

# MOLECULAR STRUCTURE AND PHYSICAL PROPERTIES

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## Abstract

## Molecular Structure and Physical Properties

### 1 Foundation

We begin with our knowledge of the structure and properties of atoms. We know that atoms have a nuclear structure, meaning that all of the positive charge and virtually all of the mass of the atom are concentrated in a nucleus which is a very small fraction of the volume of the atom. In addition, we know that many of the properties of atoms can be understood by a model in which the electrons in the atom are arranged in “shells” about the nucleus, with each shell farther from the nucleus than the previous. The electrons in outer shells are more weakly attached to the atom than the electrons in the inner shells, and only a limited number of electrons can fit in each shell. Within each shell are subshells, each of which can also hold a limited number of electrons. The electrons in different subshells have different energies and different locations for motion about the nucleus. We also assume a knowledge of the a **Lewis structure** model for chemical bonding based on valence shell electron pair sharing and the octet rule. A covalent chemical bond is formed when the two bonded atoms share a pair of valence shell electrons between them. In general, atoms of Groups IV through VII bond so as to complete an octet of valence shell electrons. We finally assume the **Electron Domain Model** for understanding and predicting molecular geometries. The pairs of valence shell electrons are arranged in bonding and non-bonding domains, and these domains are separated in space to minimize electron-electron repulsions. This electron domain arrangement determines the molecular geometry.

### 2 Goals

We should expect that the properties of molecules, and correspondingly the substances which they comprise, should depend on the details of the structure and bonding in these molecules. Now that we have developed an understanding of the relationship between molecular structure and chemical bonding, we analyze physical properties of the molecules and compounds of these molecules to relate to this bonding and structure. Simple examples of

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physical properties which can be related to molecular properties are the melting and boiling temperatures. These vary dramatically from substance to substance, even for substances which appear similar in molecular formulae, with some melting temperatures in the hundreds or thousands of degrees Celsius and others well below 0°C. We seek to understand these variations by analyzing molecular structures.

To develop this understanding, we will have to apply more details of our understanding of atomic structure and electronic configurations. In our covalent bonding model, we have assumed that atoms “share” electrons to form a bond. However, our knowledge of the properties of atoms reveals that different atoms attract electrons with different strengths, resulting in very strong variations in ionization energies, atomic radii, and electron affinities. We seek to incorporate this information into our understanding of chemical bonding

### 3 Observation 1: Compounds of Groups I and II

We begin by analyzing compounds formed from elements from Groups I and II ( e.g. sodium and magnesium). These compounds are not currently part of our Lewis structure model. For example, Sodium, with a single valence electron, is unlikely to gain seven additional electrons to complete an octet. Indeed, the common valence of the alkali metals in Group I is 1, not 7, and the common valence of the alkaline earth metals is 2, not 6. Thus, our current model of bonding does not apply to elements in these groups.

To develop an understanding of bonding in these compounds, we focus on the halides of these elements. In Melting Points and Boiling Points of Chloride Compounds, we compare physical properties of the chlorides of elements in Groups I and II to the chlorides of the elements of Groups IV, V, and VI, and we see enormous differences. All of the alkali halides and alkaline earth halides are solids at room temperature and have melting points in the hundreds of degrees centigrade. The melting point of NaCl is 808°C, for example. By contrast, the melting points of the non-metal halides from Periods 2 and 3, such as  $CCl_4$ ,  $PCl_3$ , and  $SCl_2$ , are below 0°C, so that these materials are liquids at room temperature. Furthermore, all of these compounds have low boiling points, typically in the range of 50°C to 80°C.

#### Melting Points and Boiling Points of Chloride Compounds

	Melting Point (°C)	Boiling Point (°C)
LiCl	610	1382
BeCl <sub>2</sub>	405	488
CCl <sub>4</sub>	-23	77
NCl <sub>3</sub>	-40	71
OCl <sub>2</sub>	-20	4
FCl	-154	-101
NaCl	808	1465
MgCl <sub>2</sub>	714	1418
SiCl <sub>4</sub>	-68	57
PCl <sub>3</sub>	-91	74
SCl <sub>2</sub>	-122	59
Cl <sub>2</sub>	-102	-35
KCl	772	1407
CaCl <sub>2</sub>	772	>1600

Second, the non-metal halide liquids are electrical insulators, that is, they do not conduct

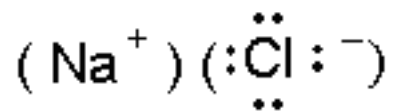


Figure 1

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an electrical current. By contrast, when we melt an alkali halide or alkaline earth halide, the resulting liquid is an excellent electrical conductor. This indicates that these molten compounds consist of ions, whereas the non-metal halides do not.

We must conclude that the bonding of atoms in alkali halides and alkaline earth halides differs significantly from bonding in non-metal halides. We need to extend our valence shell electron model to account for this bonding, and in particular, we must account for the presence of ions in the molten metal halides. Consider the prototypical example of NaCl. We have already deduced that Cl atoms react so as to form a complete octet of valence shell electrons. Such an octet could be achieved by covalently sharing the single valence shell electron from a sodium atom. However, such a covalent sharing is clearly inconsistent with the presence of ions in molten sodium chloride. Furthermore, this type of bond would predict that NaCl should have similar properties to other covalent chloride compounds, most of which are liquids at room temperature. By contrast, we might imagine that the chlorine atom completes its octet by taking the valence shell electron from a sodium atom, without covalent sharing. This would account for the presence of  $\text{Na}^+$  and  $\text{Cl}^-$  ions in molten sodium chloride.

In the absence of a covalent sharing of an electron pair, though, what accounts for the stability of sodium chloride as a compound? It is relatively obvious that a negatively charged chloride ion will be attracted electrostatically to a positively charged sodium ion. We must also add to this model, however, the fact that individual molecules of NaCl are not generally observed at temperatures less than  $1465^\circ\text{C}$ , the boiling point of sodium chloride. Note that, if solid sodium chloride consists of individual sodium ions in proximity to individual chloride ions, then each positive ion is not simply attracted to a single specific negative ion but rather to all of the negative ions in its near vicinity. Hence, solid sodium chloride cannot be viewed as individual NaCl molecules, but must be viewed rather as a lattice of positive sodium ions interacting with negative chloride ions. This type of “ionic” bonding, which derives from the electrostatic attraction of interlocking lattices of positive and negative ions, accounts for the very high melting and boiling points of the alkali halides.

We can now draw modified Lewis structures to account for ionic bonding, but these are very different from our previous drawings. Sodium chloride can be represented as shown in Figure 1.

This indicates explicitly that the bonding is due to positive-negative ion attraction, and not due to sharing of an electron pair. The only sense in which the  $\text{Na}^+$  ion has obeyed an octet rule is perhaps that, in having emptied its valence shell of electrons, the remaining outer shell of electrons in the ion has the same octet as does a neon atom. We must keep in mind, however, that the positive sodium ion is attracted to many negative chloride ions, and not just the single chloride ion depicted in the Lewis structure.

## 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**,  $\mu$  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  $6.17 \times 10^{-30} (Cm) = 1.85\text{debye}$ . (The debye is a unit used to measure dipole moments:  $1\text{debye} = 3.33 \times 10^{-30} (Cm)$ .) Water is not unique: the molecules of most substances have dipole moments. A sampling of molecules and their dipole moments is given in Dipole Moments of Specific Molecules.

### Dipole Moments of Specific Molecules

	$\mu$ (debye)
$H_2O$	1.85
$HF$	1.91
$HCl$	1.08
$HBr$	0.80
$HI$	0.42
$CO$	0.12
$CO_2$	0
$NH_3$	1.47
$PH_3$	0.58
$AsH_3$	0.20
$CH_4$	0
$NaCl$	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  $+\delta$  and negative partial

charge  $-\delta$ . 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 Dipole Moments of Specific Molecules. There are several important trends in these data. Note that each hydrogen halide ( $HF$ ,  $HCl$ ,  $HBr$ , and  $HI$ ) 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  $HF$  has a greater dipole moment than  $H_2O$ , which is in turn greater than that of  $NH_3$ . 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 Electronegativities of Selected Atoms.

### Electronegativities of Selected Atoms

	$\chi$
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

### 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.*  $CH_4$  ) does *not* possess a dipole moment, as we see in Dipole Moments of Specific Molecules. Similarly, oxygen is significantly more electronegative than carbon, yet  $CO_2$  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  $CO_2$  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  $CO_2$  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  $\text{SiH}_4$ ,  $\text{PH}_3$ , and  $\text{SH}_2$  from the third period. The boiling points at standard pressure for these molecules are, respectively,  $-111.8^\circ\text{C}$ ,  $-87.7^\circ\text{C}$ , and  $-60.7^\circ\text{C}$ . 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  $\text{SiH}_4$ , is 0.0D, the dipole moment of  $\text{PH}_3$  is 0.58D, and the dipole moment of  $\text{SH}_2$  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 molecules, 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

## 6 Review and Discussion Questions

### Exercise 1:

Compare and contrast the chemical and physical properties of  $\text{KCl}$  and  $\text{CCl}_4$ , and compare and contrast how the chemical bonding model can be used to account for these properties.

### Exercise 2:

Why is the dipole moment of  $\text{NaCl}$  extremely large?

### Exercise 3:

Explain why  $\text{CO}$  has a dipole moment but  $\text{CO}_2$  does not.

### Exercise 4:

Explain why an atom with a high ionization energy is expected to have a high electronegativity. Explain why an atom with a high electron affinity is expected to have a high electronegativity.

### Exercise 5:

Would you predict that a Kr atom has high electronegativity or low electronegativity? Predict the relative electronegativity of Kr and F.

### Exercise 6:

Explain why S has a greater electronegativity than P but a smaller electronegativity than O.

**Exercise 7:**

N atoms have a high electronegativity. However, N atoms have no electron affinity, meaning that N atoms do not attract electrons. Explain how and why these facts are not inconsistent.

**Exercise 8:**

Explain why compounds formed from elements with large differences in electronegativities are ionic.

**Exercise 9:**

Explain why ionic compounds have much higher melting points than covalent compounds.