon and hydrogen (e.g. CH₄) does not possess a dipole moment, as we see in Table. Similarly, oxygen is significantly more electronegative than carbon, yet CO₂ is a non-polar molecule. An analysis of molecular dipole moments in polyatomic molecules requires us to apply our understanding of molecular geometry.

Note that each CO bond is expected to be polar, due to the unequal sharing of the electron pairs between the carbon and the oxygen. Thus, the carbon atom should have a slight positive charge and the oxygen atom a slight negative charge in each CO bond. However, since each oxygen atom should have the same net negative charge, neither end of the molecule would display a greater affinity for an electric field. Moreover, because CO₂ is linear, the dipole in one CO bond is exactly offset by the dipole in the opposite direction due to the other CO bond. As measured by an electric field from a distance, the CO₂

molecule does not appear to have separated positive and negative charges and therefore does not display polarity. Thus, in predicting molecular dipoles we must take into account both differences in electronegativity, which affect bond polarity, and overall molecular geometry, which can produce cancellation of bond polarities.

Using this same argument, we can rationalize the zero molecular dipole moments observed for other molecules, such as methane, ethene and acetylene. In each of these molecules, the individual CH bonds are polar. However, the symmetry of the molecule produces a cancellation of these bond dipoles overall, and none of these molecules have a molecular dipole moment.

As an example of how a molecular property like the dipole moment can affect the macroscopic property of a substance, we can examine the boiling points of various compounds. The boiling point of a compound is determined by the strength of the forces between molecules of the compound: the stronger the force, the more energy is required to separate the molecules, the higher the temperature required to provide this energy. Therefore, molecules with strong intermolecular forces have high boiling points.

We begin by comparing molecules which are similar in size, such as the hydrides SiH₄, PH₃, and SH₂ from the third period. The boiling points at standard pressure for these molecules are, respectively, -111.8°C, -87.7°C, and -60.7°C. All three compounds are thus gases at room temperature and well below. These molecules have very similar masses and have exactly the same number of electrons. However, the dipole moments of these molecules are very different. The dipole moment of SiH₄, is 0.0D, the dipole moment of PH₃ is 0.58D, and the dipole moment of SH₂ is 0.97D. Note that, for these similar molecules, the higher the dipole moment, the higher the boiling point. Thus, molecules with larger dipole moments generally have stronger intermolecular forces than similar molecules with smaller dipole moments. This is because the positive end of the dipole in one molecule can interact electrostatically with the negative end of the dipole in another molecule, and vice versa.

We note, however, that one cannot generally predict from dipole moment information only the relative boiling points of compounds of very dissimilar molecules

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