SCH4U-C

3

Molecular Shape and Polarity

Introduction

Dry cleaning involves washing clothes made of delicate fabrics in a solvent other than water. Dry-cleaning solvents have had a notorious environmental track record. Over the years, some were found to be carcinogenic (cancer-causing), while others contributed to the thinning of the ozone layer. Ozone, O_3, is a key molecule to our survival because it blocks most of the sun's ultraviolet radiation. A safer and more environmentally friendly dry-cleaning alternative is being developed that uses liquid carbon dioxide as the cleaning solvent.

Carbon dioxide occurs naturally in the environment and is relatively non-polluting. What makes this process so unusual is that carbon dioxide is normally a gas, at room temperature. Therefore, special pressurized "washing machines" are being developed to keep carbon dioxide in the liquid state as it washes. Why go to all this trouble to liquefy carbon dioxide? The non-polar nature of the carbon dioxide molecule makes it an ideal cleaning solvent. However, as you'll find out in this lesson, many technical challenges still need to be overcome before this technology can be used at your local dry cleaner.

Planning Your Study

You may find this time grid helpful in planning when and how you will work through this lesson.

Suggested Timing for This Lesson (Hours)	
Molecular Shapes and Valence Shell Electron Pair Repulsion (VSEPR) Theory	½
VSEPR Theory for Multiple Bonds and Ions	1
Dipoles and Molecular Polarity	1
Key Questions	1

What You Will Learn

After completing this lesson, you will be able to

- use VSEPR theory to predict the shape of molecules or ions
- determine the polarity of molecules or ions
- understand the benefits and environmental hazards of the use of dry-cleaning solvents
- predict the polarity of various chemical compounds, based on their molecular shapes, as well as the difference in the electronegativity values of atoms

Introduction to Molecular Shapes

At first glance, water, H_2O, and carbon dioxide, CO_2, have a lot in common. Both are molecular compounds found in the atmosphere that contain oxygen. Since oxygen is more electronegative than either hydrogen or carbon, water and carbon dioxide contain polar covalent bonds. However, that's where the similarity ends. The physical properties of these compounds are quite different. Water is a liquid at room temperature, while carbon dioxide is a gas. Liquid carbon dioxide readily dissolves greasy stains off fabrics, while water and grease do not mix. This difference in properties can be explained by examining the shapes of these molecules.

In this section, you will learn a systematic way of determining the shape of a molecule or complex ion using electron dot diagrams. Then, you'll learn how molecular shape influences molecular polarity.

Valence Shell Electron Pair Repulsion (VSEPR) Theory

Valence shell electron pair repulsion theory (developed in 1957 by Canadian chemist Ron Gillespie at McMaster University) is widely used to explain and predict molecular shape. VSEPR theory is based on the observation that the inherent, negative charges of the electrons inside an atom repel one another. Because of these repulsions, the orbitals that these electrons occupy try to get as far away from one another as possible. Therefore, the bond angles in (or the angles at which other atoms connect to) the central atom are determined by the orientation of these valence electron pairs.

You know from previous courses that angles are typically described in degrees, using the degree symbol (°). If you slice a pie into three equal pieces, you will need to make the first cut, then a second cut at 120°, and then a third cut at 240°. The total pie is 360° and each slice represents 120°. Later in this lesson, you will learn that a central atom bonded identically to three identical atoms will have 120° bond angles when there are no lone electron pairs.

In Lesson 2, you learned that the atoms within a molecule are usually surrounded by electron pairs. Some of these electron pairs form covalent bonds with other atoms. Electron pairs that are not used to form bonds are called lone pairs. In the following discussion, hydrogen compounds of the second-period elements are used to show how VSEPR theory is used to determine molecular shape.

Linear Molecules

Consider beryllium hydride, which is a molecular compound. Experimental evidence shows that this compound has a beryllium atom at its centre. The bonds to the hydrogen atoms are identical in length and make an angle of 180°. The shape of this molecule is described as linear.

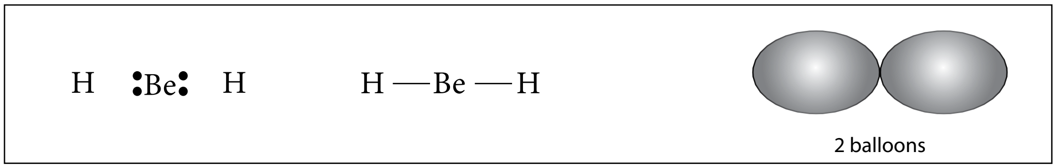


Figure 3.1: Beryllium hydride is a linear molecule. Its shape is similar to two balloons connected end to end.

Now take a look at how this structure can be explained or predicted using VSEPR theory. The electron dot diagram of beryllium hydride shows two pairs of electrons on opposite sides of a central beryllium atom. To minimize repulsions, these electrons are arranged 180° apart from one another. Note that the beryllium atom is surrounded by only four electrons, which violates the octet rule. This explains why this molecule is reactive.

Recall from Lesson 2 how the hybrid orbitals of Be were drawn. The hybrids were the *sp* type. The two identical hybrid orbitals would orient themselves on opposite sides of the Be atom. This would support the shape predicted by VSEPR theory. VSEPR theory is just another way to predict shape of molecules.

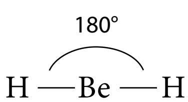


Figure 3.2: A bond angle of 180° minimizes repulsions between the bonding pairs of electrons in the two covalent bonds.

The angle that the bonds make with each other is called a bond angle. A bond angle of 180° is characteristic of a linear molecule.

Trigonal Planar Molecules

Next, you are going to examine the molecule boron hydride, BH_3. The electron dot diagram for this molecule is shown in Figure 3.3. This molecule is also an exception to the octet rule because the central boron atom is surrounded by only six electrons.

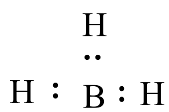


Figure 3.3: Electron dot diagram of boron hydride. Electron dot diagrams show how atoms are bonded but do not indicate the shape of the molecule.

VSEPR theory predicts that the bonding electron pairs should be as far apart as possible. Figure 3.4 shows two possible arrangements of the bonds around boron.

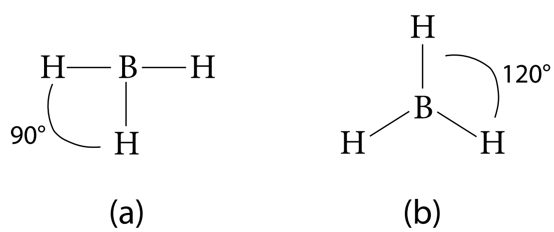


Figure 3.4: Two possible geometries for BH_3. Which minimizes repulsions?

According to VSEPR theory, structure (b) has the most stable arrangement of bonds because they are as far away from each other as possible. Therefore, the actual bond angles for boron hydride are 120°. This molecular shape is called trigonal planar. "Trigonal" implies that the molecule forms the shape of a triangle. "Planar" means that the molecule is flat (not shaped like a tripod). Visualize the B atom and the H atoms as all lying on the surface (plane) of this page. This is what is meant by planar.

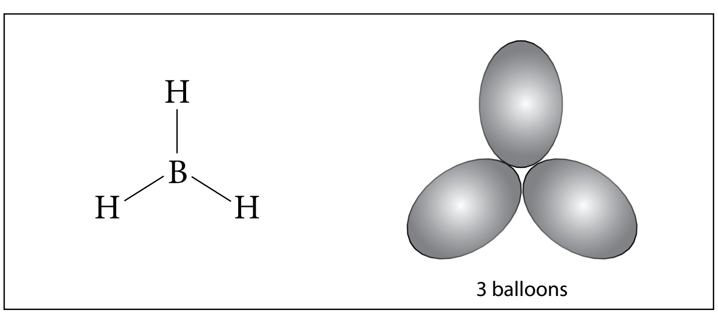


Figure 3.5: Molecules similar to BH_3 have a trigonal planar shape. This shape is similar to three balloons connected at their ends.

Tetrahedral Molecules

Methane, CH_4, a major component of natural gas, has the following electron dot diagram (Figure 3.6). In the following activity you will create a model of this molecule to help you to visualize its shape.

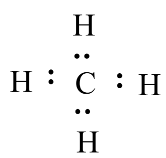


Figure 3.6: The electron dot diagram of methane

Activity: Molecular Modelling

To do this optional activity, you will create model molecules by using a few marshmallows to represent atoms, and toothpicks to represent bonds.

Procedure

Step 1: Create a model of this molecule to help you visualize the largest angle that these bonds make. Use a toothpick to represent each bond (electron pair), and a marshmallow to represent the central carbon atom.

Step 2: Arrange the toothpicks around the marshmallow so that they are placed at a 90° angle to each other (Figure 3.7). This produces a flat, two-dimensional molecule.

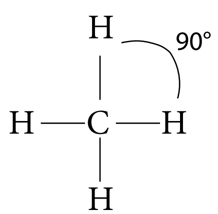


Figure 3.7: An unstable bonding arrangement for methane, CH_4

Step 3: Construct another model in which all four toothpicks are placed at a slightly larger angle to each other (approximately 110°). The shape you produce should look like a pyramid. If the toothpick angles (that is, the bond angles) are all identical, then the model should look the same, regardless of which three toothpicks it is standing on. This shape is a triangular pyramid called a tetrahedron and has a bond angle of 109.5°. The name "tetrahedral" has two parts. The prefix "tetra-" means four. The suffix "-hedral" comes from the Greek word *hedros*, which means faces. Therefore, tetrahedral means "four faces" or the four sides of a triangular pyramid. In Lesson 2, you learned that sp^3 hybrid orbitals are arranged in this shape. Therefore, any molecule or ion that has a tetrahedral shape involves sp^3 hybrid orbitals.

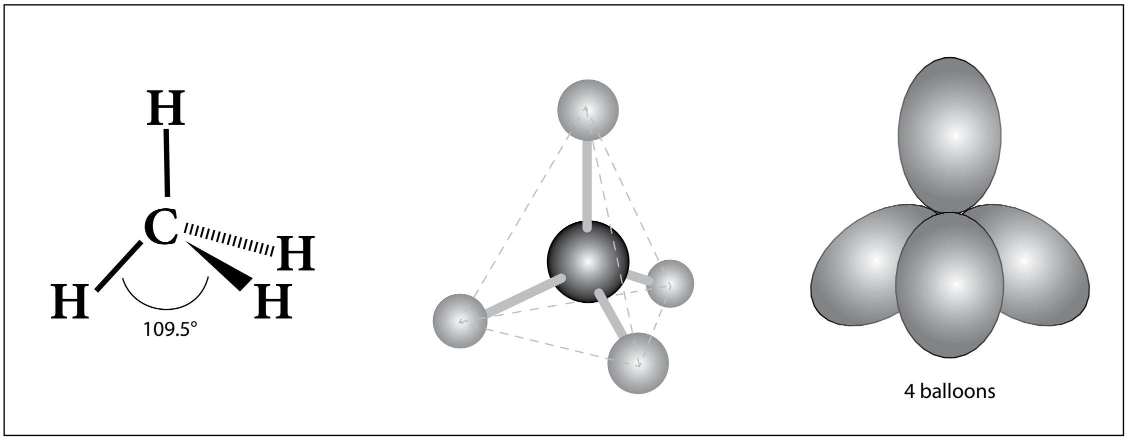


Figure 3.8: The bonds of methane are arranged in a tetrahedral geometry. The four corners of the molecule (if connected by strings or joined by lines) would form a triangular pyramid.

Pyramidal Molecules

Figure 3.9 shows the electron dot diagram and structural formula of ammonia, NH_3. The bonds for the three hydrogen atoms form a sort of squashed tripod. Since there are four pairs of electrons around nitrogen, you would expect the shape of the ammonia molecule to be similar to that of a tetrahedral pyramid. But does the lone pair have any effect on shape?

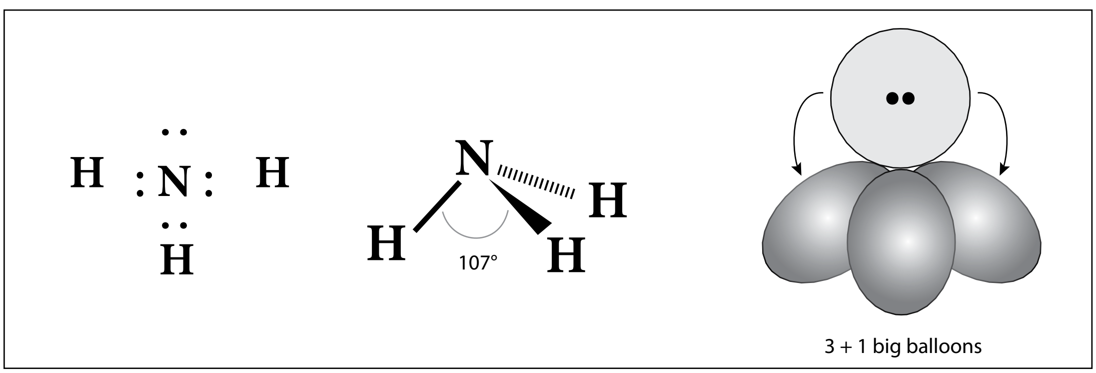


Figure 3.9: The bonds in ammonia are arranged in a pyramidal geometry. The nitrogen lone pair repels the bonding electron pairs downward.

Experimental evidence shows that the bond angle in this molecule is 107°, which is slightly smaller than the tetrahedral bond angle. VSEPR theory explains that the smaller bond angle is a result of greater repulsions from the lone pair.

This ammonia example is the first case shown where we have a lone pair of electrons on the central atom, the N atom, creating extra repulsions. In this case, we see Electron Pair Repulsions (the EPR in VSEPR) between the lone pair on the N atom and the bonding pairs on each H atom. Study the balloon diagram in Figure 3.9, which shows the lone pair pushing the 3 H atoms away from it. This creates the shape we call pyramidal. Some also describe this as being like a tripod, with the N on top of the tripod and the three H atoms forming the feet of the tripod. The similarity to the tetrahedral bond angle suggests that sp^3 hybrid orbitals are also playing a role in shaping this molecule.

Angular or Bent Molecules

The electron dot diagram for water shows four electron pairs around the central oxygen atom—two bonding pairs and two lone pairs (Figure 3.10). As with ammonia, you would expect the shape of the orbitals around the central atom to be similar to that of a tetrahedral pyramid. However, since there are two lone pairs of electrons around a water molecule's central atom, an even greater distortion of the tetrahedral bond angle is expected. This prediction agrees with the experimentally determined bond angle, which is 104.5°. The combination of two bonding pairs and two lone pairs results in a shape known as an angular or bent shape. Since this shape is related to the tetrahedral pyramid, the four electron pairs around oxygen are in sp^3 hybrid orbitals.

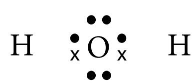


Figure 3.10: Electron dot diagram for water

As seen in Figure 3.11, the repulsion of the two lone pairs shrinks the bond angle to 104.5° in H_2O, and in other molecules that are angular.

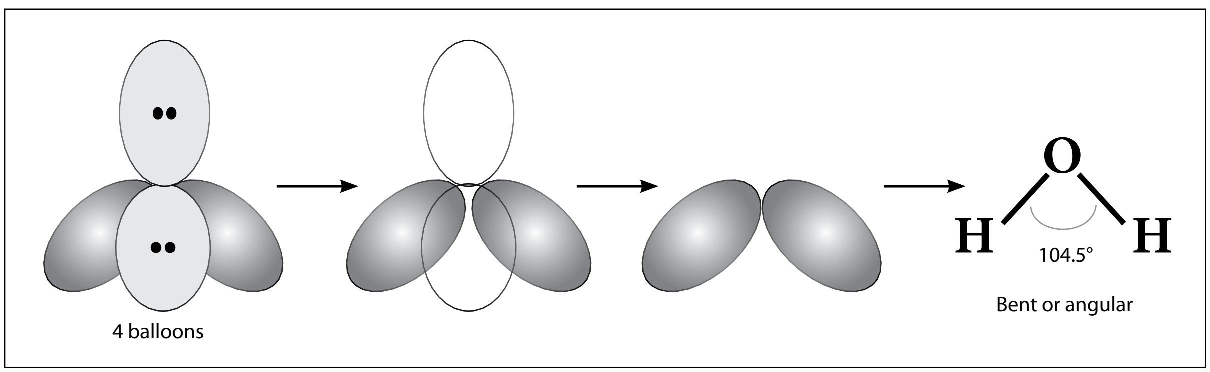
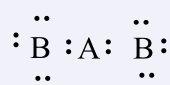
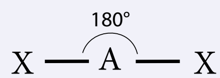
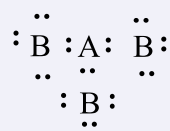
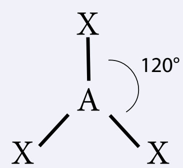
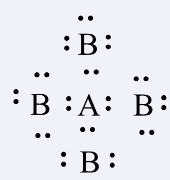
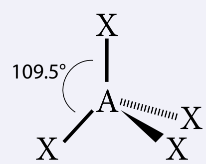
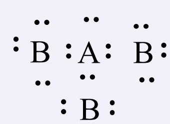
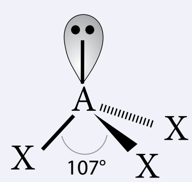
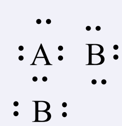
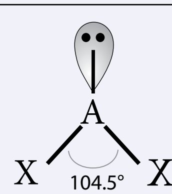


Figure 3.11: Imagine four balloons tied together and then imagine making the two balloons that are lone pairs (the balloons with the paired dots inside them) invisible. This visualization can help you to see why H_2O is a bent (or angular) molecule.

VSEPR Summary

As you've seen so far, the shape of a molecule can be predicted by determining the number of electrons that exist as bonding pairs and lone pairs around a central atom. Table 3.1 summarizes these combinations.

Table 3.1: VSEPR summary of molecular shapes

General formula	Bonding pairs	Lone pairs on central atom	Electron dot diagram	Shape	Example molecule
AB_2	2	0		 AX_2 Linear	BeH_2
AB_3	3	0		 AX_3 Trigonal planar	BH_3
AB_4	4	0		 AX_4 Tetrahedral	CH_4
AB_3	3	1		 AX_3 Pyramidal	NH_3
AB_2	2	2		 AX_2 Bent or angular	H_2O

Support Question

Be sure to try the Support Questions on your own before looking at the suggested answers provided.

19. Draw the electron dot diagram for each of the following molecules. Use this diagram to predict the molecule's shape. Draw a structural formula for each molecule.

a) H_2S. Why will we expect a shape similar to a water molecule?

b) AsF_3. Why will we expect a shape similar to the ammonia molecule seen earlier?

c) CH_3F. How does this differ from methane?

Suggested answer

VSEPR Theory for Multiple Bonds and Ions

So far, you've learned how VSEPR theory can predict the shape of molecules involving single covalent bonds. It can also be used to predict the shape of molecules with double or triple bonds and complex ions.

Multiple Bonding

Molecules such as carbon dioxide, CO_2, and hydrogen cyanide, HCN (Figure 3.12), both contain multiple bonds.

Figure 3.12: Electron dot diagram and structural formula for hydrogen cyanide, HCN (left) and carbon dioxide, CO_2 (right)

Both central atoms in these molecules are surrounded by four bonding pairs of electrons and no lone pairs. According to Table 3.1, this combination should give them a tetrahedral shape. However, experimental evidence suggests that both molecules are linear, as if both central atoms had two bonds and no lone pairs. The method described above for determining molecular shape still works if you consider either a double or triple bond as one bond. Therefore, both central atoms in carbon dioxide and hydrogen cyanide have two bonds around them and no lone pairs. This arrangement confirms that the molecule is linear. Now have a look and see if the slight alteration of the method of determining molecular shape applies to larger molecules. For example, consider methanal, which is commonly known as formaldehyde (Figure 3.13).

Figure 3.13: Electron dot diagram and structural formula for methanal (formaldehyde)

Note that there are three bonds (two singles and one double) and no lone pairs around the central carbon atom. Therefore, the formaldehyde molecule should have a trigonal planar shape. Experimental evidence confirms this prediction.

Shapes of Complex Ions

VSEPR theory can also be used to determine the shape of complex ions. For example, the electron dot diagram and structural formula for the sulfite ion are given in Figure 3.14. The central sulfur atom is surrounded by three bonds and one lone pair. According to Table 3.1, this combination results in a pyramidal shape.

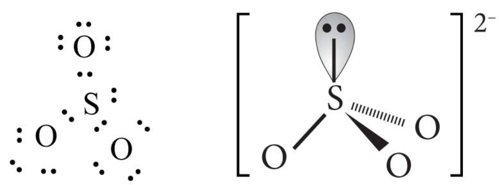


Figure 3.14: Electron dot diagram and structural formula for the sulfite ion, SO_3^{2-}. Sulfite is pyramidal in shape.

Molecules with More than One Central Atom

The method for determining molecular shape is based on there being one central atom within the molecule. Larger molecules often have multiple centres. For these situations, chemists find it useful to describe the shape around each centre, rather than invent a new name for each new shape. Consider, for example, the two hydrocarbon molecules given in Figure 3.15.

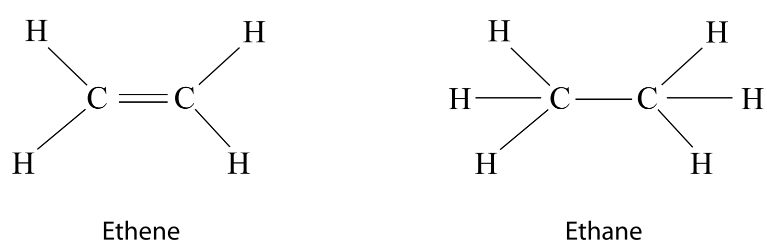


Figure 3.15: Structural formula for ethene and ethane

In ethene, each carbon atom is surrounded by three bonds (two single bonds and one double bond). This bond arrangement is similar to the structure of formaldehyde, which you saw earlier. Therefore, these bonds are in a trigonal planar arrangement around carbon. In the ethane (on the right-hand side of Figure 3.15), both carbon atoms are surrounded by four bonds. Therefore, these bonds form a tetrahedral arrangement around carbon.

Support Questions

20. Draw the Lewis structure for each of the following molecules or ions. The complex ion structure must be shown inside a square bracket and the charge on the ion is shown in the upper right corner. Use the diagram and Table 3.1 to predict the shape of the molecule. Remember to treat a double or triple bond as if it was one bond when thinking of shape.

a) C_2H_2

b) CO_3^{2-}

c) NH_4^+

Suggested answer

Dipoles and Molecular Polarity

In Lesson 2, you learned that electrons in a bond can be polarized if there's a difference in the electron-attracting ability of the two atoms that comprise the bond. The ability of an atom to attract the electrons in a chemical bond is called electronegativity. For example, the electrons that make up the bond in hydrogen chloride are drawn towards chlorine because chlorine is more electronegative than hydrogen. The result is an increase in the negative charge of chlorine and of the molecule, producing a polar covalent bond. The unequal distribution of charge between the bonding atoms is called a dipole. Since the hydrogen chloride molecule has only one bond, it is polar as well (Figure 3.16).

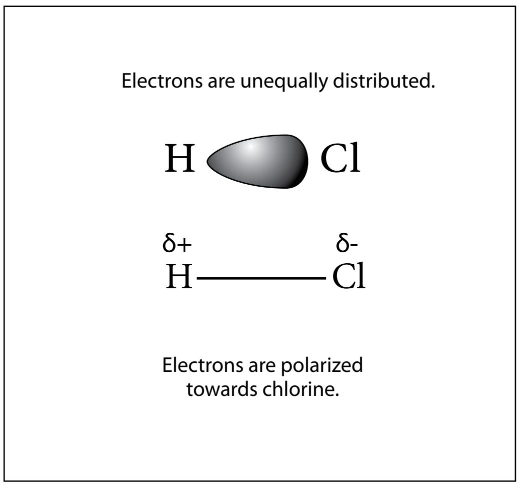


Figure 3.16: The electrons in a polar bond are polarized towards the more electronegative element. This produces a dipole (or two poles) in the bond. Since the molecule has only one bond, the molecule is polar as well.

Activity: The Great Water Bend

Like hydrogen chloride, the water molecule is also a polar molecule. As you'll see in this activity, the polarity of water gives it some rather unusual physical properties.

In order to do this optional activity, you will need access to a faucet and a plastic/rubber object (a pen or balloon).

Procedure

Step 1: Open the water tap and adjust the water flow so that the stream of water is as thin as possible. The stream of water should be as thin as the graphite (pencil lead) in the centre of a pencil.

Step 2: Put a static charge on a plastic/rubber object, such as a pen or balloon, by rubbing the object in your hair. (**Hint:** Try rubbing it in the same direction each time, as if you were combing your hair with the object.)

Step 3: Bring the charged object close to the water stream, but don't allow it to touch the water stream.

Step 4: The stream should bend towards the charged object.

Why was the thin stream of water attracted to the charged object? Think about this question for a moment and then read on to find the answer.

Predicting Molecular Polarity

The peculiar response of the stream of water in the presence of a charged object is evidence that the water molecules contain charges. Otherwise, the water stream would have flowed without deflection.

Polarity of Water

Now take a closer look at the water molecule to find out the origin of these charges. Notice that both bonds in the water molecule are polar covalent bonds (Figure 3.17).

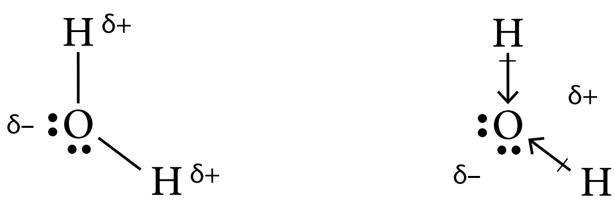


Figure 3.17: The polarity of the bonds in a water molecule (left) is indicated by one δ– and two δ+ dipoles. Because of the bent shape, the bond dipoles don't cancel each other out. The molecule has a net molecule dipole, as indicated by the arrows (right), and the electrons are held closer to the oxygen side of the molecule.

The polarity of these bonds results in oxygen being slightly negative, while the hydrogen ends are slightly positive. In the diagram, the dipole arrows are used to indicate the polar bonds. The negative side is the arrow's head and the positive side is the arrow's tail (the plus sign). Note that both dipole arrows point in the direction of oxygen, which is the most electronegative element in the molecule. The direction of the arrow also indicates the shift of the shared pair of electrons towards the oxygen side of the bond. The net result is that one end of the molecule is negative, while the other end is positive.

When we consider the two polar bonds that exist in the water molecule and the fact that both of those bonds create a shift of negative electrons toward the O on the V-shape, the whole structure of the water molecule is said to have a molecular dipole and is classified as being a polar molecule. In Figure 3.17, the diagram on the right shows the overall polarity of the water molecule where the side where the oxygen atom is located has taken on a partial negative charge, and the side where the two hydrogen atoms are located has taken on a partial positive charge (because the electrons have moved away from the H atoms).

In all cases where the whole molecule is polar, we see that one side is slightly negative while the opposite side is slightly positive.

Now consider carbon dioxide. This molecule also contains polar covalent bonds and therefore, bond dipoles. However, in this case, the bond dipoles are equally (or symmetrically) distributed around the central atom. As a result, they cancel each other out, producing a molecule with no net molecular dipole. That's why carbon dioxide is a non-polar molecule. Even though the molecule contains one or more polar bonds, it does not result in one side being slightly positive and the opposite side being slightly negative. Look at Figure 3.18, 3.19, and 3.20, which illustrate this fact.

Oil and fat also consist of non-polar molecules. Substances of similar polarity tend to dissolve in each other. For example, this property allows egg yolks, but not water or vinegar, to mix with cooking oil. This property explains why liquid carbon dioxide and other non-polar solvents used by dry cleaners can lift oil and grease off fabrics. Similarly, polar liquids like water don't mix with non-polar liquids like oil.

What do you think would happen if you repeated the water-bending activity using a stream of liquid carbon dioxide instead? Since carbon dioxide has no molecular dipole, its flow would be unaffected by the charged object.

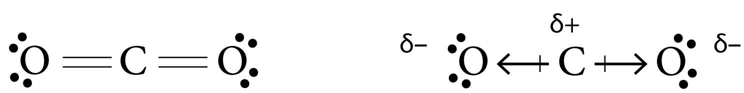


Figure 3.18: Carbon dioxide has no molecular dipole because its bond dipoles cancel each other out.

Now consider boron trifluoride, BF_3. Figure 3.19 shows the structural formula for this compound. The bond dipole of the boron to the fluorine bond is in the direction of fluorine. Note that because of the symmetry of this molecule, the bond dipoles cancel each other out. As a result, boron trifluoride is a non-polar molecule.

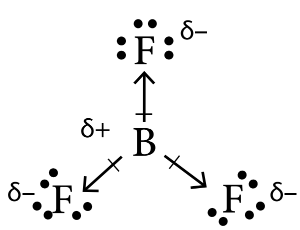


Figure 3.19: The bond dipoles in boron trifluoride cancel each other out, resulting in no molecular dipole.

Carbon tetrachloride also contains polar bonds. Chlorine is more electronegative than carbon. However, because of the symmetry of the dipole arrangement, the dipoles cancel each other out. The result is a non-polar molecule (Figure 3.20).

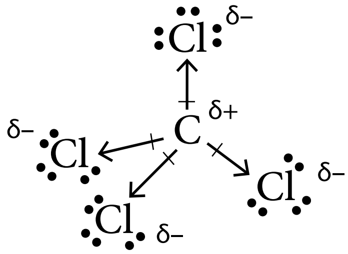


Figure 3.20: The bond dipoles in carbon tetrachloride cancel each other out, resulting in no molecular dipole.

Steps for Determining Molecular Polarity

As you've seen from the previous examples, a molecule can possess polar bonds and still be non-polar. The only way to determine molecular polarity is to consider the distribution of bond dipoles around a central atom. Here is a series of steps you can follow to determine molecular polarity.

Step 1: Draw an electron dot diagram of the molecule or ion.

Step 2: Determine the polarity of each bond using electronegativity differences (ΔEN). If $\Delta EN > 1.7$, then the bond is ionic, not covalent. If $0.4 < \Delta EN < 1.7$, the bond is polar covalent. If ΔEN is less than 0.4, the bond is essentially non-polar.

Step 3: Examine the central atom and the groups around it.

- If all of the bonds around the central atom are identical and the central atom has no lone pairs, then the molecule is non-polar.
- If the central atom has one or more different groups attached to it, then the molecule may be polar. Go to step 4.

Step 4: Draw a sketch of the molecule and determine its shape.

Step 5: Determine the symmetry of the polar bonds around the central atom.

- Draw dipole arrows on each bond pointing towards the more electronegative element. Use the length of the dipole to show the relative polarity of the bonds. A longer arrow represents a bond that is more polar than the others in the molecule.
- If the dipoles are identical in strength and are arranged equally (symmetrically), then the molecule is non-polar. In this situation, you will notice on the diagram drawn that one side of the structure does not end up slightly positive and the opposite side slightly negative.
- If the dipoles are not arranged symmetrically, then the molecule is polar.
- If the dipoles are different and don't cancel each other out, then the molecule is polar.

Support Questions

21. Predict whether each of the following molecules are polar or non-polar. Justify your predictions.

a) C_2H_2

b) NH_3

c) NH_4^+

Suggested answer

Key Questions

Now work on your Key Questions in the online submission tool. You may continue to work at this task over several sessions, but be sure to save your work each time. When you have answered all the unit's Key Questions, submit your work to the ILC.

8. For the ion IO_3^-,

a) draw the electron dot diagram and structural formula using the method as taught in this course. **(4 marks)**

b) predict the shape. **(1 mark)**

c) predict whether it is polar or non-polar, and justify your prediction. Indicate the positive and negative poles. **(2 marks)**

9. For the molecule $CHCl_3$,

a) draw the electron dot diagram and structural formula. **(4 marks)**

b) predict the shape. **(1 mark)**

c) predict whether it is polar or non-polar, and justify your prediction. Indicate the positive and negative poles. **(2 marks)**

10. The molecular shapes of water and methane are based on sp^3 hybrid orbitals attached to the central atoms. Why are the bond angles in these molecules not identical? **(2 marks)**

11. Imagine that you are the owner of a small dry-cleaning business that is considering switching from using the "normal" organic solvents to liquid carbon dioxide, as described in the lesson introduction.

a) Provide a brief explanation of why carbon dioxide is a suitable solvent to use. **(2 marks)**

b) Research two pros and two cons of using liquid carbon dioxide for dry cleaning. **(2 marks)**

Now go on to Lesson 4. Send your answers to the Key Questions to the ILC when you have completed Unit 1 (Lessons 1 to 4).