CH 221 Chapter Five Concept Guide

According to **valence bond theory**, the s and p orbitals of any atom give a maximum of four hybrid orbitals. Atoms of second-period elements, which have only s and p orbitals, may form up to four hybrid orbitals and no more than four covalent bonds around the central atom. Atoms of the elements in the third and higher periods can form a larger number of covalent bonds by involving d orbitals in hybridization. For sp^3d hybridization, the number of hybrid orbitals is 5 and the electronic geometry is trigonal bipyramidal. For sp^3d^2 hybridization, there are 6 hybrid orbitals and the electronic geometry is octahedral.

1. Valence Bond Theory

Problem

Describe the bonding in BrF_3 in terms of valence bond theory.

Solution

The Lewis structure shows that 3 single bonds and two lone pairs surround the bromine atom:

Five equivalent hybridized orbitals on the bromine atom are necessary. The outer electron configuration for the bromine atom is: $4s^2 4p^5$. By using the 4s orbital, 3 4p orbitals, and one of the empty 4d orbitals in sp^3d hybridization, five hybrid orbitals can be formed. Two of the hybrid orbitals contain lone pairs of electrons. The other hybrid orbitals contain single electrons, which will form single bonds with the fluorine atoms.

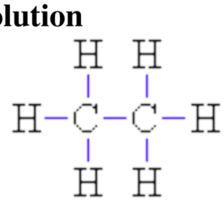
The five hybridized orbitals will be arranged in the shape of a trigonal bipyramid.

2. Valence Bond Theory

Problem

Describe the bonding in C_2H_6 in terms of valence bond theory.

Solution



Each carbon atom must have four equivalent hybridized orbitals that are formed by sp^3 hybridization. Three of these orbitals on each carbon atom contain a single electron that will form a single bond with a hydrogen atom. The fourth orbital contains a single electron that will form a single bond with the other carbon atom.

3. Valence Bond Theory

Problem
Describe the bonding in H_2O_2 in terms of valence bond theory.

Solution

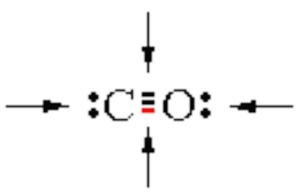
Each oxygen has four equivalent hybrid orbitals formed by sp^3 hybridization. Two of these orbitals contain lone pairs of electrons, one contains a single electron that forms a single bond with a hydrogen atom, and one contains a single electron that will form a single bond with the other oxygen atom.

4. Multiple Bonds

Problem
Describe the bonding in carbon monoxide, CO, using hybrid orbital theory.

Solution
The Lewis structure depicts C and O being bonded by a triple bond and each having a single lone pair.
C O

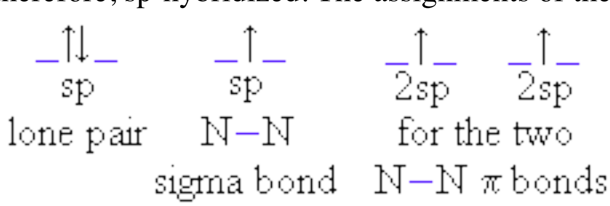
Each atom has a half-filled sp hybrid orbital it uses for sigma bond formation. Each atom also has a sp hybrid orbital that contains a lone electron pair. In addition, two pairs of electrons occur in unhybridized p orbitals and are used to form two π bonds.



5. Multiple Bonds

Problem
Describe the bonding in a nitrogen molecule, N_2, using hybrid orbital theory.

Solution
The bonding in a nitrogen molecule is identical to that in CO, except that both atoms are nitrogen: there is one sigma bond, two π bonds, and one lone pair on each atom. Each N has linear electron-pair geometry and is, therefore, sp-hybridized. The assignments of the five valence electrons on each N and their roles in bonding are:



6. Multiple Bonds

Problem

Describe the hybridization of both carbon atoms and of the nitrogen atom in acetonitrile:

CH_3-C≡N

Solution

The CH_3 carbon has tetrahedral electron-pair geometry, and is, therefore, sp^3 hybridized. The CN carbon has linear electron-pair geometry and is, therefore, sp-hybridized. Last, the N atom has linear electron-pair geometry and is sp-hybridized. Two unhybridized orbitals on the central carbon and two on the nitrogen are used to form two π bonds.

7. Molecular Orbitals and Bond Order

Question

Write the electron configuration of the H_2^- ion in molecular orbital terms. What is the bond order of this ion?

Solution

This molecular ion has three electrons: one from each H atom and one due to the negative charge. Its configuration, therefore, is $(\sigma_{1s})^2\ (\sigma^*_{1s})^1$.

H_2^- has a net bond order of $^1/_2$ and the ion is predicted to exist under special circumstances:

$^1/_2$(2 bonding electrons - 1 antibonding electron) = $^1/_2$

8. Molecular Orbitals and Bond Order

Question

Write the configuration of the H_2^+ ion in molecular orbital terms. Compare the bond order of this ion to He_2^+ and H_2^-. Do you expect H_2^+ to exist?

Solution

The molecular orbital configuration for H_2^+ is $(\sigma_{1s})^1$. This ion has a bond order of $^1/_2$, as do He_2^+ and H_2^-:

$^1/_2$(2 bonding electrons - 1 antibonding electron) = $^1/_2$

H_2^+, therefore, is expected to exist.

9. Molecular Orbitals in Diatomic Molecules

Question

Knowing that Be_2 does not exist, describe the electron configuration in molecular orbital terms for Be_2^+ and give its net bond order. Do you expect Be_2^+ to exist?

Solution

The Be_2^+ molecular ion has seven electrons. Four of the seven electrons are core electrons, and are assigned to σ_{1s} and σ_{1s}^* molecular orbitals. The remaining three electrons are assigned to the σ_{2s} and σ_{2s}^* orbitals. The molecular orbital configuration is:

[core electrons] $(\sigma_{2s})^2\ (\sigma_{2s}^*)^1$

The net bond order is: $^1/_2$(2 bonding electrons - 1 antibonding electron) = $^1/_2$

Be_2^+ has a net bond order of $^1/_2$, thus it is expected to exist.