Models versus reality
In this experiment, molecular models are used to explore a number of aspects of molecular structure and an important molecular property, polarity. You will also examine some of the instances in which models prove too simple to successfully represent the reality at the molecular level. In order to be able to make proper use of models it is important to understand the relationship between a model and the reality it tries to reproduce.

Models are imperfect things, often very useful when applied to the problems for which they were designed, frequently misleading when extended beyond their range of applicability. Let’s consider the Framework Molecular Model Kit (see Appendix 1) used in this experiment. It is designed to reproduce some basic geometric features of bonding, specifically, bond angles and lengths. These models are at their most valuable in showing how the structure of molecules arises as a consequence of the geometry of bonds about the individual atoms. Pauling and Corey’s determination of the structure of simple proteins and Watson and Crick’s discovery of the base pairing in DNA were some early triumphs of the use of simple model kits like the one you will use in this experiment.

The model kits do not convey information about the energetics of bonding, i.e., why a particular bond forms between two atoms. The kits do not allow for the distortions of the geometry away from the perfect tetrahedral, octahedral, etc. The kits do not really attempt to depict the distribution of electrons around the atoms and in the bonds with any accuracy. You need to be aware of these limitations when you draw conclusions from your model building. (You will see what we mean in this experiment.) These limitations, however, are also the reason why the models are as simple to use (and, hence, as useful) as they are.

Bonding and valence shell electrons
When an atom forms a single covalent bond it in effect gains one electron into its valence shell.

An isolated F atom has 7 valence electrons (F is in Periodic Group 17). An HF molecule can be represented by an electron dot (Lewis – see Appendix 2) structure as

\[ H \cdot F \]

In the formation of the one covalent bond, both the H and the F atoms have gained one electron each and now have the stable electronic configuration of the next noble gas atom in the periodic table.

An isolated O atom has 6 valence electrons (O is in Periodic Group 16). The H₂O molecule can be represented as

\[ H \cdot O \cdot H \]

In the formation of the two covalent bonds, the O atom has gained two electrons and now has a stable octet of valence electrons.

Building with the model kit
Where one of the electron pairs is a bonding pair, join the cluster representing the first atom to the coloured tubing representing the covalent radius of that atom. The outer end of the tubing must then be joined to another length of tubing representing the covalent radius of the bonded atom. Where one of the electron pairs is a nonbonding pair, the coloured tubing is cut to the appropriate van der Waals radius length of that atom and represents the extent of the electron pair. A nonbonding electron pair is also called a lone pair.
A prediction of the geometry of a molecule can be made based on the simple idea that the electron pairs in the valence shell (non-bonding pairs as well as bonding pairs) seek to maximise their distance from one another in order to minimise the Coulombic repulsions. This idea is referred to as Valence Shell Electron Pair Repulsion (or VSEPR, for short). For example, consider an atom which, in a molecule, has 4 electron pairs in its valence shell. The VSEPR model would predict that those 4 pairs would arrange themselves tetrahedrally about the atom, as this is the arrangement which maximises the distance of all the pairs from each other.

**Constructing bonds with the model kit**

Single bonds have axial symmetry (like the tubing which represents them). Bonds with axial symmetry are termed σ bonds (sigma bonds).

**C-C Bond**

A bond between a pair of like atoms is cut from tubing of one colour. The atomic radius of carbon is represented by black tubing, 0.77 inch long. A C-C bond will then be represented by two of these lengths joined together. (Refer to the tables in Appendix 1 for the radii of different atoms).

**C-H Bond**

As shown in Figure E11-1, a C-H bond could be constructed by joining in sequence:

- 0.77 inch length of black tubing representing the covalent radius of carbon.
- A 0.30 inch length of white tubing representing the covalent radius of hydrogen, and which has a permanently attached linear fastener at both ends.
- 1.20 inch length of white tubing representing the van der Waals radius of hydrogen.

![Figure E11-1](image1)

The hydrogen atom occupies a sphere centred at the nucleus. You should mentally fill in the volume of the atom on this framework.

**C-F Bond**

A 0.77 inch length of black tubing (covalent radius of carbon 0.77 Å) is attached to a 0.64 inch length of light-green tubing (covalent radius of fluorine 0.64 Å) by means of a linear fastener, to form the carbon-fluorine bond, as shown in Figure E11-2.

![Figure E11-2](image2)
APPENDIX 1 - THE FRAMEWORK MOLECULAR MODEL KIT

© Acknowledgment is made to Prentice-Hall Inc. for permission to reprint sections of the instruction manual which accompanies their "Framework Molecular Models" kits.

The FMM kit is composed of two basic construction units, metal “valence clusters” and plastic tubing, by means of which atoms of all elements can be represented. Each type of atom is colour-coded (see Table E11-1). For example, red tubing represents oxygen, white is hydrogen, blue is nitrogen, black is carbon, and so on. Valence clusters are coloured silver, brass, and copper for easy identification.

Table E11-1 Colour Coding Of Atoms

<table>
<thead>
<tr>
<th>Atom</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>white</td>
</tr>
<tr>
<td>B</td>
<td>dark yellow</td>
</tr>
<tr>
<td>C</td>
<td>black</td>
</tr>
<tr>
<td>N</td>
<td>blue</td>
</tr>
<tr>
<td>O</td>
<td>red</td>
</tr>
<tr>
<td>F</td>
<td>light green</td>
</tr>
<tr>
<td>Si</td>
<td>purple</td>
</tr>
<tr>
<td>P</td>
<td>violet</td>
</tr>
<tr>
<td>S</td>
<td>light yellow</td>
</tr>
<tr>
<td>Cl</td>
<td>dark green</td>
</tr>
<tr>
<td>Br</td>
<td>orange</td>
</tr>
<tr>
<td>I</td>
<td>brown</td>
</tr>
</tbody>
</table>

Each valence cluster has metal prongs joined at a common point representing the centre of the atom. These prongs, which fit snugly into the plastic tubing, point along the symmetry axes of the valence orbitals, and the angles formed determine bond angles in the assembled models.

Models built from the FMM kit show to scale the mutual relations of atoms of a given structure. The scale is 1 inch = 1 ångstrom (1 Å) = 10⁻¹ nanometre = 10⁻¹⁰ metre = 100 picometre. Note that one inch is approximately 25 millimetre on your metric ruler.

The molecular framework is specified by
- The internuclear distances, which measure the separation between the centres of two neighbouring atoms.
- The bond angles which measure whether two atoms both bonded to a third are collinear or at an angle.

For example, take methane. The points H and C are the centres of hydrogen and carbon atoms, and the distance between them is called the internuclear (or interatomic) distance. This distance can be conveniently thought of as composed of two parts:
- The C to X or C-X distance (0.77 Å), measuring the size of carbon in the direction of the bond, and known as the covalent radius of carbon.
- The X-H distance (0.30 Å), the covalent radius of hydrogen.

![Figure E11-3](image-url)
Values of covalent radii are listed in Table E11-2. The bond length is the distance between the two nuclei and is the sum of the covalent radii, in this case 1.07 Å.

**Table E11-2 Single Bond Covalent Radii (Å)**

<table>
<thead>
<tr>
<th>Element</th>
<th>Covalent Radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0.30</td>
</tr>
<tr>
<td>Be</td>
<td>0.89</td>
</tr>
<tr>
<td>B</td>
<td>0.80</td>
</tr>
<tr>
<td>C</td>
<td>0.77</td>
</tr>
<tr>
<td>N</td>
<td>0.74</td>
</tr>
<tr>
<td>O</td>
<td>0.74</td>
</tr>
<tr>
<td>F</td>
<td>0.64</td>
</tr>
<tr>
<td>Si</td>
<td>1.17</td>
</tr>
<tr>
<td>P</td>
<td>1.10</td>
</tr>
<tr>
<td>S</td>
<td>1.04</td>
</tr>
<tr>
<td>Cl</td>
<td>1.00</td>
</tr>
<tr>
<td>Br</td>
<td>1.14</td>
</tr>
<tr>
<td>I</td>
<td>1.33</td>
</tr>
<tr>
<td>Xe</td>
<td>1.31</td>
</tr>
</tbody>
</table>

3rd transition metals ~ 1.25

In CH₄, the H-C-H bond angle is 109.47° (109° 28'), and is called the tetrahedral angle. In less symmetric molecules, such as CH₃Cl or NH₃, the bond angles vary slightly from the tetrahedral angle.

When molecules aggregate to form a crystal, or when they collide at moderate speed, their closest contact occurs at a distance corresponding to the van der Waals envelope. This envelope denotes how far the atoms within a molecule extend outwards. The size of van der Waals radii are given in Table E11-3. Note that such radii are not measurable precisely, but estimates, as given here, are nevertheless very useful.

**Table E11-3 Van Der Waals Radii (Å)**

<table>
<thead>
<tr>
<th>Element</th>
<th>Van Der Waals Radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1.2</td>
</tr>
<tr>
<td>C</td>
<td>1.8</td>
</tr>
<tr>
<td>N</td>
<td>1.5</td>
</tr>
<tr>
<td>O</td>
<td>1.4</td>
</tr>
<tr>
<td>F</td>
<td>1.4</td>
</tr>
<tr>
<td>P</td>
<td>1.9</td>
</tr>
<tr>
<td>S</td>
<td>1.8</td>
</tr>
<tr>
<td>Cl</td>
<td>1.8</td>
</tr>
<tr>
<td>Br</td>
<td>2.0</td>
</tr>
<tr>
<td>I</td>
<td>2.2</td>
</tr>
<tr>
<td>Xe</td>
<td>2.1</td>
</tr>
</tbody>
</table>

With the axis of the C-H bond as example (see Figure E11-3), the distance C-X denotes the covalent radius of carbon (black tubing), the distance X-H denotes the covalent radius of H (0.30 Å), and the section H to W extending in the nonbonded direction corresponds to the van der Waals radius of hydrogen (1.20 Å). In Figure E11-3, one must imagine that the volume occupied by each hydrogen atom is a portion of a sphere with centre H and radius H-W. Space-filling models, which show the outer surface of molecules, are available for comparison. With experience it is not difficult to visualise the volume of a molecule, given the framework of the molecule in an FMM model.

For the preparation of bonds, coloured tubing is supplied, which can be used either by itself for a bond between like atoms, or joined by a linear fastener to tubing of another colour to represent a bond joining different atoms.
APPENDIX 2 - LEWIS (ELECTRON DOT) STRUCTURES

Lewis structures are useful aids in the understanding of how atoms bond together to form molecules, and are often used to conceptualise molecular properties. Lewis structures are combinations of chemical symbols, dots and lines, used to denote nuclei, electrons and bonds, respectively. An understanding of valency, the octet rule and hybridisation are a necessary prerequisite.

Valency
Valence orbitals are simply those orbitals that occupy the outermost energy shell of the atomic structure (ie. the valence shell). Valence electrons are those electrons that occupy these orbitals. Note, that whilst each orbital can contain two electrons, it does not necessarily do so in the ground, elemental state. For instance, nitrogen has one s and 3 p valence orbitals, and so could have 8 valence electrons, but it only has 5. The number of valence electrons present in an atom of an element can be readily determined from the Periodic Table.

The octet rule
The octet rule states that bonded atoms tend to possess or share a total of 8 valence electrons. An octet of electrons can be thought of as four pairs of valence electrons arranged around the atom. Each pair can be entirely shared (dative covalent) with another atom or a single electron from a valence pair can be shared with another atom which likewise shares an electron to form the (covalent) bonding pair.

Not all elements obey the octet rule. Whether or not an element follows the octet rule will depend on two things: (i) how many valence electrons can the element have, and (ii) is the atom a central atom. When an atom bonds with another atom, the valence electrons of each are shared in such a way that both atoms will tend to get 8 valence electrons, providing that there are enough valence positions within the outer shell of each atom for this to occur. For instance, N has 5 valence electrons and in forming N₂, the 10 valence electrons available are shared such that there are 3 bonding pairs (6 shared electrons, as a triple bond) between the 2 nitrogen atoms and one lone pair of electrons on each atom. But, in BF₃, the boron can only take 6 valence electrons of the 21 available because it only has 1 s and 2 p valence orbitals, so boron can not obey the octet rule.

The distinction between being a "central" atom and "external" atom is quite simple. Any atom bonded to more than one atom is a central atom; when bonded to only one atom it can be thought of as an external atom. For external atoms, the octet rule applies in all cases except for those elements smaller than carbon in the Periodic Table (eg. boron). For central atoms, only carbon, nitrogen and oxygen will always obey the octet rule; for elements below carbon, there are not enough available valence orbitals to accept more than 6 electrons, and for elements above oxygen the d orbitals are often available, thus allowing hybridisation.

Despite these limitations, the octet rule is viewed as representing the ideal or default situation.

Hybridisation
Although the idea of orbital overlap allows us to understand the formation of covalent bonds, understanding how molecular shapes arise using the simple s, p and d orbitals is not always possible, especially for polyatomic molecules. The approach taken by valence bond theory to rationalise geometries involves mixing together (or hybridising) these simple orbitals, all of which are perpendicular to each other, in order to obtain a different set of orbitals in a different geometrical arrangement (ie. with different angles between them). Hence, by mixing one s orbital with 3 p orbitals (each at 90° to the others) we can make 4 sp³ orbitals, each lying at 109° to the others. In this way, we can in part explain the bond angles observed in polyatomic molecules like H₂O.

With regard to Lewis structures, hybridisation is of importance in that elements that have available d orbitals can mix these with the usually considered s and p orbitals to produce either 5 sp³d or 6 sp³d² hybrid orbitals, thus allowing more than 8 valence electrons (10 and 12 respectively) to surround the central atom.

Drawing Lewis structures
In drawing Lewis structures, the simple procedure outlined below should be followed.

1. **Sum the valence electrons from all atoms** within the molecule you wish to draw. For an anion, add one more electron for each negative charge, and for a cation, subtract one electron for each positive charge. [Note: do not worry about keeping track of where each electron comes from as it is only the total number of electrons which is important.]

2. **Write down the symbols of each external atom and connect them to the central atom by a single (s-) bond.** Atoms are usually written in the order in which they are connected within the molecule or ion. When one atom is an atom to which other atoms are bonded, this "central" atom is usually written first. For example, carbon is the central atom in carbon dioxide, CO₂. Occasionally, however, further information may be required to
determine the order of bonding.

The representation of the bond itself is achieved either by using a pair of dots or by a single line between the chemical symbols for each atom joined. Each method represents two electrons covalently shared between the atoms in forming the bond.

3. **Complete the octets of the atoms surrounding the central atom**
   Remember the restrictions on those atoms smaller than carbon. For instance, hydrogen can only ever have two electrons.

4. **Place any remaining electrons as pairs around the central atom** even if doing so results in more than the octet.

5. **If there are not enough electrons available to complete step 3, then try introducing multiple bonds.**
   Introduce the multiple bonds one at a time, between the central atom and one of the other atoms, using one or more of the lone pairs on the external atom.

**Example - The Lewis structure of HCN.**

Hydrogen has one valence electron, carbon has 4 and nitrogen 5, for a total of 10 valence electrons. There are various ways in which these elements can be combined (HCN, HNC, CHN) but hydrogen can only accommodate 2 valence electrons and so can only bond to one other atom. Therefore, the H atom can not be a central atom. Thus, there are really only two choices, HCN and HNC. Given that the molecule is written as HCN, the best starting point would be to assume that the carbon is a central atom, and construct the Lewis structure from there. We begin with a skeletal structure that joins each atom with one pair of electrons. These two "bonds" account for 4 valance electrons.

\[
\begin{align*}
H & \equiv C & N
\end{align*}
\]

If we then place the remaining valence electrons as pairs around the nitrogen atom to give it its stable octet, we find that carbon is left with less than the octet.

\[
\begin{align*}
H & \equiv C & \equiv N
\end{align*}
\]

Therefore, in order to produce a structure where carbon obeys the octet rule, we must introduce multiple bonds (between C and N, remembering that H can only bond once).

\[
\begin{align*}
H & \equiv C = & N
\end{align*}
\]

A double bond still leaves carbon short of the octet and so we arrive at a situation where the bond between C and N is a triple bond. This gives both C and N the stable octet structure.

\[
\begin{align*}
H & \equiv C \equiv N
\end{align*}
\]

A structure drawn with N as the central atom would end up similarly, with a bond between N and C. Without any other information, both Lewis structures are viable. However, it is found through experiment that the structure is HCN. In most cases it is always best to assume that the way a formula is written gives a clue to the identity of the central atom.

**Example - The Lewis structure of BrO₃⁻**

Total valence electrons is 26 (7 from Br, 6 from each O, and 1 for the negative charge). Again assuming that the central atom is written first, and following the steps outlined in the previous example, we get
Note that this ion is drawn within square brackets with the charge indicated at the upper right. This is the correct formulation that must be used for all Lewis structures of ions.

**Example - The Lewis structure of O₃**
Total valence electrons is 18, six from each O atom. Bonding these atoms together by single bonds results in a structure where the central O atom is deficient in electrons (only 6 instead of 8).

![Lewis structure of O₃ with single bonds](image)

Multiple bonding is therefore required. Bonding one of the external O atoms to the central O atom with a double bond sufficiently shares the electrons such that all 3 O atoms now have the stable octet of electrons.

![Lewis structure of O₃ with double bond](image)

Note that this structure could also have been drawn like this.

![Alternative Lewis structure of O₃ with double bond](image)

These two structures are called *resonance* structures, which simply means that each Lewis structure is equivalent to the other.