Chemistry 2e
8: Advanced Theories of Covalent Bonding
8.1: Valence Bond Theory

1. Explain how σ and π bonds are similar and how they are different.

Solution

Similarities: Both types of bonds result from overlap of atomic orbitals on adjacent atoms and contain a maximum of two electrons. Differences: σ bonds are stronger and result from end-to-end overlap and all single bonds are σ bonds; π bonds between the same two atoms are weaker because they result from side-by-side overlap, and multiple bonds contain one or more π bonds (in addition to a σ bond).

3. Explain why bonds occur at specific average bond distances instead of the atoms approaching each other infinitely close.

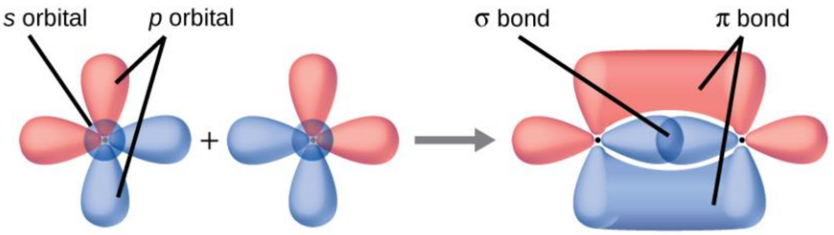
Solution

The specific average bond distance is the distance with the lowest energy. At distances less than the bond distance, the positive charges on the two nuclei repel each other, and the overall energy increases.

5. Use valence bond theory to explain the bonding in O_2. Sketch the overlap of the atomic orbitals involved in the bonds in O_2.

Solution

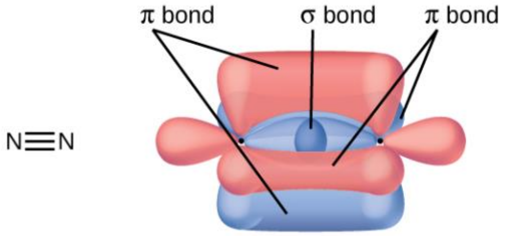
Bonding: One σ bond and one π bond. The *s* orbitals are filled and do not overlap. The *p* orbitals overlap along the axis to form a σ bond and side by side to form the π bond.



7. A friend tells you N_2 has three π bonds due to overlap of the three *p*-orbitals on each N atom. Do you agree?

Solution

No, two of the *p* orbitals (one on each N) will be oriented end to end and will form a σ bond.



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Chemistry 2e
8: Advanced Theories of Covalent Bonding
8.2: Hybrid Atomic Orbitals

9. Why is the concept of hybridization required in valence bond theory?

Solution

Hybridization is introduced to explain the geometry of bonding orbitals in valance bond theory.

11. Explain why a carbon atom cannot form five bonds using sp^3d hybrid orbitals.

Solution

There are no *d* orbitals in the valence shell of carbon.

13. A molecule with the formula AB_3 could have one of four different shapes. Give the shape and the hybridization of the central A atom for each.

Solution

trigonal planar, sp^2, trigonal pyramidal (one lone pair on A) sp^3, T-shaped (two lone pairs on Asp^3d, or (three lone pair on A) sp^3d^2

15. Sulfuric acid is manufactured by a series of reactions represented by the following equations:

$$S_8(s) + 8O_2(g) \longrightarrow 8SO_2(g)$$

$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$$

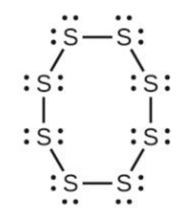
$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(l)$$

Draw a Lewis structure, predict the molecular geometry by VSEPR, and determine the hybridization of sulfur for the following:

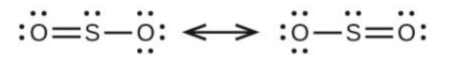
(a) circular S_8 molecule
(b) SO_2 molecule
(c) SO_3 molecule
(d) H_2SO_4 molecule (the hydrogen atoms are bonded to oxygen atoms)

Solution

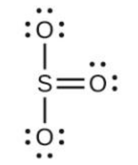
(a) S_8,each S has a bent (109°) geometry, sp^3



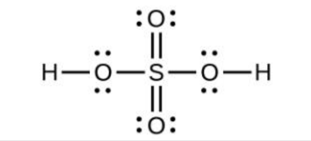
(b) SO_2, bent (120°), sp^2



(c) SO_3, trigonal planar, sp^2



(d) H_2SO_4, tetrahedral, sp^3



17. Analysis of a compound indicates that it contains 77.55% Xe and 22.45% F by mass.
(a) What is the empirical formula of the compound? *(Assume this is also the molecular formula when responding to the remaining parts of this exercise).*
(b) Write a Lewis structure for the compound.
(c) Predict the shape of the molecules of the compound.
(d) What hybridization is consistent with the shape you predicted?

Solution
(a) A 100-g sample contains 77.55 g Xe and 22.45 g F. Divide each mass by the atomic weight to find the number of moles. Then, compare the ratio of moles of the two elements.

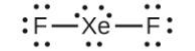
$$\frac{77.55\text{ g}}{131.29\text{ g mol}^{-1}} = 0.5907\text{ mol}$$

$$\frac{22.45\text{ g}}{18.998\text{ g mol}^{-1}} = 1.182\text{ mol}$$

Find the ratio by dividing by the smaller value.

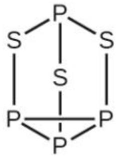
$$\frac{1.182}{0.5907} = 2.001$$

That is, there are two atoms of F for each atom of Xe. Therefore, the empirical formula is XeF_2.
(b) Assuming the empirical formula is also the molecular formula, the Lewis structure is



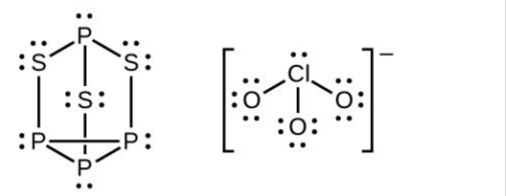
(c) The central Xe atom is surrounded by five electron pairs in a trigonal bipyramid geometry. To minimize the greater repulsion between nonbonded electrons, the three lone pairs occupy the trigonal plane of the molecule, with the two bonding pairs above and below the plane, resulting in a linear geometry for XeF_2.
(d) sp^3d hybridization is consistent with the linear shape.

19. Strike-anywhere matches contain a layer of $KClO_3$ and a layer of P_4S_3. 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. $KClO_3$ contains the ClO_3^- ion. P_4S_3 is an unusual molecule with the skeletal structure.



(a) Write Lewis structures for P_4S_3 and the ClO_3^- 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 P_4S_3 and the ClO_3^- ion.

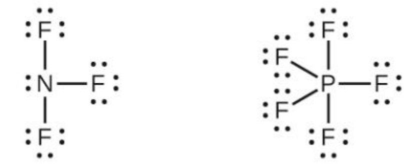
Solution
(a)



(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, sp^3; (d) Oxidation states P +1, S $-1\frac{1}{3}$, Cl +5, O –2.Formal charges: P 0; S 0; Cl +2: O –1

21. Write Lewis structures for NF_3 and PF_5. On the basis of hybrid orbitals, explain the fact that NF_3, PF_3, and PF_5 are stable molecules, but NF_5 does not exist.

Solution



Phosphorus and nitrogen can form sp^3 hybrids to form three bonds and hold one lone pair in PF_3 and NF_3, respectively. However, nitrogen has no valence *d* orbitals, so it cannot form a set of sp^3d hybrid orbitals to bind five fluorine atoms in NF_5. Phosphorus has *d* orbitals and can bind five fluorine atoms with sp^3d hybrid orbitals in PF_5.

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8.3: Multiple Bonds

23. The bond energy of a C–C single bond averages 347 kJ mol^{-1}; that of a $C \equiv C$ triple bond averages 839 kJ mol^{-1}. Explain why the triple bond is not three times as strong as a single bond.

Solution

A triple bond consists of one σ bond and two π bonds. A σ bond is stronger than a π bond due to greater overlap.

25. A useful solvent that will dissolve salts as well as organic compounds is the compound acetonitrile, H_3CCN. It is present in paint strippers.

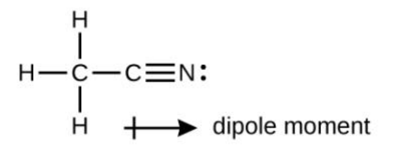
(a) Write the Lewis structure for acetonitrile, and indicate the direction of the dipole moment in the molecule.

(b) Identify the hybrid orbitals used by the carbon atoms in the molecule to form σ bonds.

(c) Describe the atomic orbitals that form the π bonds in the molecule. Note that it is not necessary to hybridize the nitrogen atom.

Solution

(a)



(b) The terminal carbon atom uses sp^3 hybrid orbitals, while the central carbon atom is *sp* hybridized. The terminal carbon atom forms four σ bonds (three to the hydrogen atoms and one to the carbon) while the central carbon forms two σ bond (one to carbon and one to nitrogen). (c) Each of the two πbonds is formed by overlap of a 2*p* orbital on carbon and a nitrogen 2*p* orbital.

27. Identify the hybridization of the central atom in each of the following molecules and ions that contain multiple bonds:

(a) ClNO (N is the central atom)
(b) CS_2
(c) Cl_2CO (C is the central atom)
(d) Cl_2SO (S is the central atom)
(e) SO_2F_2 (S is the central atom)
(f) XeO_2F_2 (Xe is the central atom)
(g) $ClOF_2^+$ (Cl is the central atom)

Solution

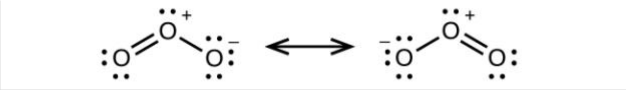
(a) sp^2; (b) sp; (c) sp^2; (d) sp^3; (e) sp^3; (f) sp^3d; (g) sp^3

29. For each of the following molecules, indicate the hybridization requested and whether or not the electrons will be delocalized:

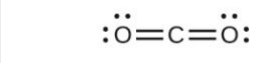
(a) ozone (O_3) central O hybridization
(b) carbon dioxide (CO_2) central C hybridization
(c) nitrogen dioxide (NO_2) central N hybridization
(d) phosphate ion $\left(PO_4^{3-}\right)$ central P hybridization

Solution

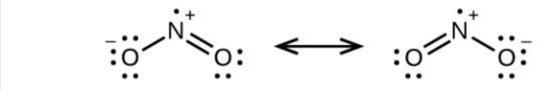
(a) sp^2, delocalized



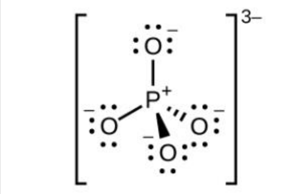
(b) *sp*, localized



(c) sp^2, delocalized

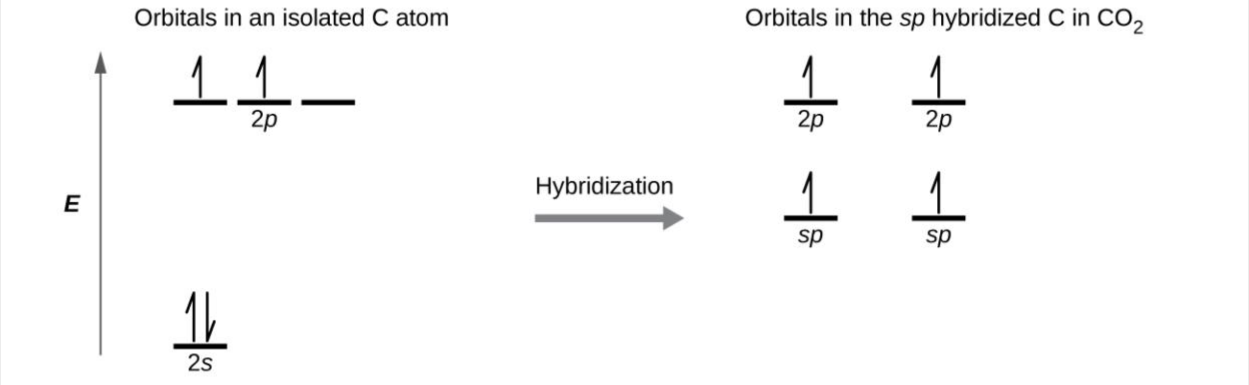


(d) sp^3, delocalized



31. Draw the orbital diagram for carbon in CO_2 showing how many carbon atom electrons are in each orbital.

Solution


Orbitals in an isolated C atom
Orbitals in the *sp* hybridized C in CO_2
E
2*p*
2*s*
Hybridization
2*p*
2*p*
sp
sp

Each of the four electrons is in a separate orbital and overlaps with an electron on an oxygen atom.

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Chemistry 2e
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8.4: Molecular Orbital Theory

33. How are the following similar, and how do they differ?
(a) σ molecular orbitals and π molecular orbitals
(b) ψ for an atomic orbital and ψ for a molecular orbital
(c) bonding orbitals and antibonding orbitals

Solution

(a) Similarities: Both are bonding orbitals that can contain a maximum of two electrons. Differences: σ orbitals are end-to-end combinations of atomic orbitals, whereas π orbitals are formed by side-by-side overlap of orbitals. (b) Similarities: Both are quantum-mechanical constructs that represent the probability of finding the electron about the atom or the molecule. Differences: ψ for an atomic orbital describes the behavior of only one electron at a time based on the atom. For a molecule, ψ represents either a mathematical combination of atomic orbitals. (c) Similarities: Both are orbitals that can contain two electrons. Differences: Bonding orbitals result in holding two or more atoms together. Antibonding orbitals have the effect of destabilizing any bonding that has occurred.

35. Can a molecule with an odd number of electrons ever be diamagnetic? Explain why or why not.

Solution

An odd number of electrons can never be paired, regardless of the arrangement of the molecular orbitals. It will always be paramagnetic.

37. Why are bonding molecular orbitals lower in energy than the parent atomic orbitals?

Solution

Bonding orbitals have electron density in close proximity to more than one nucleus. The interaction between the bonding positively charged nuclei and negatively charged electrons stabilizes the system.

39. Explain why an electron in the bonding molecular orbital in the H_2 molecule has a lower energy than an electron in the 1*s* atomic orbital of either of the separated hydrogen atoms.

Solution

The pairing of the two bonding electrons lowers the energy of the system relative to the energy of the nonbonded electrons.

41. Determine the bond order of each member of the following groups, and determine which member of each group is predicted by the molecular orbital model to have the strongest bond.

(a) H_2, H_2^{+}, H_2^{-}

(b) O_2, O_2^{2+}, O_2^{2-}

(c) Li_2, Be_2^{+}, Be_2

(d) F_2, F_2^{+}, F_2^{-}

(e) N_2, N_2^{+}, N_2^{-}

Solution

The bond order is equal to half the difference between the number of bonding electrons and the number of antibonding electrons. The bond with the greatest bond order is predicted to be the strongest. (a) H_2 bond order = 1, H_2^{+} bond order = 0.5, H_2^{-} bond order = 0.5, strongest bond is H_2; (b) O_2 bond order = 2, O_2^{2+} bond order = 3; O_2^{2-} bond order = 1, strongest bond is O_2^{2+};

(c) Li_2 bond order = 1, Be_2^+ bond order = 0.5, Be_2 bond order = 0, strongest bond is Li_2; (d) F_2 bond order = 1, F_2^+ bond order = 1.5, F_2^- bond order = 0.5, strongest bond is F_2^+; (e) N_2 bond order = 3, N_2^+ bond order = 2.5, N_2^- bond order = 2.5, strongest bond is N_2.

43. Compare the atomic and molecular orbital diagrams to identify the member of each of the following pairs that has the highest first ionization energy (the most tightly bound electron) in the gas phase:

(a) H and H_2
(b) N and N_2
(c) O and O_2
(d) C and C_2
(e) B and B_2

Solution

(a) H_2; (b) N_2; (c) O; (d) C_2; (e) B_2

45. A friend tells you that the 2*s* orbital for fluorine starts off at a much lower energy than the 2*s* orbital for lithium, so the resulting σ_{2s}molecular orbital in F_2 is more stable than in Li_2. Do you agree?

Solution

Yes, fluorine is a smaller atom than Li, so atoms in the 2*s* orbital are closer to the nucleus and more stable.

47. What charge would be needed on F_2 to generate an ion with a bond order of 2?

Solution

2+

49. Explain why N_2^{2+} is diamagnetic, while O_2^{4+}, which has the same number of valence electrons, is paramagnetic.

Solution

N_2 has s-p mixing, so the π orbitals are the last filled in N_2^{2+}. O_2 does not have s-p mixing, so the σ_p orbital fills before the π orbitals.

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8.4: Molecular Orbital Theory

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