

Section 4: Observation 2: Molecular Dipole Moments

Our Lewis model of bonding, as currently developed, incorporates two extreme views of the distribution of electrons in a bond. In a covalent bond, we have assumed up to this point that the electron pair is shared perfectly. In complete contrast, in ionic bonding we have assumed that the electrons are not shared at all. Rather, one of the atoms is assumed to entirely extract one or more electrons from the other. We might expect that a more accurate description of the reality of chemical bonds falls in general somewhere between these two extremes. To observe this intermediate behavior, we can examine molecular dipole moments.

An electric dipole is a spatial separation of positive and negative charges. In the simplest case, a positive charge Q and a negative charge $-Q$ separated by a distance R produce a measurable dipole moment, μ equal to $Q \times R$.

. An electric field can interact with an electric dipole and can even orient the dipole in the direction of the field.

We might initially expect that molecules do not in general have dipole moments. Each atom entering into a chemical bond is electrically neutral, with equal numbers of positive and negative charges. Consequently, a molecule formed from neutral atoms must also be electrically neutral. Although electron pairs are shared between bonded nuclei, this does not affect the total number of negative charges. We might from these simple statements that molecules would be unaffected by electric or magnetic fields, each molecule behaving as a single uncharged particle.

This prediction is incorrect, however. To illustrate, a stream of water can be deflected by an electrically charged object near the stream, indicating that individual water molecules exhibit a dipole moment. A water molecule is rather more complicated than a simple separation of a positive and negative charges, however. Recall though that a water molecule has equal total numbers of positive and negative charges, consisting of three positively charged nuclei surrounded by ten electrons. Nevertheless, measurements reveal that water has a dipole moment of $6.17 \times 10^{-30} \text{ (Cm)} = 1.85 \text{ debye}$.

. (The debye is a unit used to measure dipole moments: $1 \text{ debye} = 3.33 \times 10^{-30} \text{ (Cm)}$.) Water is not unique: the molecules of most substances have dipole moments. A sampling of molecules and their dipole moments is given in Table.

	μ (debye)
	1.85
	1.91
	1.08
	0.80
	0.42
	0.12
	0

	1.47
	0.58
	0.20
	0
	9.00

Focusing again on the water molecule, how can we account for the existence of a dipole moment in a neutral molecule? The existence of the dipole moment reveals that a water molecule must have an internal separation of positive partial charge and negative partial charge

. Thus, it must be true that the electrons in the covalent bond between hydrogen and oxygen are not **equally** shared. Rather, the shared electrons must spend more time in the vicinity of one nucleus than the other. The molecule thus has one region where, on average, there is a net surplus of negative charge and one region where, on average, there is a compensating surplus of positive charge, thus producing a molecular dipole. Additional observations reveal that the oxygen "end" of the molecule holds the partial negative charge. Hence, the covalently shared electrons spend more time near the oxygen atom than near the hydrogen atoms. We conclude that oxygen atoms have a greater ability to attract the shared electrons in the bond than do hydrogen atoms.

We should not be surprised by the fact that individual atoms of different elements have differing abilities to attract electrons to themselves. We have previously seen that different atoms have greatly varying ionization energies, representing great variation in the extent to which atoms cling to their electrons. We have also seen great variation in the electron affinities of atoms, representing variation in the extent to which atoms attract an added electron. We now define the electronegativity of an atom as the ability of the atom to attract electrons in a chemical bond. This is different than either ionization energy or electron affinity, because electronegativity is the attraction of electrons **in a chemical bond**, whereas ionization energy and electron affinity refer to removal and attachment of electrons in free atoms. However, we can expect electronegativity to be correlated with electron affinity and ionization energy. In particular, the electronegativity of an atom arises from a combination of properties of the atom, including the size of the atom, the charge on the nucleus, the number of electrons about the nuclei, and the number of electrons in the valence shell.

Because electronegativity is an abstractly defined property, it cannot be directly measured. In fact, there are many definitions of electronegativity, resulting in many different scales of electronegativities. However, relative electronegativities can be observed indirectly by measuring molecular dipole moments: in general, the greater the dipole moment, the greater the separation of charges must be, and therefore, the less equal the sharing of the bonding electrons must be.

With this in mind, we refer back to the dipoles given in [Table](#). There are several important trends in these data. Note that each hydrogen halide (

, , , and) has a significant dipole moment. Moreover, the dipole moments increase as we move **up** the periodic table in the halogen group. We can conclude that fluorine atoms have a greater electronegativity than do chlorine atoms, etc. Note also that has a greater dipole moment than , which is in turn greater than that of

. We can conclude that electronegativity increases as we move **across** the periodic table from left to right in a single period. These trends hold generally in comparisons of the electronegativities of the individual elements. One set of relative electronegativities of

atoms in the first three rows of the periodic table is given in [Table](#).

Electronegativities of Selected Atoms

		χ
H		2.1
He		-
Li		1.0
Be		1.5
B		2.0
C		2.5
N		3.0
O		3.5
F		4.0
Ne		-
Na		0.9
Mg		1.2
Al		1.5
Si		1.8
P		2.1
S		2.5
Cl		3.0
Ar		-
K		0.8
Ca		1.0

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