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The structure that minimizes repulsions is a trigonal bipyramid, which consists of two trigonal pyramids that share a base (Figure R.2.2): 3. With three nuclei and three lone pairs of electrons, the molecular geometry of I_3^- is linear. The Lewis electron structure is Trigonal Planar Structure of boron trifluoride 2. The three lone pairs of electrons have equivalent interactions with the three iodine atoms, so we do not expect any deviations in bonding angles. Once again, both groups around the central atom are bonding pairs (BP), so CO_2 is designated as AX2. The central atom, sulfur, contributes six valence electrons, and each fluorine atom has seven valence electrons, so the Lewis electron structure is With an expanded valence, that this species is an exception to the octet rule. The carbon atom forms two double bonds. We must now decide how to arrange the lone pairs of electrons in a trigonal bipyramid in a way that minimizes repulsions. 1. With four electron groups, we must learn to show molecules and ions in three dimensions. The VSEPR model is not a theory; it does not attempt to explain observations. The structure of CO_2 is shown in above. With only bonding pairs, SF_6 is designated as AX6. Instead, it is a counting procedure that accurately predicts the three-dimensional structures of a large number of compounds, which cannot be predicted using the Lewis electron-pair approach. Each group around the central atom is designated as a bonding pair (BP) or lone (nonbonding) pair (LP). There are four electron groups around the central atom. There are three electron groups around the central atom. The Faxial-B-Fequatorial angles are 85.1° , less than 90° because of LP-BP repulsions. However, we predict a deviation in bond angles because of the presence of the two lone pairs of electrons. Our first example is a molecule with two bonded atoms and no lone pairs of electrons, (BeH_2). With five bonding pairs and one lone pair, BrF_5 is designated as AX5E; it has a total of six electron pairs. There are six nuclei, so the molecular geometry of SF_6 is octahedral. All electron groups are bonding pairs (BP). This is essentially a trigonal bipyramid that is missing two equatorial vertices. We expect the LP-BP interactions to cause the bonding pair angles to deviate significantly from the angles of a perfect tetrahedron. This causes a deviation from ideal geometry (an H-C-H bond angle of 116.5° rather than 120°). Placing them in the axial positions eliminates 90° LP-LP repulsions and minimizes the number of 90° LP-BP repulsions. Due to LP-LP, LP-BP, and BP-BP interactions, we expect a significant deviation from idealized tetrahedral angles. Figure R.2.1 Common Structures for Molecules and Polyatomic Ions That Consist of a Central Atom Bonded to Two or Three Other Atoms We can use the VSEPR model to predict the geometry of most polyatomic molecules and ions by focusing on only the number of electron pairs around the central atom, ignoring all other valence electrons present. However, because the axial and equatorial positions are not chemically equivalent, where do we place the lone pair? With four nuclei and one lone pair of electrons, the molecular structure is based on a trigonal bipyramid with a missing equatorial vertex; it is described as a seesaw. With three bonding groups around the central atom, the structure is designated as AX3. The central atom, carbon, contributes four valence electrons, and each hydrogen atom has one valence electron, so the full Lewis electron structure is 2. Groups are positioned around the central atom in a way that produces the molecular structure with the lowest energy, as illustrated in Figures R.2.1 and R.2.2. Figure R.2.2 Geometries for Species with Two to Six Electron Groups. We will demonstrate with methyl isocyanate ($\text{CH}_3\text{-N=C=O}$), a volatile and highly toxic molecule that is used to produce the pesticide Sevin. 1. In SO_2 , we have one BP-BP interaction and two LP-BP interactions. With five nuclei surrounding the central atom, the molecular structure is based on an octahedron with a vertex missing. 3. In the VSEPR model, the molecule or polyatomic ion is given an AXmEn designation, where A is the central atom, X is a bonded atom, E is a nonbonding valence electron group (usually a lone pair of electrons), and m and n are integers. These structures can generally be predicted, when A is a nonmetal, using the "valence-shell electron-pair repulsion model (VSEPR) discussed in the next section. There are six electron groups around the central atom, each a bonding pair. The Lewis electron structure is 2. We expect all Faxial-B-Fequatorial angles to be less than 90° because of the lone pair of electrons, which occupies more space than the bonding electron pairs. From Figure R.2.3 we see that with three bonding pairs around the central atom, the molecular geometry of BCl_3 is trigonal planar, as shown in above 1. The central atom, carbon, has four valence electrons, and each oxygen atom has six valence electrons. From Figure R.2.3 we see that with two bonding pairs, the molecular geometry that minimizes repulsions in BeH_2 is linear. There are five groups around the central atom, three bonding pairs and two lone pairs. There are two bonding pairs and one lone pair, so the structure is designated as AX2E. From the BP and LP interactions we can predict both the relative positions of the atoms and the angles between the bonds, called the bond angles. The axial and equatorial positions are not chemically equivalent, as we will see in our next example. We again direct the groups toward the vertices of a trigonal bipyramid. The central atom, bromine, has seven valence electrons, as does each fluorine, so the Lewis electron structure is With its expanded valence, this species is an exception to the octet rule. 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. 2. Six electron groups form an octahedron, a polyhedron made of identical equilateral triangles and six identical vertices (Figure R.2.2). 1. 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_3 , as we would expect because of the presence of two lone pairs of electrons on the central atom rather than one. The central atom, sulfur, has 6 valence electrons, as does each oxygen atom. Using this information, we can describe the molecular geometry, the arrangement of the bonded atoms in a molecule or polyatomic ion. There are six electron groups around the central atom, four bonding pairs and two lone pairs. This procedure is summarized as follows: Draw the Lewis electron structure of the molecule or polyatomic ion. With three bonding pairs and one lone pair, the structure is designated as AX3E. With two bonding pairs and two lone pairs, the structure is designated as AX2E2 with a total of four electron pairs. All electron groups are bonding pairs, so the structure is designated as AX5. If one lone pair is axial and the other equatorial, we have one LP-LP repulsion at 90° and three LP-BP repulsions at 90° : Structure (c) can be eliminated because it has a LP-LP interaction at 90° . There are no lone pair interactions. There are four electron groups around nitrogen, three bonding pairs and one lone pair. We can treat methyl isocyanate as linked AXmEn fragments beginning with the carbon atom at the left, which is connected to three H atoms and one N atom by single bonds. In addition, there was significant damage to livestock and crops. With four bonding pairs, the molecular geometry of methane is tetrahedral (Figure R.2.3). As you learned previously, the Lewis electron structure of one of three resonance forms is represented as Trigonal Structure of Carbonate Ion 2. Like BeH_2 , the arrangement that minimizes repulsions places the groups 180° apart. The central atom, beryllium, contributes two valence electrons, and each hydrogen atom contributes one. The structure of CO_2 is a resonance hybrid. We encounter this situation for the first time with five electron groups. Thus according to the VSEPR model, the C-N=C fragment should be bent with an angle less than 120° . Similarly, the carbon atom on the right has two double bonds that are similar to that in CO_2 , so its geometry, like that of CO_2 , is linear. Phosphorus has five valence electrons and each chlorine has seven valence electrons, so the Lewis electron structure of PCl_5 is 2. Recognizing similarities to simpler molecules will help you predict the molecular geometries of more complex molecules. The molecular geometry of PCl_5 is trigonal bipyramidal, as shown in Figure R.2.3. The molecule has three atoms in a plane in equatorial positions and two atoms above and below the plane in axial positions. With two bonding pairs and three lone pairs, I_3^- has a total of five electron pairs and is designated as AX2E3. We minimize repulsions by placing the three groups 120° apart (Figure R.2.2). This can be described as a trigonal bipyramid with three equatorial vertices missing. VSEPR only recognizes groups around the central atom. All electron groups are bonding pairs (BP), so the structure is designated as AX3. There are six electron groups around the Br, five bonding pairs and one lone pair. 1. We continue our discussion of structure and bonding by introducing the valence-shell electron-pair repulsion (VSEPR) model (pronounced "vesper"), which can be used to predict the shapes of many molecules and polyatomic ions. The three nuclei in BrF_3 determine its molecular structure, which is described as T shaped. Determine the electron group arrangement around the central atom that minimizes repulsions. 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. With three bonding pairs and two lone pairs, the structural designation is AX3E2 with a total of five electron pairs. This molecular shape is essentially a tetrahedron with two missing vertices. The resulting highly exothermic reaction caused a rapid increase in pressure that ruptured the tanks, releasing large amounts of methyl isocyanate that killed approximately 3800 people and wholly or partially disabled about 50,000 others. The central atom, boron, contributes three valence electrons, and each chlorine atom contributes seven. Structure (b), with fewer LP-BP repulsions at 90° than structure (a), is lower in energy. The structure that minimizes LP-LP, LP-BP, and BP-BP repulsions is 3. We initially place the groups in a trigonal planar arrangement to minimize repulsions (Figure R.2.2). Keep in mind, however, that the VSEPR model, like any model, is a limited representation of reality; the model provides no information about bond lengths or the presence of multiple bonds. The N=C=O angle should therefore be 180° , or linear. Both groups around the central atom are bonding pairs (BP). There are five groups around sulfur, four bonding pairs and one lone pair. 4. The experimentally determined structure of methyl isocyanate confirms our prediction (Figure R.2.7). With 18 valence electrons, the Lewis electron structure is shown below. In our discussion we will refer to Figure R.2.2 and Figure R.2.3, which summarize the common molecular geometries and idealized bond angles of molecules and ions with two to six electron groups. With two hydrogen atoms and two lone pairs of electrons, the structure has significant lone pair interactions. The sulfur atom has six valence electrons and each fluorine has seven valence electrons, so the Lewis electron structure is With an expanded valence, this species is an exception to the octet rule. Because the axial and equatorial positions are not equivalent, we must decide how to arrange the groups to minimize repulsions. Therefore, we do not expect any deviation in the Cl-I-Cl bond angles. We see from Figure R.2.2 that the arrangement that minimizes repulsions places the groups 180° apart. There are three electron groups around the central atom, two double bonds and one lone pair. The central atom, carbon, contributes four valence electrons, and each oxygen atom contributes six. There are four groups around the central oxygen atom, two bonding pairs and two lone pairs. This image table was borrowed from Paul Groves LibreText, and the rotating molecules were created by Robyn Rindge. One of the limitations of Lewis structures is that they depict molecules and ions in only two dimensions. Assign an AXmEn designation; then identify the LP-LP, LP-BP, or BP-BP interactions and predict deviations from ideal bond angles. With fewer 90° LP-BP repulsions, we can predict that the structure with the lone pair of electrons in the equatorial position is more stable than the one with the lone pair in the axial position. This approach gives no information about the actual arrangement of atoms in space, however. Figure 9.2.4: 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. Each double bond is a group, so there are two electron groups around the central atom. 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 R.2.2 and R.2.3). Because a lone pair is not shared by two nuclei, it occupies more space near the central atom than a bonding pair (Figure R.2.4). The bromine atom has seven valence electrons, and each fluorine has seven valence electrons, so the Lewis electron structure is Once again, we have a compound that is an exception to the octet rule. If we place the lone pair in the equatorial position, we have three LP-BP repulsions at 90° . To minimize repulsions, the groups are directed to the corners of a trigonal bipyramid. If we place both lone pairs in the axial positions, we have six LP-BP repulsions at 90° . Each chlorine contributes seven, and there is a single negative charge. In essence, this is a tetrahedron with a vertex missing (Figure R.2.3). This molecular structure is square pyramidal. In 1984, large quantities of Sevin were accidentally released in Bhopal, India, when water leaked into storage tanks. The three fragments combine to give the following structure: We predict that all four nonhydrogen atoms lie in a single plane, with a C-N-C angle of approximately 120° . In our next example we encounter the effects of lone pairs and multiple bonds on molecular geometry for the first time. Lone pairs are shown using a dashed line. The carbon in the -N=C=O fragment is doubly bonded to both nitrogen and oxygen, which in the VSEPR model gives carbon a total of two electron pairs. The central atom, iodine, contributes seven electrons. Placing five F atoms around Br while minimizing BP-BP and LP-BP repulsions gives the following structure: 3. The relationship between the number of electron groups around a central atom, the number of lone pairs of electrons, and the molecular geometry is summarized in Figure R.2.6. Figure R.2.6 Overview of Molecular Geometries Table 1 shows some examples of geometries with a central atom (A) is bonded to two or more (X) atoms. Groups are placed around the central atom in a way that produces a molecular structure with the lowest energy. For example, in a molecule such as CH_2O (AX3), whose structure is shown below, the double bond repels the single bonds more strongly than the single bonds repel each other. In some cases, however, the positions are not equivalent. To minimize repulsions, the groups are placed 120° apart (Figure R.2.2). All electron groups are bonding pairs, so the structure is designated as AX4. Because electrons repel each other electrostatically, the most stable arrangement of electron groups (i.e., the one with the lowest energy) is the one that minimizes repulsions. With five nuclei, the ICl_4^- ion forms a molecular structure that is square planar, an octahedron with two opposite vertices missing. Figure R.2.3 Common Molecular Geometries for Species with Two to Six Electron Groups. This designation has a total of four electron pairs, three X and one E. The VSEPR model can be used to predict the structure of somewhat more complex molecules with no single central atom by treating them as linked AXmEn fragments. The Faxial-S-Faxial angle is 173° rather than 180° because of the lone pair of electrons in the equatorial plane. The molecular geometry is described only by the positions of the nuclei, not by the positions of the lone pairs. All positions are chemically equivalent, so all electronic interactions are equivalent. As shown in Figure R.2.2, repulsions are minimized by placing the groups in the corners of a tetrahedron with bond angles of 109.5° . The BrF_5 structure has four fluorine atoms in a plane in an equatorial position and one fluorine atom and the lone pair of electrons in the axial positions. It has three identical bonds, each with a bond order of $(1 \frac{1}{3})$. We can therefore predict the $\text{CH}_3\text{-N}$ portion of the molecule to be roughly tetrahedral, similar to methane: The nitrogen atom is connected to one carbon by a single bond and to the other carbon by a double bond, producing a total of three bonds, C-N=C. Thus bonding pairs and lone pairs repel each other electrostatically in the order BP-BP < LP-BP < LP-LP. If we place it in the axial position, we have two 90° LP-BP repulsions at 90° . There are five bonding groups around phosphorus, the central atom. The four bonds around carbon mean that it must be surrounded by four bonding electron pairs in a configuration similar to AX_4 . According to this model, valence electrons in the Lewis structure form groups, which may consist of a single bond, a double bond, a triple bond, a lone pair of electrons, or even a single unpaired electron, which in the VSEPR model is counted as a lone pair. We see from Figure R.2.2 that the geometry that minimizes repulsions is octahedral. The Faxial-Br-Faxial angle is 172° , less than 180° because of LP-BP repulsions (figure above) Note Because lone pairs occupy more space around the central atom than bonding pairs, electrostatic repulsions are more important for lone pairs than for bonding pairs. There are three nuclei and one lone pair, so the molecular geometry is trigonal pyramidal. The three equatorial positions are separated by 120° from one another, and the two axial positions are at 90° to the equatorial plane. Contributors Anonymous, Modified by Bob Belford, Joshua Halpern, Scott Sinex and Scott Johnson Page 2 UALR 1402: General Chemistry I Belford: LibreText Handout 8.6.1: Overview of Structures: api/deki/files/60818/VESPR_Geometry_Handout.pdf T Handout 8.6.2: VSEPR Worksheet api/deki/files/61155/vsepr2_Worksheet.pdf The Lewis electron-pair approach can be used to predict the number and types of bonds between the atoms in a substance, and it indicates which atoms have lone pairs of electrons. Thus BeH_2 is designated as AX2. This designation has a total of three electron pairs, two X and one E. In previous examples it did not matter where we placed the electron groups because all positions were equivalent. Repulsions are minimized by directing the bonding pairs and the lone pairs to the corners of a tetrahedron Figure R.2.2. 3. The VSEPR Model The VSEPR model can predict the structure of nearly any molecule or polyatomic ion in which the central atom is a nonmetal, as well as the structures of many molecules and polyatomic ions with a central metal atom. That is, the one that minimizes repulsions. We designate SF_4 as AX4E; it has a total of five electron pairs. ICl_4^- is designated as AX4E2 and has a total of six electron pairs. We also expect a deviation from ideal geometry because a lone pair of electrons occupies more space than a bonding pair. In ammonia, the central atom, nitrogen, has five valence electrons and each hydrogen donates one valence electron, producing the Lewis electron structure 2. Repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron. There are two electron groups around the central atom. Thus the lone pairs on the oxygen atoms do not influence the molecular geometry. For example, carbon atoms with four bonds (such as the carbon on the left in methyl isocyanate) are generally tetrahedral. 1. The Lewis electron structure is 2. We will illustrate the use of this procedure with several examples, beginning with atoms with two electron groups. Each iodine atom contributes seven electrons and the negative charge one, so the Lewis electron structure is 2.

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