



## **Example for sp hybridization**

Why is hybridization important? Why do we need hybridization? Do lone pairs affect hybridization? What is hybridization and its types? What is hybridization? What is hybridization and its types? What is hybridization? What is hybridization? there? How do I calculate bond order? How is sp3 hybridization, the s orbital overlaps with only one p orbital. Any central atom surrounded by just two regions of valence electron density in a molecule will exhibit sp hybridization. sp orbitals are oriented at 180 degrees to each other. In sp hybridization, the s orbital overlaps with only one p orbitals that are linearly oriented; two sp orbitals will be at 180 degrees to each other. Any central atom surrounded by just two regions of valence electron density in a molecule will exhibit sp hybridization. Some examples include the mercury atom in the linear HgCl2 molecule, the zinc atom in BeCl2. This last example will be discussed in more detail below. The beryllium atom in a gaseous BeCl2 molecule is an example of a central atom with no lone pairs of electrons in a linear arrangement of three atoms. There are two regions of valence electron domains, two of the Be atom's four valence orbitals will mix to yield two hybrid orbitals. When atomic orbitals hybridize, the valence electrons occupy the newly created orbitals. The Be atom had two valence electrons, so each of these electrons, so each of these electrons pairs up with the unpaired electrons at the valence electrons. Each of these electrons occupy the newly created orbitals and a chlorine atom when a hybrid orbital and a chlorine atom when a hybrid orbital electrons. of the Be-Cl bonds. The hybridization process involves mixing of the valence s orbitals to yield two equivalent sp hybrid orbitals. Each hybrid orbital is oriented primarily in just one direction. Note that each sp orbital contains one lobe that is significantly larger than the other. The set of two sp orbitals are oriented at 180°, which is consistent with the geometry for two domains. The set of sp orbitals appears similar in shape to the original p orbital, but there is an important difference. The number of atomic orbitals combined always equals the number of hybrid orbitals formed. The p orbital is one orbital that can hold up to two electrons. The sp set is two equivalent orbitals, which are half filled. In gaseous BeCl2, these half-filled hybrid orbitals from the chlorine atoms to form two identical  $\sigma$  bonds. Energy Level Diagrams for sp Orbitals from the chlorine atom and in the bonded Be a horizontal line (indicating its energy) and each electron by an arrow. Energy increases toward the top of the diagram. We use one upward arrows (up and down) to indicate two electrons of opposite spin. Orbital Energy-Level Diagrams For Isolated and Bonded BeThe left orbital energy-level diagram shows both electrons of Be in the 2s orbital. The right energy-level diagrams shows sp hybridized orbitals on Be in the linear BeCl2 molecule. Each of the two sp hybrid orbitals holds one electron and is thus half filled and available for bonding via overlap with a Cl 3p orbital. By the end of this section, you will be able to: Explain the concept of atomic orbital hybridization Determine the hybrid orbitals associated with various molecules. However, to understand how molecules with more than two atoms form stable bonds, we require a more detailed model As an example, let us consider the water molecule, in which we have one oxygen atom bonding to two hydrogen atoms. Oxygen has the electrons (one in each of the two 2p orbitals). Valence bond theory would predict that the two O-H bonds form from the overlap of these two 2p orbitals with the 1s orbitals of the hydrogen atoms. If this were the case, the bond angle is 104.5°, not 90°. The prediction of the valence bond theory model does not match the real-world observations of a water molecule; a different model is needed. Figure 1. The hypothetical overlap of two of the 2p orbitals on an oxygen atom (red) with the 1s orbitals of two hydrogen atoms (blue) would produce a bond angles in H2O differ from those predicted by the overlap of the 1s orbital of the hydrogen atoms with the 2p orbitals of the oxygen atom. The mathematical expression known as the wave function,  $\psi$ , contains information about each orbital and the wave functions combine to produce new mathematical descriptions that have different shapes. This process of combining the wave functions for atomic orbitals, LCAO, (a technique that we will encounter again later). The new orbitals that result are called hybrid orbitals. The valence orbitals in an isolated oxygen atom are a 2s orbital and three 2p orbitals. The valence orbitals in an oxygen atom in a water molecule differ; they consist of four equivalent hybrid orbitals that point approximately toward the corners of a tetrahedron (Figure 2). Consequently, the overlap of the O and H orbitals should result in a tetrahedral bond angle (109.5°). The observed angle of 104.5° is experimental evidence for which quantum-mechanical calculations. Figure 2. (a) A water molecule has four regions of electron density, so VSEPR theory predicts a tetrahedral arrangement of hybrid orbitals. (b) Two of the hybrid orbitals on oxygen contain lone pairs, and the other two overlap with the experimental structure. The following ideas are important in understanding hybridization: Hybrid orbitals do not exist in isolated atoms. They are formed only in covalently bonded atoms. A set of hybrid orbitals in a set is equal to the number of atomic orbitals that were combined to produce the set. All orbitals in a set of hybrid orbitals are equivalent in shape and energy. The type of hybrid orbitals formed in a bonded atom depends on its electron-pair geometry as predicted by the VSEPR theory. Hybrid orbitals formed in a bonded atom depends on its electron-pair geometry as predicted by the vertage to form σ bonds. In the following sections, we shall discuss the common types of hybrid orbitals. The beryllium atom in a gaseous BeCl2 molecule is an example of a central atom with no lone pairs of electrons in a linear arrangement of three atoms. There are two regions of valence electron density in the BeCl2 molecule that correspond to the two covalent Be-Cl bonds. To accommodate these two electron domains, two of the Be atom's four valence orbitals will mix to yield two hybrid orbitals. This hybridization process involves mixing of the valence s orbitals that are oriented in a linear geometry (Figure 3). In this figure, the set of sp orbitals appears similar in shape to the original p orbital, but there is an important difference. The number of atomic orbitals combined always equals the number of hybrid orbitals formed. The p orbital is one orbital that can hold up to two electrons. The sp set is two equivalent orbitals that point 180° from each other. The two electrons that were originally in the s orbital are now distributed to the two sp orbitals, which are half filled. In gaseous BeCl2, these half-filled hybrid orbitals from the chlorine atoms to form two identical  $\sigma$  bonds. Figure 3. Hybridization of an s orbital (blue) and a p orbital (red) of the same atom produces two sp hybrid orbitals (purple). Each hybrid orbital is oriented primarily in just one direction. Note that each sp orbital contains one lobe that is significantly larger than the other. The set of two sp orbitals are oriented at 180°, which is consistent with the geometry for two domains. We illustrate the electronic differences in an isolated Be atom and in the bonded Be atom in the orbital energy-level diagram in Figure 4. These diagrams represent each orbital by a horizontal line (indicating its energy) and each electron by an arrow. Energy increases toward the top of the diagram. We use one upward arrow to indicate one electron in an orbital and two arrows (up and down) to indicate two electrons of opposite spin. Figure 4. This orbital energy-level diagram shows the sp hybridized orbitals on Be in the linear BeCl2 molecule. Each of the two sp hybrid orbitals holds one electrons, so each of the sp orbitals gets one of these electrons. Each of these electrons pairs up with the unpaired electron on a chlorine atom when a hybrid orbital and a chlorine orbital overlap during the formation of the Be-Cl bonds. Any central atom surrounded by just two regions of valence electron density in a molecule will exhibit sp hybridization. Other examples include the mercury atom in the linear HgCl2 molecule, the zinc atom in Zn(CH3)2, which contains a linear C-Zn-C arrangement, and the carbon atoms in HCCH and CO2. Check out the University of Wisconsin-Oshkosh website to learn about visualizing hybrid orbitals in three dimensions. The valence orbitals of a central atom surrounded by three regions of electron density consist of a set of three sp2 hybrid orbitals and one unhybridized p orbitals from sp2 hybridization, the mixing of one s orbital sto produce three identical hybrid orbitals (red) produces three equivalent sp2 hybridized orbitals (purple) oriented at 120° with respect to each other. The remaining unhybridized p orbital is not shown here, but is located along the z axis. Although quantum mechanics yields the "plump" orbital lobes as depicted in Figure 5, sometimes for clarity these orbitals are drawn thinner and without the minor lobes, as in Figure 6, to avoid obscuring other features of a given illustration. We will use these "thinner" representations whenever the trugonal planar sp2 hybrid orbitals is sometimes used in more crowded figures. The observed structure of the borane molecule, BH3, suggests sp2 hybridization for boron in this compound. The molecule is trigonal planar, and the boron atom is involved in three bonds to hydrogen atoms (Figure 7). We can illustrate the comparison of orbital energy level diagram in Figure 8. We redistribute the three valence electrons of the boron atom in the three sp2 hybrid orbitals, and each boron electron when B-H bonds form. Figure 7. BH3 is an electron-deficient molecule with a trigonal planar structure. Figure 8. In an isolated B atom, there are one 2s and three 2p valence orbitals. When boron is in a molecule with three regions of electron density, three of the orbitals hybridized 2p orbitals and one unhybridized 2p orbitals and create a set of three regions of electron density will exhibit sp2 hybridization. This includes molecules with a lone pair on the central atom, as in formaldehyde, CH2O, and ethene, H2CCH2. Figure 9. The central atom(s) in each of the structures shown contain three regions of electron density and are sp2 hybridized. As we know from the discussion of VSEPR theory, a region of electron density contains all of the electron, a single bond, or a multiple bond would each count as one region of electron density. The valence orbitals of an atom surrounded by a tetrahedral arrangement of bonding pairs and lone pairs consist of a set of four sp3 hybrid orbitals. The hybrids result from the mixing of one s orbital and all three p orbitals that produces four identical sp3 hybrid orbitals. The hybridization of an s orbital (blue) and three p orbitals (red) produces four equivalent sp3 hybridized orbitals (purple) oriented at 109.5° with respect to each other. A molecule of a tetrahedron. The carbon atom in methane exhibits sp3 hybridization. We illustrate the orbitals hybridize when the carbon bonds in a molecule like CH4 with four regions of electron density. This creates four equivalent sp3 hybridized orbitals. Overlap of each of the four hydrogen atoms overlaps with one of the four sp3 orbitals of the carbon atom to form a sigma (o) bond. This results in the formation of four strong, equivalent covalent bonds between the carbon atom and each of the hydrogen atoms to produce the methane molecule, CH4. The structure of ethane, C2H6, is similar to that of methane in that each carbon in ethane has four neighboring atoms arranged at the corners of a tetrahedron—three hydrogen atoms and one carbon atom (Figure 12). However, in ethane an sp3 orbital of a second carbon atom to form a σ bond between the two carbon atoms. Each of the remaining sp3 hybrid orbitals overlaps with an sp3 orbital of a hydrogen atom to form carbon-hydrogen σ bonds. The structure and overall outline of the bonding orbitals of ethane are shown in Figure 12. The orientation of the two CH3 groups is not fixed relative to each other. Experimental evidence shows that rotation around σ bonds occurs easily. Figure 12. (a) In the ethane molecule, C2H6, each carbon has four sp3 orbitals. (b) These four orbitals overlap to form seven  $\sigma$  bonds. An sp3 hybrid orbital can also hold a lone pair of electrons. For example, the nitrogen atom is surrounded by three bonding pairs and a lone pair of electrons directed to the four corners of a tetrahedron. The nitrogen atom is sp3 hybridized with one hybrid orbital occupied by the lone pair. The molecular structure of water is consistent with a tetrahedral arrangement of two lone pairs and two bonding pairs. Since lone pairs and two by bonding pairs, structures that contain lone pairs have bond angles slightly distorted from the ideal. Perfect tetrahedra have angles of 109.5°, but the observed angles in ammonia (107.3°) and water (104.5°) are slightly smaller. Other examples of sp3 hybridization include CCl4, PCl3, and NCl3. To describe the five bonding orbitals in a trigonal bipyramidal arrangement, we must use five of the valence shell atomic orbitals, and one of the d orbitals, we must use six valence shell), which gives six sp3d2 hybrid orbitals. With an octahedral arrangement of six hybrid orbitals, we must use six valence shell atomic orbitals. These hybridizations are only possible for atoms that have d orbitals in their valence subshells (that is, not those in the first or second period). In a molecule of phosphorus atom) directed toward the corners of a trigonal bipyramid. We use the 3s orbital, the three 3p orbitals, and one of the 3d orbitals to form the set of five sp3d hybrid orbitals (Figure 14) that are involved in the P-Cl bonds. Other atoms in ClF3 and in ClF4+. (The electrons on fluorine atoms are omitted for clarity.) Figure 13. The three compounds pictured exhibit sp3d hybridization in the central atom and a trigonal bipyramid form. SF4 and ClF4+ have one lone pairs giving it the T-shape shown. Figure 14. (a) The five regions of electron density around phosphorus in PCl5 require five hybrid sp3d orbitals. (b) These orbitals combine to form a trigonal bipyramidal structure with each large lobe of the hybrid orbital pointing at a vertex. As before, there are also small lobes pointing in the opposite direction for each orbital (not shown for clarity). The sulfur atom in sulfur hexafluoride, SF6, exhibits sp3d2 hybridization. A molecule of sulfur hexafluoride has six bonding pairs of electrons connecting six fluorine atoms to a single sulfur atom. There are no lone pairs of electrons on the central atom. To bond six fluorine atoms, the 3s orbitals, each directed toward a different corner of an octahedron. Other atoms that exhibit sp3d2 hybridization include the phosphorus atom in PCl6-, the iodine atom in the interhalogens IF6+, IF5, ICl4-, IF4- and the xenon atom in XeF4. Figure 15. (a) Sulfur hexafluoride, SF6, has an octahedral structure that requires sp3d2 hybridization. (b) The six sp3d2 orbitals form an octahedral structure that requires sp3d2 hybridization. orbital is not shown for clarity. The hybridization of an atom is determined based on the number of regions of electron density that surround it. The geometrical arrangements are identical to those of the electron-pair geometries predicted by VSEPR theory. VSEPR theory predicts the shapes of molecules, and hybrid orbital theory provides an explanation for how those shapes are formed. To find the hybridization of a central atom, we can use the following guidelines: Determine the Lewis structure of the molecule. Determine the number of regions of electron density around an atom using VSEPR theory, in which single bonds, multiple bonds, radicals, and lone pairs each count as one region. Assign the set of hybridized orbitals from Figure 16 that corresponds to this geometry. Figure 16. The shapes of hybridized orbital sets are consistent with the electron-pair geometries. For example, an atom surrounded by three regions of electron density is sp2 hybridized, and the three sp2 orbitals are arranged in a trigonal planar fashion. It is important to remember that hybridization was devised to rationalize experimentally observed molecular geometries. The model works well for molecules containing small central atoms, in which the valence electron pairs are close together in space. However, for larger central atoms, the valence-shell electron pairs are farther from the nucleus, and there are fewer repulsions. Their compounds exhibit structures that are often not consistent with VSEPR theory, and hybridized orbitals are not necessary to explain the observed data. For example, we have discussed the H-O-H bond angle in H2O, 104.5°, which is more consistent with sp3 hybrid orbitals (109.5°) on the central atom than with 2p orbitals (90°). Sulfur is in the same group as oxygen, and H2S has a similar Lewis structure. However, it has a much smaller bond angle (92.1°), which indicates much less hybridization on sulfur than oxygen. Continuing down the group, tellurium is even larger than sulfur, and for H2Te, the observed bond angle (90°) is consistent with overlap of the 5p orbitals, without invoking hybridization. We invoke hybridization Ammonium sulfate is important as a fertilizer. What is the hybridization of the sulfur atom in the sulfate ion, SO42-? Solution The Lewis structure of sulfate shows there are four regions of electron density. The hybridization is sp3. Check Your Learning What is the hybridization of the selenium atom in SeF4? The selenium atom is sp3d hybridized. Assigning Hybridization Urea, NH2C(O)NH2, is sometimes used as a source of nitrogen in fertilizers. What is the hybridization of each nitrogen and carbon density, which arrange themselves in a tetrahedral electron-pair geometry. The hybridization in a tetrahedral electron-pair geometry. The hybridization of the nitrogen atoms are surrounded by four regions of electron density, which arrange themselves in a tetrahedral electron-pair geometry. in urea. The carbon atom is surrounded by three regions of electron density, positioned in a trigonal planar arrangement. The hybridization of the carbon atom in urea. Check Your Learning Acetic acid, H3CC(O)OH, is the molecule that gives vinegar its odor and sour taste. What is the hybridization of the two carbon atoms in acetic acid? We can use hybrid orbitals, which are mathematical combinations of some or all of the valence atomic orbitals, to describe the electron density around covalently bonded atoms. These hybrid orbitals either form sigma (o) bonds directed toward other atoms of the molecule or contain lone pairs of electrons. We can determine the type of hybridization; four, sp3 hybridiz atomic orbitals (p or d orbitals). Chemistry End of Chapter Exercises Why is the concept of hybridization required in valence bond theory? Give the shape that describes each hybrid orbitals. What is the hybridization of the central atom in each of the following? (a) BeH2 (b) SF6 (c) PO43- (d) PCl5 A molecule with the formula AB3 could have one of four different shapes. Give the shape and the hybridization of the central A atom for each. Methionine, CH3SCH2CH2CH(NH2)CO2H, is an amino acid found in proteins. Draw a Lewis structure of this compound. What is the hybridization type of each carbon, oxygen, the nitrogen, and the sulfur? Sulfuric acid is manufactured by a series of reactions represented by the following equations: [latex]/text{SO}\_2(g) + \text{O}\_2(g) \longrightarrow 8\text{SO}\_2(g) + \text{O}\_2(g) \longrightarrow 8\text{SO}\_2(g) + \text{O}\_2(g) + \text{O}\_2( \text{O}(1) \longrightarrow \text{H}\_2 \text{SO}\_4(1)[/latex] Draw a Lewis structure, predict the molecule (b) SO2 molecule (c) SO3 molecule (d) H2SO4 molecule (the hydrogen atoms) Two important industrial chemicals, ethene, C2H4, and propene, C3H6, are produced by the steam (or thermal) cracking process: [latex]2\text{C}\_3 \text{H}\_6(g) + \text{C}\_3 \text{H}\_2(g)[/latex] For each of the four carbon compounds, do the following: (a) Draw a Lewis structure. (b) Predict the geometry about the carbon atom. (c) Determine the hybridization of each type of carbon atom. For many years after they were discovered, it was believed that the noble gases could not form compounds. Now we know that belief to be incorrect. A mixture of xenon and fluorine gases, confined in a quartz bulb and placed on a windowsill, is found to slowly produce a white solid. Analysis of the compound indicates that it contains 77.55% Xe and 22.45% F by mass. (a) What is the formula of the compound. (b) Write a Lewis structure for the compound. (c) Predict the shape of the molecules of the compound? (b) Write a Lewis structure for the compound? (b) Write a Lewis structure for the compound. (c) Predict the shape of the molecules of the molecules of the molecules of the compound? HNO2 (HONO). (a) Write a Lewis structure. (b) What are the electron pair and molecular geometries of the internal oxygen and nitrogen atoms in HNO2? Strike-anywhere matches contain a layer of KClO3 and a layer of P4S3. The heat produced by the friction of striking the match causes these two compounds to react vigorously, which sets fire to the wooden stem of the match. KClO3 contains the ClO3- ion. (b) Describe the geometry about the P atoms, the S atom, and the Cl atom in these species. (c) Assign a hybridization to the P atoms, the S atom, and the Cl atom in these species. (d) Determine the oxidation states and formal charge of the atoms in P4S3 and the ClO3- ion. Identify the hybridization of each carbon atom in the following molecule. (The arrangement of atoms is given; you need to determine how many bonds connect each pair of atoms.) Write Lewis structures for NF3 and PF5. On the basis of hybrid orbitals, explain the fact that NF3, PF3, and PF5 are stable molecules, but NF5 does not exist. In addition to NF3, two other fluoro derivatives of nitrogen are known: N2F4 and N2F2. What shapes do you predict for these two molecules? What is the hybridization for the nitrogen in each molecule? hybrid orbital created by combining atomic orbitals on a central atom hybridization model that describes the changes in the atomic orbitals with a linear arrangement that results from combining one s and one p orbital sp2 hybrid orbital one of a set of three orbitals with a trigonal planar arrangement that results from combining one s and two p orbitals sp3 hybrid orbital sp3 hybrid orbitals sp3 hybrid orbitals with a trigonal planar arrangement that results from combining one s and three p orbitals sp3 hybrid orbital one of a set of five orbitals with a trigonal planar arrangement that results from combining one s and two p orbitals sp3 hybrid orbital one of a set of five orbitals with a trigonal planar arrangement that results from combining one s and two p orbitals sp3 hybrid orbital one of a set of five orbitals with a trigonal planar arrangement that results from combining one s and two p orbitals with a trigonal planar arrangement that results from combining one s and two p orbitals with a trigonal planar arrangement that results from combining one s and two p orbitals with a trigonal planar arrangement that results from combining one s and two p orbitals with a trigonal planar arrangement that results from combining one s and two p orbitals with a trigonal planar arrangement that results from combining one s and two p orbitals with a trigonal planar arrangement that results from combining one s and two p orbitals with a trigonal planar arrangement that results from combining one s and two p orbitals with a trigonal planar arrangement that results from combining one s and two p orbitals with a trigonal planar arrangement that results from combining one s and two p orbitals with a trigonal planar arrangement that results from combining one s are set of four orbitals with a trigonal planar arrangement that results from combining one s are set of four orbitals with a trigonal planar arrangement that results from combining one s are set of four orbitals with a trigonal planar arrangement that results from combining one s are set of four orbitals with a trigonal planar arrangement that results from combining one s are set of four orbitals with a trigonal planar arrangement that results from combining one s are bipyramidal arrangement that results from combining one s, three p, and one d orbital sp3d2 hybrid orbital sp3d2 hybrid orbitals Answers to Chemistry End of Chapter Exercises 1. Hybridization is introduced to explain the geometry of bonding orbitals in valance bond theory. 3. There are no d orbitals in the valence shell of carbon. 5. trigonal planar, sp2; trigonal planar, sp2; trigonal planar, sp2; trigonal planar, sp3d, or (three lone pairs on A) sp3d2 7. (a) Each S has a bent (109°) geometry, sp3 (b) Bent (120°), sp2 (c) Trigonal planar, sp2 (d) Tetrahedral, sp3 9. a) XeF2 (b) (c) linear (d) sp3d 11. (a) (b) P atoms, trigonal pyramidal; S atoms, bent, with two lone pairs; Cl atoms, trigonal pyramidal; (c) Hybridization about P, S, and Cl is, in all cases, sp3; (d) Oxidation states P +1, [latex]\text{S} - 1\frac{1}{3}[/latex], Cl +5, O -2. Formal charges: P 0; S 0; Cl +2: O -1 13. Phosphorus and nitrogen can form sp3 hybrids to form three bonds and hold one lone pair in PF3 and NF3, respectively. However, nitrogen has no valence d orbitals to bind five fluorine atoms in NF5. Phosphorus has d orbitals and can bind five fluorine atoms with sp3d hybrid orbitals in PF5.

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