Objectives

After completing this section, you should be able to

1. draw Lewis Dot Symbols for main group elements and ions.
2. describe the three-dimensional nature of molecules.
4. make a ball-and-stick model of a simple tetrahedral molecule such as methane, CH₄.
5. draw Lewis Dot Structures for 2 electron group molecules.
6. draw Lewis Dot Structures for 3 electron group molecules.
7. draw Lewis Dot Structures for 4 electron group molecules.

Study Notes

When drawing any organic structure, you must remember that a neutral carbon atom will almost always have four bonds. Similarly, hydrogen always has one bond; neutral oxygen atoms have two bonds; and neutral nitrogen atoms have three bonds. By committing these simple rules to memory, you can avoid making unnecessary mistakes later in the course.

The “wedge-and-broken-line” type of representation, which helps to convey the three-dimensional nature of organic compounds, will be used throughout the course.

Bonding Overview

Why are some substances chemically bonded molecules and others are an association of ions? The answer to this question depends upon the electronic structures of the atoms and nature of the chemical forces within the compounds. Although there are no sharply defined boundaries, chemical bonds are typically classified into three main types: ionic bonds, covalent bonds, and metallic bonds. In this chapter, each type of bond and the general properties found in typical substances in which the bond type occurs will be discussed.

1. Ionic bonds result from **electrostatic forces that exist between ions of opposite charge**. These bonds typically involve a metal with a nonmetal.
2. Covalent bonds **result from the sharing of electrons between two atoms**. The bonds typically involve one nonmetallic element with another.
3. Metallic bonds are found in solid metals (copper, iron, aluminum) with each metal atom bonded to several neighboring metal atoms and the bonding electrons are free to move throughout the 3-dimensional structure.

Each bond classification is discussed in detail in subsequent sections of the chapter. Let's look at the preferred arrangements of electrons in atoms when they form chemical compounds.
Lewis Symbols

At the beginning of the 20th century, the American chemist G. N. Lewis (1875–1946) devised a system of symbols—now called Lewis electron dot symbols, often shortened to Lewis dot symbols—that can be used for predicting the number of bonds formed by most elements in their compounds. Each Lewis dot symbol consists of the chemical symbol for an element surrounded by dots that represent its valence electrons.

Lewis Dot symbols:

- provide a convenient representation of valence electrons
- allows you to keep track of valence electrons during bond formation
- consists of the chemical symbol for the element plus a dot for each valence electron

To write an element’s Lewis dot symbol, we place dots representing its valence electrons, one at a time, around the element’s chemical symbol. Up to four dots are placed above, below, to the left, and to the right of the symbol (in any order, as long as elements with four or fewer valence electrons have no more than one dot in each position). The next dots, for elements with more than four valence electrons, are again distributed one at a time, each paired with one of the first four. For example, the electron configuration for atomic sulfur is [Ne]3s²3p⁴, thus there are six valence electrons. Its Lewis symbol would therefore be:

\[
\text{S} \quad \text{S} \quad \text{S} \quad \text{S} \quad \text{S} \quad \text{S}
\]

Fluorine, for example, with the electron configuration [He]2s²2p⁵, has seven valence electrons, so its Lewis dot symbol is constructed as follows:
The number of dots in the Lewis dot symbol is the same as the number of valence electrons, which is the same as the last digit of the element's group number in the periodic table. Lewis dot symbols for the elements in period 2 are given in Figure 1.4.2.

Lewis used the unpaired dots to predict the number of bonds that an element will form in a compound. Consider the symbol for nitrogen in Figure 1.4.2. The Lewis dot symbol explains why nitrogen, with three unpaired valence electrons, tends to form compounds in which it shares the unpaired electrons to form three bonds. Boron, which also has three unpaired valence electrons in its Lewis dot symbol, also tends to form compounds with three bonds, whereas carbon, with four unpaired valence electrons in its Lewis dot symbol, tends to share all of its unpaired valence electrons by forming compounds in which it has four bonds.

<table>
<thead>
<tr>
<th>Element</th>
<th>Electron config.</th>
<th>Electron dot symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>[He]2s(^1)</td>
<td>Li⁺</td>
</tr>
<tr>
<td>Be</td>
<td>[He]2s(^2)</td>
<td>Be⁺</td>
</tr>
<tr>
<td>B</td>
<td>[He]2s(^2)2p(^1)</td>
<td>B⁺</td>
</tr>
<tr>
<td>C</td>
<td>[He]2s(^2)2p(^2)</td>
<td>C⁺</td>
</tr>
<tr>
<td>N</td>
<td>[He]2s(^2)2p(^3)</td>
<td>N∶</td>
</tr>
<tr>
<td>O</td>
<td>[He]2s(^2)2p(^4)</td>
<td>O∶</td>
</tr>
<tr>
<td>F</td>
<td>[He]2s(^2)2p(^5)</td>
<td>F∶</td>
</tr>
<tr>
<td>Ne</td>
<td>[He]2s(^2)2p(^6)</td>
<td>Ne∶</td>
</tr>
</tbody>
</table>

*Figure 1.4.2: Lewis Dot Symbols for the Elements in Period 2*

**The Octet Rule**

Lewis's major contribution to bonding theory was to recognize that atoms tend to lose, gain, or share electrons to reach a total of eight valence electrons, called an *octet*. This so-called *octet rule* explains the stoichiometry of most compounds in the s and p blocks of the periodic table. We now know from quantum mechanics that the number eight corresponds to one *ns* and three *np* valence orbitals, which together can accommodate a total of eight electrons. Remarkably, though, Lewis's insight was made nearly a decade before Rutherford proposed the nuclear model of the atom. Common
exceptions to the octet rule are helium, whose $1s^2$ electron configuration gives it a full $n = 1$ shell, and hydrogen, which tends to gain or share its one electron to achieve the electron configuration of helium.

Lewis dot symbols can also be used to represent the ions in ionic compounds. The reaction of cesium with fluorine, for example, to produce the ionic compound CsF can be written as follows:

$$
\text{Cs}^+ + \cdot \cdot \cdot \rightarrow \text{Cs}^+ [\cdot \cdot \cdot ]^{-}
$$

No dots are shown on Cs$^+$ in the product because cesium has lost its single valence electron to fluorine. The transfer of this electron produces the Cs$^+$ ion, which has the valence electron configuration of Xe, and the F$^-$ ion, which has a total of eight valence electrons (an octet) and the Ne electron configuration. This description is consistent with the statement that among the main group elements, ions in simple binary ionic compounds generally have the electron configurations of the nearest noble gas. The charge of each ion is written in the product, and the anion and its electrons are enclosed in brackets. This notation emphasizes that the ions are associated electrostatically; no electrons are shared between the two elements.

Atoms often gain, lose, or share electrons to achieve the same number of electrons as the noble gas closest to them in the periodic table.

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**Molecular Shape**

A stick and wedge drawing of methane shows the tetrahedral angles...(The wedge is coming out of the paper and the dashed line is going behind the paper. The solid lines are in the plane of the paper.)

The following examples make use of this notation, and also illustrate the importance of including non-bonding valence shell electron pairs when viewing such configurations.
Bonding configurations are readily predicted by valence-shell electron-pair repulsion theory, commonly referred to as **VSEPR** in most introductory chemistry texts. This simple model is based on the fact that electrons repel each other, and that it is reasonable to expect that the bonds and non-bonding valence electron pairs associated with a given atom will prefer to be as far apart as possible. The bonding configurations of carbon are easy to remember, since there are only three categories.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Bonding Partners</th>
<th>Bond Angles</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrahedral</td>
<td>4</td>
<td>109.5°</td>
<td><img src="image" alt="C tetrahedral" /></td>
</tr>
<tr>
<td>Trigonal Planar</td>
<td>3</td>
<td>120°</td>
<td><img src="image" alt="C trigonal" /></td>
</tr>
<tr>
<td>Linear</td>
<td>2</td>
<td>180°</td>
<td><img src="image" alt="O=C=O" /></td>
</tr>
</tbody>
</table>

Figure 1.4.3 In the three examples shown above, the central atom (carbon) does not have any non-bonding valence electrons; consequently the configuration may be estimated from the number of bonding partners alone. However, for molecules of water and ammonia, the non-bonding electrons must be included in the calculation. In each case there are four regions of electron density associated with the valence shell so that a tetrahedral bond angle is expected. The measured bond angles of these compounds (H\(_2\)O 104.5° & NH\(_3\) 107.3°) show that they are closer to being tetrahedral than trigonal planar or linear. Of course, it is the configuration of atoms (not electrons) that defines the the shape of a molecule, and in this sense ammonia is said to be pyramidal (not tetrahedral). The compound boron trifluoride, BF\(_3\), does not have non-bonding valence electrons and the configuration of its atoms is trigonal. Nice treatments of VSEPR theory have been provided by Oxford and Purdue. The best way to study the three-dimensional shapes of molecules is by using molecular models. Many kinds of model kits are available to students and professional chemists.
Two Electron Groups

Our first example is a molecule with two bonded atoms and no lone pairs of electrons, \( \text{AX}_2 \): BeH\(_2\).

1. The central atom, beryllium, contributes two valence electrons, and each hydrogen atom contributes one. The Lewis electron structure is:

\[
\begin{align*}
\text{H:Be:} & \text{H} \quad \text{or} \quad \text{H–Be–H} \\
\text{Figure 1.4.4: Lewis Structure for BeH}_2
\end{align*}
\]

2. There are two electron groups around the central atom. We see from Figure 1.4.3 that the arrangement that minimizes repulsions places the groups 180° apart.

3. Both groups around the central atom are bonding pairs (BP). Thus BeH\(_2\) is designated as \( \text{AX}_2 \).

4. From Figure 1.4.3 we see that with two bonding pairs, the molecular geometry that minimizes repulsions in BeH\(_2\) is linear.

\( \text{AX}_2 \): CO\(_2\)

1. The central atom, carbon, contributes four valence electrons, and each oxygen atom contributes six. The Lewis electron structure is:

\[
\begin{align*}
\text{O} & \text{C:} \text{O} \\
\text{Figure 1.4.5: Lewis Structure for CO}_2
\end{align*}
\]

2. The carbon atom forms two double bonds. Each double bond is a group, so there are two electron groups around the central atom. Like BeH\(_2\), the arrangement that minimizes repulsions places the groups 180° apart.

3. Once again, both groups around the central atom are bonding pairs (BP), so CO\(_2\) is designated as \( \text{AX}_2 \).

4. VSEPR only recognizes groups around the central atom. Thus the lone pairs on the oxygen atoms do not influence the molecular geometry. With two bonding pairs on the central atom and no lone pairs, the molecular geometry of CO\(_2\) is linear (Figure 1.4.3).

Three Electron Groups
**AX₃: BCl₃**

1. The central atom, boron, contributes three valence electrons, and each chlorine atom contributes seven valence electrons. The Lewis electron structure is

   ![](image)

2. There are three electron groups around the central atom. To minimize repulsions, the groups are placed 120° apart (Figure 1.4.3).

3. All electron groups are bonding pairs (BP), so the structure is designated as AX₃.

4. From Figure 1.4.3 we see that with three bonding pairs around the central atom, the molecular geometry of BCl₃ is **trigonal planar**.

**AX₃: CO₃²⁻**

1. The central atom, carbon, has four valence electrons, and each oxygen atom has six valence electrons. As you learned previously, the Lewis electron structure of one of three resonance forms is represented as

   ![](image)

2. The structure of CO₃²⁻ is a resonance hybrid. It has three identical bonds, each with a bond order of 4/3. We minimize repulsions by placing the three groups 120° apart (Figure 1.4.3).

3. All electron groups are bonding pairs (BP). With three bonding groups around the central atom, the structure is designated as AX₃.

4. We see from Figure 1.4.3 that the molecular geometry of CO₃²⁻ is **trigonal planar**.
In our next example we encounter the effects of lone pairs and multiple bonds on molecular geometry for the first time.

**AX\_2E: SO\_2**

1. The central atom, sulfur, has 6 valence electrons, as does each oxygen atom. With 18 valence electrons, the Lewis electron structure is shown below.

![Lewis structure of SO2](image)

2. There are three electron groups around the central atom, two double bonds and one lone pair. We initially place the groups in a trigonal planar arrangement to minimize repulsions (Figure 1.4.3).

3. There are two bonding pairs and one lone pair, so the structure is designated as AX\_2E. This designation has a total of three electron pairs, two X and one E. Because a lone pair is not shared by two nuclei, it occupies more space near the central atom than a bonding pair (Figure 1.4.4). Thus bonding pairs and lone pairs repel each other electrostatically in the order BP–BP < LP–BP < LP–LP. In SO\_2, we have one BP–BP interaction and two LP–BP interactions.

4. The molecular geometry is described only by the positions of the nuclei, not by the positions of the lone pairs. Thus with two nuclei and one lone pair the shape is bent, or V shaped, which can be viewed as a trigonal planar arrangement with a missing vertex (Figures 1.4.2.1 and 1.4.3).
Figure 1.4.4: The Difference in the Space Occupied by a Lone Pair of Electrons and by a Bonding Pair

As with SO\(_2\), this composite model of electron distribution and negative electrostatic potential in ammonia shows that a lone pair of electrons occupies a larger region of space around the nitrogen atom than does a bonding pair of electrons that is shared with a hydrogen atom.

Like lone pairs of electrons, multiple bonds occupy more space around the central atom than a single bond, which can cause other bond angles to be somewhat smaller than expected. This is because a multiple bond has a higher electron density than a single bond, so its electrons occupy more space than those of a single bond. For example, in a molecule such as CH\(_2\)O (AX\(_3\)), whose structure is shown below, the double bond repels the single bonds more strongly than the single bonds repel each other. This causes a deviation from ideal geometry (an H–C–H bond angle of 116.5° rather than 120°).

Four Electron Groups

One of the limitations of Lewis structures is that they depict molecules and ions in only two dimensions. With four electron groups, we must learn to show molecules and ions in three dimensions.
**AX₄: CH₄**

1. The central atom, carbon, contributes four valence electrons, and each hydrogen atom has one valence electron, so the full Lewis electron structure is

```
    H
   /   \\
H-C-H
   \
    H
```

2. There are four electron groups around the central atom. As shown in Figure 1.4.2, repulsions are minimized by placing the groups in the corners of a tetrahedron with bond angles of 109.5°.

3. All electron groups are bonding pairs, so the structure is designated as AX₄.

4. With four bonding pairs, the molecular geometry of methane is **tetrahedral** (Figure 1.4.3).

![Molecular geometry (tetrahedral)](tetrahedral)

**AX₃E: NH₃**

1. In ammonia, the central atom, nitrogen, has five valence electrons and each hydrogen donates one valence electron, producing the Lewis electron structure

```
     .
H-N-H
     .
```

2. There are four electron groups around nitrogen, three bonding pairs and one lone pair. Repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.
3. With three bonding pairs and one lone pair, the structure is designated as AX\textsubscript{3}E. This designation has a total of four electron pairs, three X and one E. We expect the LP–BP interactions to cause the bonding pair angles to deviate significantly from the angles of a perfect tetrahedron.

4. There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*. In essence, this is a tetrahedron with a vertex missing (Figure 1.4.3). However, the H–N–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsions.

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**AX\textsubscript{2}E\textsubscript{2}: H\textsubscript{2}O**

1. Oxygen has six valence electrons and each hydrogen has one valence electron, producing the Lewis electron structure

   ![Lewis Structure of H\textsubscript{2}O](image)

2. There are four groups around the central oxygen atom, two bonding pairs and two lone pairs. Repulsions are minimized by directing the bonding pairs and the lone pairs to the corners of a tetrahedron Figure 1.4.3.

3. With two bonding pairs and two lone pairs, the structure is designated as AX\textsubscript{2}E\textsubscript{2} with a total of four electron pairs. Due to LP–LP, LP–BP, and BP–BP interactions, we expect a significant deviation from idealized tetrahedral angles.

4. With two hydrogen atoms and two lone pairs of electrons, the structure has significant lone pair interactions. There are two nuclei about the central atom, so the molecular shape is *bent*, or *V shaped*, with an H–O–H angle that is even less than the H–N–H angles in NH\textsubscript{3}, as we would expect because of the presence of two lone pairs of electrons on the central atom rather than one. This molecular shape is essentially a tetrahedron with two missing vertices.

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**Exercises**

**Questions**

**Q1.4.1**

List the bond angles for each of the following compounds: BH\textsubscript{3}, CF\textsubscript{4}, H\textsubscript{2}O.
Q1.4.2

Why is sulfur dioxide a bent molecule (bond angle less than 180°)?

Solutions

S1.4.1

HBH = 120°

FCF = 109.5°

OHO = 104°

S1.4.2

This deviation is due to the lone pairs on the sulfur. These force the molecule to exhibit a “bent” geometry and therefore a deviation from the 180°.