three-dimensional structure the threedimensional arrangement of ions or atoms making up a pure substance

Figure 1 A queen bee secretes a chemical that the worker bees immediately recognize. This chemical prevents the worker bees from competing against the queen bee.

valence shell electron-pair repulsion

(VSEPR) theory a method to determine the geometry of a molecule based on the idea that electron pairs are as far apart as possible

electron-pair repulsion the repulsive force that occurs between electron pairs, causing them to be positioned as far apart as possible in a molecule

4.2 Three-Dimensional Structure

Chemical bonds play an important role in determining the nature of various substances. So does the three-dimensional structure. The three-dimensional structure of a substance refers to the arrangement in three dimensions of atoms that the substance comprises. Three-dimensional structure often helps determine how the pure substance will behave in chemical reactions. It also influences interactions with other substances, especially in biological systems, where reactions have to be efficient and highly specific.

For example, enzymes, an important group of molecules in living organisms, interact with other molecules primarily based on molecular shape (molecular geometry). Enzymes and the molecules they act on interact in a manner similar to locks and keys. You cannot use just any key to open a lock. The ridges and shape of the key must be complementary to the shape of the inside of the lock. Receptor proteins on the surfaces of cells function very much like a lock. A specific molecule, such as a hormone or a neurotransmitter, must fit perfectly in the receptor pocket before it will signal the cell interior. At the cellular level, communication, growth, defence, and differentiation all ultimately depend on molecular shape. Beyond the cellular level, entire organisms can communicate through a process called semiochemical communication, where chemicals act as messengers to relay information from one organism to another. For example, queen bees secrete a unique chemical, or pheromone, to prevent worker bees from rebelling (Figure 1). WEB LINK

The VSEPR Theory

Many sophisticated and highly accurate methods, such as X-ray crystallography and nuclear magnetic resonance (NMR) spectroscopy, exist for determining threedimensional structure. We must use these methods when we need precise information about a molecule's structure, but they require lengthy experiments and expensive equipment. However, you can predict the approximate structure of a molecule or ionic compound using the valence shell electron-pair repulsion (VSEPR) theory. The main idea behind the VSEPR theory is that you can determine the structure around an atom by minimizing the repulsive force between electron pairs. Remember that electrons are all negatively charged and, thus, repel each other. Atoms can share electron pairs in a covalent bond (bonding electron pairs), and can also have lone electron pairs that do not participate in chemical bonds. You saw examples of this in the previous section when you drew Lewis structures. According to VSEPR theory, bonded and lone pair electrons position themselves as far apart as possible in a molecule to minimize the repulsive forces between them, a concept called **electron-pair repulsion**.

To illustrate VSEPR theory, consider beryllium chloride, BeCl₂. Beryllium chloride is a rather unusual substance. It is a molecule, not an ionic compound. Although covalent bonds typically occur between atoms of non-metals, in beryllium chloride covalent bonds occur between a metal atom and a non-metal atom. You will learn more about how this happens in Section 4.6. Beryllium chloride can be represented by the following structural formula and ball-and-stick model:

Note that there are 2 bonding electron pairs around the beryllium atom. What geometric arrangement of these electron pairs allows them to be as far apart as possible to minimize the repulsive forces between them? The best arrangement is to place the electron pairs on opposite sides of the atom, or 180° apart.

the central atom, you can specify the three-dimensional structure of beryllium Now that you have determined the optimal arrangement of the electron pairs around

chloride. Since the beryllium atom shares each bonding electron pair with a chlorine atom, the molecule has a linear structure with a 180° bond angle.

$$
Cl - Be - Cl
$$

180°

Next, consider boron trifluoride, BF_3 , which can be represented by the following simplified Lewis structure.

$$
\begin{array}{c}\n \vdots \ddots \\
 \vdots \ddots \\
 \vdots \ddots \ddots \ddots\n \end{array}
$$

In this Lewis structure, 3 bonding electron pairs surround the boron atom. What arrangement will minimize electron-pair repulsion? The bonding electron pairs are the farthest apart at angles of 120° in a two-dimensional plane.

Since the boron atom shares an electron pair with each fluorine atom, the threedimensional structure can be represented as

trigonal planar structure. The shape of this molecule is planar (flat) and triangular, and it is described as a

structural formula. Next, consider the methane molecule, $CH₄$, which can be represented by this

$$
\begin{array}{c}\nH \\
| \\
H\neg C\neg H \\
| \\
H\n\end{array}
$$

Increase 4 bonded electron pairs surrounding the central earbon atom. What arrangement of these electron pairs minimizes the electron-pair repulsions? First, try to arrange the molecule into a square planar arrangement, where all 4 bonds lie There are 4 bonded electron pairs surrounding the central carbon atom. What in the same plane:

$$
\begin{array}{c}\nH \\
 \hline\n|\nabla 90^{\circ} \\
H - C \rightarrow H \\
\hline\n\vdots \\
H\n\end{array}
$$

1st pass In this arrangement, the carbon atom and the electron pairs are centred in the plane of the paper, and the angles between the electron pairs are all 90°.

There is another arrangement that would put the electron pairs even farther away from each other. The tetrahedral structure has angles of 109.5°, and the atoms are Deborah Crowle be represented by the following structural formula and ball-and-stick model: equally positioned in four locations around the central atom. This arrangement can

Table 1 Conventions for Depicting Bonds in Three Dimensions

This three-dimensional arrangement allows the maximum possible separation of 4 pairs of electrons around a central atom. In the structural formula for the methane molecule, some bonds are represented as dashes or wedges to better communicate the arrangement of the atoms. **Table 1** summarizes the conventions for representing the three-dimensional arrangement of atoms in structural formulas. Blue lines were added to the ball-and-stick model of methane on the previous page to emphasize the tetrahedron. Whenever 4 pairs of electrons are present around a central atom, always place them at the vertices of a regular tetrahedron.

Recall from Section 4.1 that the central atom of phosphorus pentachloride, PCl₅, is overfilled. There are 5 covalent bonds between the phosphorus atom and the 5 chlorine atoms. In this case, the geometric structure that minimizes electron repulsion is a trigonal bipyramidal structure. In a phosphorus pentachloride molecule, 3 P–Cl bonds are in the same plane and 120° apart from each other, and the remaining 2 P–Cl bonds are 90° from these bonds and 180° from each other (Figure **2(a)**). Similarly, sulfur hexafluoride, SF_6 , forms 6 covalent bonds. The predicted VSEPR theory structure for this molecule is an octahedral structure. In this structure, 4 S–F bonds are in the same plane separated by 90° angles. The other 2 S–F bonds are Cl perpendicular to this plane, 1 above it and 1 below it (**Figure 2(b)**). эу

Figure 2 (a) The trigonal bipyramidal structure of PCI₅ and (b) the octahedral structure of SF₆

VSEPR theory helps you to determine the arrangement of electron pairs around a central atom that minimizes electron-pair repulsions. The lone electron pairs surrounding tral atom that minimizes electron-pair repulsions. The lone electron pairs surrounding
non-central atoms do not play a role in determining molecular shape. However, when the central atom has 1 or more lone pairs of electrons, the geometric structure of the molecule and the positions of the surrounding atoms are affected. Consider ammonia, F NH₃, which has a single lone electron pair on the central atom: \sum_{1}

$$
\stackrel{\rm H: N:H}{\underset{\rm H}{\rm H}}
$$

You might predict that this molecule has a tetrahedral structure because there are 4 pairs of electrons around the central nitrogen atom. However, the lone electron pair repels a little more than the bonding pairs, and thus pushes the bonding pairs closer together. As a result, the bond angles decrease from 109.5° to 107°. This forms a trigonal pyramidal structure, because the central atom is at the vertex of a pyramid with a triangular base (**Figure 3**).

Note that the three-dimensional structure classification depends only on the spatial arrangement of the atoms bonded to the central atom. Although the lone pairs strongly influence the angles between the bonds and thus the structure of the molecule, the lone pairs are disregarded when describing the overall shape of the molecule. Consider water, H_2O . Its Lewis structure is

$H:O:H$

Ignoring the lone pairs around oxygen, you would predict a linear structure, like beryllium chloride. However, the lone pairs of electrons on the central atom repel the bonding pairs, thereby decreasing the angle between them. If you place the bonding and non-bonding electron pairs around the oxygen atom as far apart as possible, the structure will be tetrahedral, as in methane. However, in the water molecule, the 2 lone pairs of electrons repel the bonding pairs with more force, making the H–O–H bond angle 104.5° instead of 109.5°. The result is a V-shaped or bent structure (**Figure 4**).

> marized in **Table 2** (on the next two pages). \bullet career link Common three-dimensional structures predicted by the VSPER theory are sum-

Figure 3 The structure of ammonia is close trigonal pyramidal due to the repulsion a of the lone pair against the 3 N–H
bonds. bonds.

Figure 4 The structure of water is bent due to the repulsion of the 2 lone pairs (blue ellipses) against the 2 0–H bonds.

Mini Investigation

Balloon Model of Electron Repulsion

Skills: Performing, Observing, Analyzing, Communicating

In this investigation you will use balloons as models for the electron repulsion of electrons in atoms.

Equipment and Materials: chemical safety goggles; 9 balloons; string

- 1. Put on your safety goggles.
- 2. Inflate all the balloons.
- 3. Tie 2 of the balloons close together, and place them on a table.
- 4. Repeat Step 3 with 3 balloons.
- 5. Repeat Step 3 with 4 balloons.
-

Three-Dimensional Shape (page 255)

Now that you have learned how to determine molecular structures, perform Investigation 4.2.1 to compare your three-dimensional structure predictions to actual molecular models.

A. How do the 2 balloons tied together orient themselves?

SKILLS **A2.3**

- B. How do the 3 balloons tied together orient themselves? T/II
- C. How do the 4 balloons tied together orient themselves? T/I
- D. Are balloons good models of valence shell electron-pair repulsion? Why or why not?
- E. What would happen in any of the models if you pushed the balloons together and then let go?
- F. With 4 balloons tied together, imagine 1 of them being a lone pair. What would the three-dimensional structure be? What if 2 balloons were lone pairs? \blacksquare

Investigation 4.2.1 Steps for Applying the VSEPR Theory

The steps below summarize how to predict the structure of a pure substance using the VSEPR theory.

- 1. Draw the simplified Lewis structure.
- 2. Count the electron pairs surrounding the central atom, including both bonded and lone electron pairs, and arrange them in a way that minimizes electron-pair repulsion. Do this by putting the electron pairs as far apart as possible in a three-dimensional space.
- 3. Place the atoms bonded to the central atom at the ends of their bonded electron pairs.
- 4. Determine the name of the structure from the positions of the atoms and lone pairs of electrons.

Tutorial 1 Using the VSEPR Theory to Predict Molecular Shapes

In this Tutorial, you will use the step-by-step approach described on the previous page to use the VSEPR theory to predict the shape of molecules and polyatomic ions.

Sample Problem 1: The Shape of a Molecule without Lone Electron Pairs

Predict the structure of carbon tetrachloride, CCl₄, using the step-by-step VSEPR approach.

Solution

Step 1. Draw the simplified Lewis structure.

$$
\begin{array}{c}\n \vdots \stackrel{\cdot}{\stackrel{\cdot}{\cdots}} \\
 \vdots \stackrel{\cdot}{\stackrel{\cdot}{\cdots}} -\stackrel{\cdot}{\stackrel{\cdot}{\cdots}} \\
 \vdots \stackrel{\cdot}{\stackrel{\cdot}{\cdots}} \\
 \vdots \stackrel{\cdot}{\stackrel{\cdot}{\cdots}} \\
 \vdots \quad \vdots\n \end{array}
$$

Step 2. Count the electron pairs surrounding the central atom, and arrange them to minimize electron-pair repulsion.

> The carbon tetrachloride molecule has 4 pairs of bonding electrons around the central atom. There are no lone electron pairs on the carbon atom. The best arrangement of the 4 bonding electron pairs around the central atom is a tetrahedral structure.

Step 3. Place the atoms bonded to the central atom at the ends of their bonded electron pairs.

Step 4. Name the three-dimensional structure.

Carbon tetrachloride has a tetrahedral structure.

Sample Problem 2: The Shape of a Polyatomic Ion

Predict the structure of the ammonium ion, NH_4^+ , using the step-by-step VSEPR approach.

Solution

Step 1. Draw the simplified Lewis structure for the polyatomic ion.

Step 2. Count the electron pairs surrounding the central atom and arrange them to minimize repulsions.

> The ammonium ion has 4 pairs of bonding electrons around the central atom. There are no lone electron pairs in the ion. The best arrangement of the 4 bonding electron pairs around the central atom is tetrahedral.

Step 3. Place the atoms bonded to the central atom at the ends of their bonded electron pairs.

Sample Problem 3: The Shape of a Molecule with Lone Electron Pairs Predict the structure of phosphine, PH_3 , using the step-by-step VSEPR approach.

Solution

Step 1. Draw the simplified Lewis structure for the molecule.

$$
\begin{array}{c}\n\mathbf{i} - \mathbf{j} - \mathbf{H} \\
\mid \\
\mathbf{H}\n\end{array}
$$

Step 2. Count the electron pairs surrounding the central atom and arrange them to minimize repulsions.

H

The phosphine molecule has 3 pairs of bonding electrons around the central atom. There is 1 lone electron pair on the phosphorus atom. The best arrangement of the 4 electron pairs (3 bonding and 1 lone pair) around the central atom is tetrahedral.

Step 3. Place the atoms bonded to the central atom at the ends of their bonded electron pairs.

$$
H\begin{array}{c} \stackrel{\cdot\cdot\cdot}{\longrightarrow} H\\ H\end{array}
$$

Step 4. Name the three-dimensional structure.

The phosphine molecule has a tetrahedral arrangement of electron pairs. However, because it has a lone electron pair, its structure is trigonal pyramidal.

Practice

- 1. Use VSEPR theory to predict the geometry of each of the following molecules: \blacksquare
	- (a) HBr [ans: linear]
- (b) SiCl₄ [ans: tetrahedral]
- (C) BF₃ [ans: trigonal planar]
- $\left(\alpha\right)$ \cdots (d) $NCI₃$ [ans: trigonal pyramidal]
- 1st pass 2. Use VSEPR theory to predict the geometry of each of the following substances. Draw the structures. The c
	- (a) BCl_3 [ans: trigonal planar]
	- (b) BH_4^- [ans: tetrahedral]
	- (c) CF_4 [ans: tetrahedral]
	- (d) H_2S [ans: bent]

The VSEPR Theory and Molecules with More Than One Central Atom

So far, you have investigated pure substances that contain just 1 central atom surrounded by other atoms. Many others have more than 1 central atom. You can still use the VSEPR theory to predict the three-dimensional structure of these more complex molecules. Consider methanol, CH₃OH, which has 2 central atoms, carbon and oxygen. Methanol can be represented by the following simplified Lewis structure:

$$
\begin{array}{c}\nH \\
| \\
H-C-\ddot{Q}-H \\
H \\
H\n\end{array}
$$

You can predict the three-dimensional structure from the arrangement of electron pairs around both the carbon and oxygen atoms. In a molecule or ionic compound with more than 1 central atom, you first need to predict the arrangement of electrons around each atom individually. Then, combine these arrangements to predict the overall structure. There are 4 pairs of electrons around the carbon atom, so it has a tetrahedral arrangement (**Figure 5(a)**). The oxygen atom also has 4 electron pairs (2 bonding pairs and 2 lone pairs), so it too has a tetrahedral arrangement. The oxygen atom has a slight distortion of the tetrahedron because of the space requirements of the lone electron pairs, so the three-dimensional structure around the oxygen atom is bent (**Figure 5(b)**). The overall geometric arrangement for the methanol molecule is shown in **Figure 5(c)**.

Figure 5 (a) The arrangement of atoms around the carbon atom is tetrahedral. (b) The arrangement of atoms and lone electron pairs around the oxygen atom is bent. (c) The three-dimensional structure of methanol.

Tutorial 2 Structures of Molecules with Two Central Atoms

In this Tutorial, you will use the VSEPR theory to predict the shape of molecules that contain more than 1 atom as the central atom.

Sample Problem 1: Molecular Shape with No Single Central Atom

Predict the structure of methylamine, CH₃NH₂, using the step-by-step VSEPR approach.

Solution

Step 1. Draw the simplified Lewis structure. There are 2 central atoms in this structure, carbon and nitrogen.

$$
\begin{array}{c}\nH & H \\
| & | \\
H - C - N \\
| & | \\
H & H\n\end{array}
$$

Step 2. Count the electron pairs surrounding the central atom, and arrange them to minimize electron-pair repulsion.

The methylamine molecule has 4 pairs of bonding electrons around the central carbon atom and 3 pairs of bonding electrons around the nitrogen atom. There is also 1 lone pair of electrons around the nitrogen atom. Both central atoms therefore have a tetrahedral arrangement.

Step 3. Place the atoms bonded to the central atom at the ends of their bonded electron pairs.

Step 4. Name the three-dimensional structure.

The carbon atom in methylamine has a tetrahedral arrangement of atoms, and the nitrogen atom has a trigonal pyramidal arrangement of atoms because it has 1 lone pair of electrons.

Practice

- 1. For each of the following molecules, use the step-by-step VSEPR approach to predict the shape of the molecule. Draw a three-dimensional structural formula to illustrate your answer, and state the shape around each central atom. The case (a) $CH₃BH₂$
	- (b) $CH₃OCH₃$
	- (c) CH_3CH_2OH
	-

VSEPR Theory and Multiple Bonds

Molecules or ionic compounds with double and triple bonds have different chemical properties than those with single bonds. For example, hydrocarbons with double or triple bonds react quickly with bromine or potassium permanganate, whereas hydrocarbons with single bonds react much more slowly. Double and triple bonds are shorter and stronger than single bonds between the same types of atoms. However, pure substances with double and triple bonds behave very similarly to pure substances with single bonds when it comes to three-dimensional structure. In a double or triple bond, there is more than 1 bonding pair of electrons. When using the VSEPR theory to determine structure, you must place all of the multiple bonding electrons together, as you will see in the following tutorial.

Tutorial 3 Structures of Molecules with Multiple Bonds

This Tutorial explains how to use the VSEPR theory to determine the shape of a molecule that contains multiple bonds.

Sample Problem 1: Predicting the Shape of a Molecule with Multiple Bonds Predict the structure of carbon dioxide, $CO₂$, using the step-by-step VSEPR approach.

Solution

Step 1. Draw the simplified Lewis structure for the molecule. In the carbon dioxide molecule, carbon is the central atom and is bonded by double bonds to each oxygen atom.

$$
\ddot{Q} = C = \ddot{Q}
$$

Step 2. Count the electron pairs surrounding the central atom, and arrange them to minimize electron-pair repulsion.

> The carbon dioxide molecule has 4 pairs of bonding electrons around the central atom. Each $C-0$ bond is a double bond that consists of 2 pairs of electrons (4 electrons) each. For the purposes of VSEPR, treat a multiple bond as a single group of electrons. In effect, you are counting the number of bonded atoms. There are 2 atoms bonded to the central carbon. Therefore the shape is linear. The generalizations outlined in Table 2 on pages 209–210 still apply to multiple bonding if you count atoms bonded to the central atom rather than electron pairs.

Step 3. Determine the positions of the atoms.

Place the atoms bonded to the central atom at the ends of their bonded electron pairs.

 $O = C = O$

Step 4. Name the three-dimensional structure.

The carbon dioxide molecule has a linear structure. Since each oxygen atom forms a double bond with the carbon atom, the configuration that maximizes the separation of electrons is a linear shape. The electrons are 180° from each other.

Practice

- 1. Use a simplified Lewis structure and VSEPR theory to predict the shape of a nitrite ion, $N0₂$ T/I c
- 2. Use VSEPR theory to predict the shapes of the following molecules. Draw structures to illustrate your answers. The c
	- (a) $SiO₂$
	- (b) HCN
	- (c) $Xe0F_4$

The VSEPR Theory: How Well Does It Work?

The VSEPR theory works well for most molecules and ionic substances that contain non-metallic elements. However, the theory fails in a few instances. For example, phosphine, PH_3 , has the same Lewis structure as ammonia, NH_3 : trigonal pyramidal. From the VSEPR theory, you would expect phosphine to have the same bond angles as NH_3 : 107°. However, the bond angles of phosphine are actually 94° (**Figure 6**). There are ways to explain this difference, but you have to add more rules to the theory. This example illustrates that simple theories are likely to have exceptions. The amazing thing about the VSEPR theory is that it correctly predicts the structures of so many pure substances.

Figure 6 Even though phosphine has the same three-dimensional structure as ammonia, the angles between bonding atoms in the molecules are different: 94° in phosphine and 107° in ammonia.

Summary

- The valence shell electron-pair repulsion (VSEPR) theory predicts the distribution of atoms covalently bonded to a central atom based on the repulsion between bonding and lone electron pairs associated with the central atom.
- You can use the VSEPR theory to predict the geometry of simple and complex pure substances with covalent bonds by minimizing electron-pair repulsion.
- The VSEPR theory predicts several common arrangements of atoms that minimize electron-pair repulsion.
- There are some exceptions in which the VSEPR theory does not accurately describe the structure of a pure substance.

Questions

- 1. How do the words that make up the initialism "VSEPR" describe the ideas of the theory? KU
- 2. Predict the three-dimensional structure and bond angles for each of the following molecules: T/I

- 3. Predict the three-dimensional structure and bond angles for each of the following ions: \overline{M}
	- (a) NO_2^-
	- (b) NO_3^-
	- (c) OCN^- (carbon is the central atom)
	- (d) N_3^-
- 4. What is the shape of molecules such as iodine chloride, ICl, and hydrogen bromide, HBr? How can you tell? What is the name of this shape? \blacksquare
- 5. Identify which of the following substances contain atoms in a trigonal planar arrangement. The
	- (a) $AlCl₃$
	- (b) B_2H_4
	- (c) $CH₃COH$, where O is double-bonded to C
	- (d) $CH₃CH₃COOH$, where one O is double-bonded to C
- 6. State whether any of the following molecules or polyatomic ions have a tetrahedral arrangement of either atoms or electrons: TII
	- (a) CH₃OH
	- (b) SO_4^2 ⁻
	- (c) CH₃NH₂
- 7. Use VSEPR theory to predict the geometry of the following molecules, then draw their structures: T/I \vert C \vert
	-
	- (a) BeI₂
	- (b) $SiBr₄$
	- (c) BBr₃
	- (d) $CH₃COCH₃$ (C is double-bonded to O)
	- (e) CH_2F_4
- 8. Use the VSEPR theory to predict the geometry of the following polyatomic ions, then draw their structures: TH C
	- (a) PO_3^3 ⁻
	- (b) CO_3^2 ⁻
	- (c) CN^-
- 9. The molecule $CH_3CH=CHCH_2CH_3$ is a 5-carbon chain with 1 double bond between the second and third carbon atoms. Use the VSEPR theory to describe the geometry around each of the carbon atoms. The
- 10. Create a table with the headings shown in **Table 3**. Then, complete the table by filling in the appropriate information for each of the following compounds: NBr_3 ; CS₂; SeH₄; SeF₆; ICl₄⁻; ICl; CH₃Cl; BrCl₅; BrF_3 Xel_3 $^-$; SBr_4 ; $\mathrm{BrO_2}$ $^-$; OF_2 ; $\mathrm{CF}_2\mathrm{Cl}_2$; $\mathrm{H}_2\mathrm{Se}$; and PBr_6^- . T/I C

Table 3

