Sample Exercise 9.1 Using the VSPER Model

Use the VSEPR model to predict the molecular geometry of (a) O_3, (b) $SnCl_3^-$.

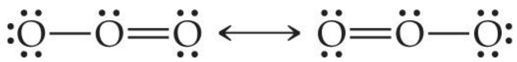
Solution

Analyze We are given the molecular formulas of a molecule and a polyatomic ion, both conforming to the general formula AB_n and both having a central atom from the *p* block of the periodic table.

Plan To predict the molecular geometries, we draw their Lewis structures and count electron domains around the central atom to get the electron-domain geometry. We then obtain the molecular geometry from the arrangement of the domains that are due to bonds.

Solve

(a) We can draw two resonance structures for O_3:

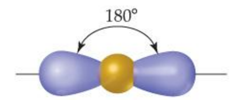
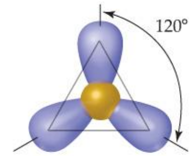
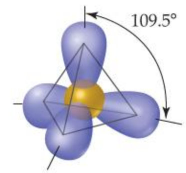
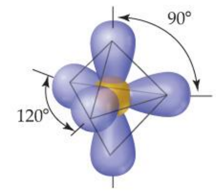
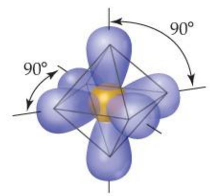


Sample Exercise 9.1 Using the VSPER Model

Continued

Because of resonance, the bonds between the central O atom and the outer O atoms are of equal length. In both resonance structures the central O atom is bonded to the two outer O atoms and has One nonbonding pair. Thus, there are three electron domains about the central O atoms. (Remember that a double bond counts as a single Electron domain.) The arrangement of three electron domains is trigonal planar (Table 9.1).

TABLE 9.1 • Electron-Domain Geometries as a Function of Number of Electron Domains

Number of Electron Domains	Arrangement of Electron Domains	Electron-Domain Geometry	Predicted Bond Angles
2		Linear	180°
3		Trigonal planar	120°
4		Tetrahedral	109.5°
5		Trigonal bipyramidal	120° 90°
6		Octahedral	90°

Sample Exercise 9.1 Using the VSPER Model

Continued

Two of the domains are from bonds, and one is due to a nonbonding pair. So, the molecule has a bent shape with an ideal bond angle of 120° (Table 9.2).

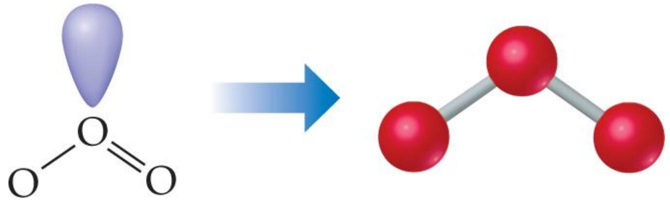


TABLE 9.2 • Electron-Domain and Molecular Geometries for Two, Three, and Four Electron Domains around a Central Atom

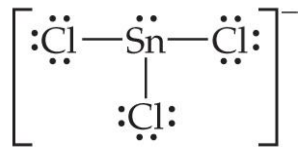
Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
2	Linear	2	0	Linear	$\ddot{O}{=}C{=}\ddot{O}$
3	Trigonal planar	3	0	Trigonal planar	F, B, F, F
		2	1	Bent	[O N O]$^-$
4	Tetrahedral	4	0	Tetrahedral	H, C, H, H, H
		3	1	Trigonal pyramidal	H, N, H, H
		2	2	Bent	H, O, H

Sample Exercise 9.1 Using the VSPER Model

Continued

Comment As this example illustrates, when a molecule exhibits resonance, any one of the resonance structures can be used to predict the molecular geometry.

(b) The Lewis structure for $SnCl_3$ is



The central Sn atom is bonded to the three Cl atoms and has one nonbonding pair; thus, we have four electron domains, meaning tetrahedral electron-domain geometry (Table 9.1) with one vertex occupied

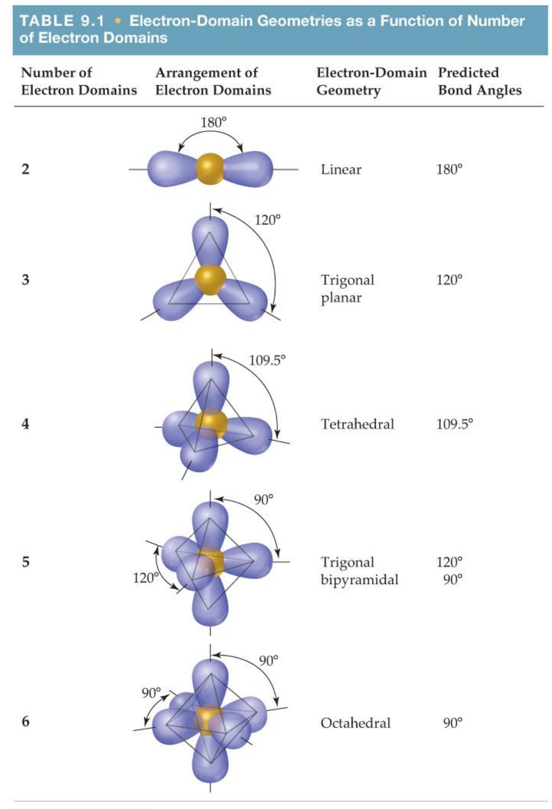


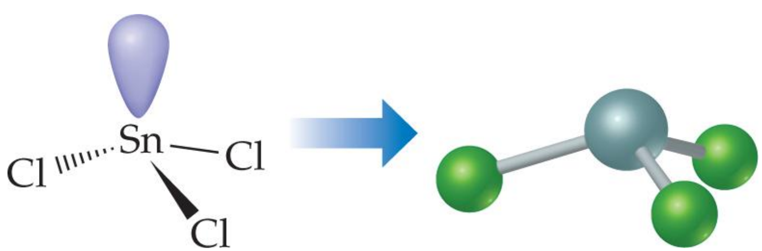
TABLE 9.1 • Electron-Domain Geometries as a Function of Number of Electron Domains

Number of Electron Domains	Arrangement of Electron Domains	Electron-Domain Geometry	Predicted Bond Angles
2	180°	Linear	180°
3	120°	Trigonal planar	120°
4	109.5°	Tetrahedral	109.5°
5	90°, 120°	Trigonal bipyramidal	120° 90°
6	90°, 90°	Octahedral	90°

Sample Exercise 9.1 Using the VSPER Model

Continued

by a nonbonding pair of electrons. Tetrahedral electron domain geometry with three bonding and one nonbonding domains means the molecular geometry is trigonal pyramidal (Table 9.2).



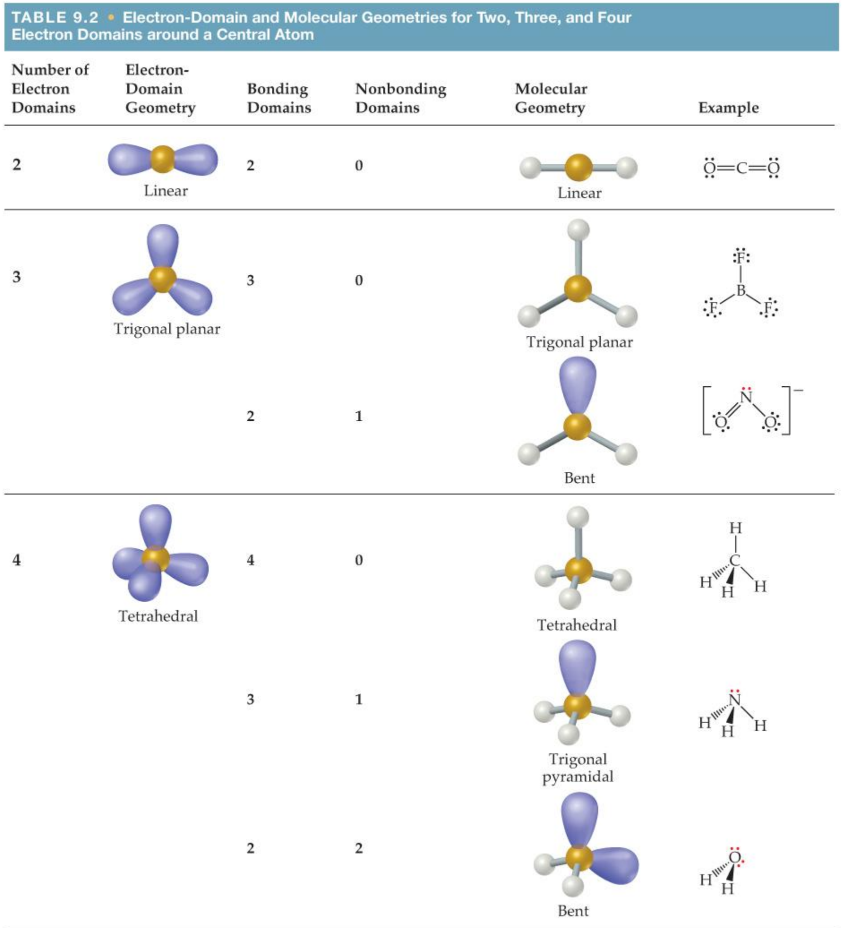


TABLE 9.2 • Electron-Domain and Molecular Geometries for Two, Three, and Four Electron Domains around a Central Atom

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
2	Linear	2	0	Linear	O=C=O
3	Trigonal planar	3	0	Trigonal planar	BF_3
		2	1	Bent	$[NO_2]^-$
4	Tetrahedral	4	0	Tetrahedral	CH_4
		3	1	Trigonal pyramidal	NH_3
		2	2	Bent	H_2O

Practice Exercise

Predict the electron-domain and molecular geometries for (a) $SeCl_2$, (b) CO_3^{2-} .

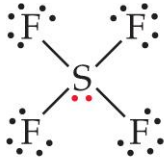
Answers: (a) tetrahedral, bent; (b) trigonal planar, trigonal planar

Sample Exercise 9.2 Molecular Geometries of Molecules with Expanded Valence Shells

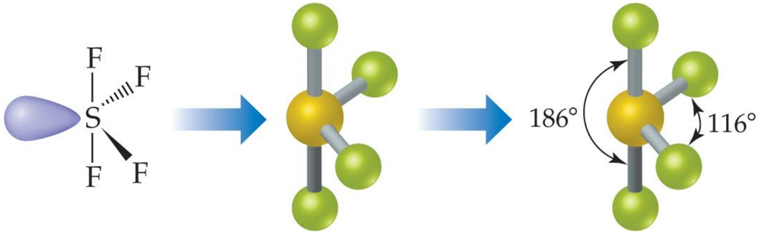
Use the VSEPR model to predict the molecular geometry of (a) SF_4, (b) IF_5.

Solution

Analyze The molecules are of the ABn type with a central p-block atom.
Plan We first draw Lewis structures and then use the VSEPR model to determine the electron-domain geometry and molecular geometry.
Solve (a) The Lewis structure for SF_4 is



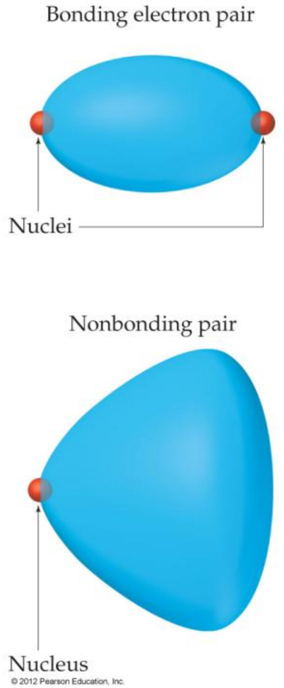
The sulfur has five electron domains around it: four from the S—F bonds and one from the nonbonding pair. Each domain points toward a vertex of a trigonal bipyramid. The domain from the nonbonding pair will point toward an equatorial position. The four bonds point toward the remaining four positions, resulting in a molecular geometry that is described as see-sawshaped:



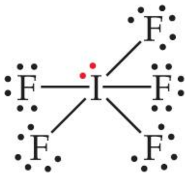
Sample Exercise 9.2 Molecular Geometries of Molecules with Expanded Valence Shells

Use the VSEPR model to predict the molecular geometry of (a) SF_4, (b) IF_5.

Comment The experimentally observed structure is shown on the right. We can infer that the nonbonding electron domain occupies an equatorial position, as predicted. The axial and equatorial S—F bonds are slightly bent away from the nonbonding domain, suggesting that the bonding domains are "pushed" by the nonbonding domain, which exerts a greater repulsion (Figure 9.7).



(b) The Lewis structure of IF_5 is



Sample Exercise 9.2 Molecular Geometries of Molecules with Expanded Valence Shells

Continued

The iodine has six electron domains around it, one of which is nonbonding. The electron-domain geometry is therefore octahedral, with one position occupied by the nonbonding pair, and the molecular geometry is square pyramidal (Table 9.3):

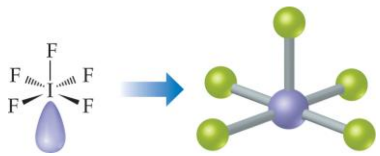


TABLE 9.3 • Electron-Domain and Molecular Geometries for Five and Six Electron Domains around a Central Atom

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
5	Trigonal bipyramidal	5	0	Trigonal bipyramidal	PCl_5
		4	1	Seesaw	SF_4
		3	2	T-shaped	ClF_3
		2	3	Linear	XeF_2
6	Octahedral	6	0	Octahedral	SF_6
		5	1	Square pyramidal	BrF_5
		4	2	Square planar	XeF_4

Comment Because the nonbonding domain is larger than the bonding domains, we predict that the four F atoms in the base of the pyramid will be tipped up slightly toward the top F atom. Experimentally, we find that the angle between the base atoms and top F atom is 82°, smaller than the ideal 90° angle of an octahedron.

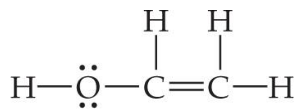
Practice Exercise

Predict the electron-domain and molecular geometries of (a) BrF_3, (b) ICl_4^-.

Answers: (a) trigonal bipyramidal, T-shaped; (b) octahedral, square planar

Sample Exercise 9.3 Predicting Bond Angles

Eyedrops for dry eyes usually contain a water-soluble polymer called *poly(vinyl alcohol)*, which is based on the unstable organic molecule *vinyl alcohol*:



Predict the approximate values for the H — O — C and O — C — C bond angles in vinyl alcohol.

Solution

Analyze We are given a Lewis structure and asked to determine two bond angles.

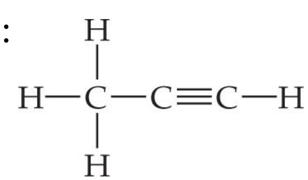
Plan To predict a bond angle,we determine the number of electron domains surrounding the middle atom in the bond. The ideal angle corresponds to the electron-domain geometry around the atom. The angle will be compressed somewhat by nonbonding electrons or multiple bonds.

Solve In H — O — C , the O atom has four electron domains (two bonding, two nonbonding). The electron-domain geometry around O is therefore tetrahedral, which gives an ideal angle of 109.5° . The H — O — C angle is compressed somewhat by the nonbonding pairs, so we expect this angle to be slightly less than 109.5° .

To predict the O — C — C bond angle, we examine the middle atom in the angle. In the molecule, there are three atoms bonded to this C atom and no nonbonding pairs, and so it has three electron domains about it. The predicted electron-domain geometry is trigonal planar, resulting in an ideal bond angle of 120° . Because of the larger size of the C = C domain, the bond angle should be slightly greater than 120° .

Practice Exercise

Predict the H — C — H and C — C — C bond angles in *propyne*:



Answers: 109.5° , 180°

Sample Exercise 9.4 Polarity of Molecules

Predict whether these molecules are polar or nonpolar: (a) BrCl, (b) SO_2, (c) SF_6.

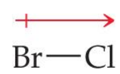
Solution

Analyze We are given three molecular formulas and asked to predict whether the molecules are polar.

Plan A molecule containing only two atoms is polar if the atoms differ in electronegativity. The polarity of a molecule containing three or more atoms depends on both the molecular geometry and the individual bond polarities. Thus, we must draw a Lewis structure for each molecule containing three or more atoms and determine its molecular geometry.We then use electronegativity values to determine the direction of the bond dipoles. Finally, we see whether the bond dipoles cancel to give a nonpolar molecule or reinforce each other to give a polar one.

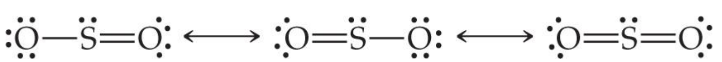
Solve

(a) Chlorine is more electronegative than bromine. All diatomic molecules with polar bonds are polar molecules. Consequently, BrCl is polar, with chlorine carrying the partial negative charge:

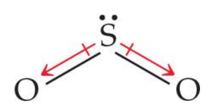


The measured dipole moment of BrCl is $\mu = 0.57$ D.

(b) Because oxygen is more electronegative than sulfur, SO2 has polar bonds. Three resonance forms can be written:



For each of these, the VSEPR model predicts a bent molecular geometry. Because the molecule is bent, the bond dipoles do not cancel, and the molecule is polar:

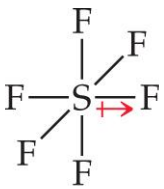


Sample Exercise 9.4 Polarity of Molecules

Continued

Experimentally, the dipole moment of SO_2 is μ = 1.63 D.

(c) Fluorine is more electronegative than sulfur, so the bond dipoles point toward fluorine. For clarity, only one S — F dipole is shown. The six S — F bonds are arranged octahedrally around the central sulfur:



Because the octahedral molecular geometry is symmetrical, the bond dipoles cancel, and the molecule is nonpolar, meaning that μ = 0.

Practice Exercise

Determine whether the following molecules are polar or nonpolar: (a) NF_3, (b) BCl_3.
Answers: (a) polar because polar bonds are arranged in a trigonal-pyramidal geometry, (b) nonpolar because polar bonds are arranged in a trigonal-planar geometry

Sample Exercise 9.5 Hybridization

Indicate the orbital hybridization around the central atom in NH_2^-.

Solution

Analyze We are given the chemical formula for a polyatomic anion and asked to describe the type of hybrid orbitals surrounding the central atom.

Plan To determine the central atom hybrid orbitals, we must know the electron-domain geometry around the atom. Thus, we draw the Lewis structure to determine the number of electron domains around the central atom. The hybridization conforms to the number and geometry of electron domains around the central atom as predicted by the VSEPR model.

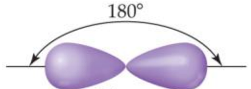
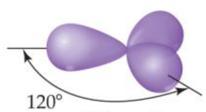
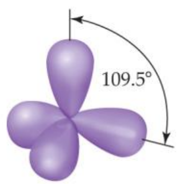
Solve The Lewis structure is

Sample Exercise 9.5 Hybridization

Indicate the orbital hybridization around the central atom in NH_2^-.

Because there are four electron domains around N, the electron-domain geometry is tetrahedral. The hybridization that gives a tetrahedral electron-domain geometry is sp^3 (Table 9.4). Two of the sp^3 hybrid orbitals contain nonbonding pairs of electrons, and the other two are used to make bonds with the hydrogen atoms.

TABLE 9.4 • Geometric Arrangements Characteristic of Hybrid Orbital Sets

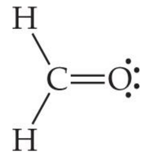
Atomic Orbital Set	Hybrid Orbital Set	Geometry	Examples
s,p	Two *sp*	180°  Linear	BeF_2, $HgCl_2$
s,p,p	Three sp^2	 120° Trigonal planar	BF_3, SO_3
s,p,p,p	Four sp^3	 109.5° Tetrahedral	CH_4, NH_3, H_2O, NH_4^+

Practice Exercise

Predict the electron-domain geometry and hybridization of the central atom in SO_3^{2-}.
Answer: tetrahedral, sp^3

Sample Exercise 9.6 Describing σ and π Bonds in a Molecule

Formaldehyde has the Lewis structure



Describe how the bonds in formaldehyde are formed in terms of overlaps of hybrid and unhybridized oribitals.

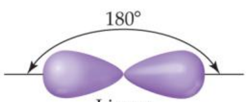
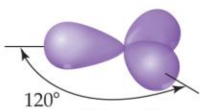
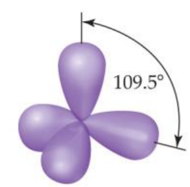
Solution

Analyze We are asked to describe the bonding in formaldehyde in terms of hybrid orbitals.

Plan Single bonds σ are bonds, and double bonds consist of one π bond and one π bond. The ways in which these bonds form can be deduced from the molecular geometry, which we predict using the VSEPR model.

Solve The C atom has three electron domains around it, which suggests a trigonal-planar geometry with bond angles of about 120° . This geometry implies sp^2 hybrid orbitals on C (Table 9.4). These hybrids are used to make the two C — H and one C — O bonds to C. There remains an unhybridized 2*p* orbital on carbon, perpendicular to the plane of the three sp^2 hybrids.

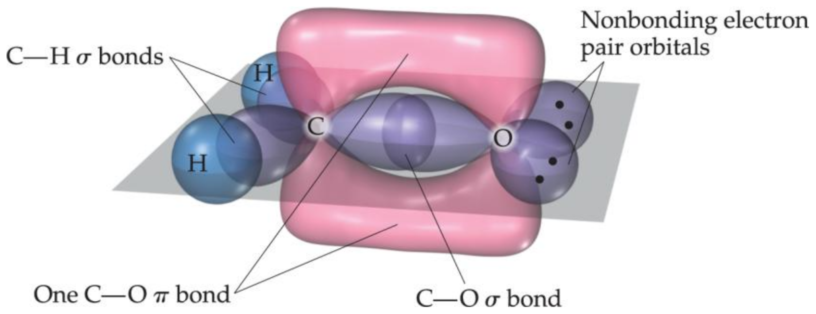
TABLE 9.4 • Geometric Arrangements Characteristic of Hybrid Orbital Sets

Atomic Orbital Set	Hybrid Orbital Set	Geometry	Examples
s,p	Two *sp*	 Linear	BeF_2, $HgCl_2$
s,p,p	Three sp^2	 Trigonal planar	BF_3, SO_3
s,p,p,p	Four sp^3	 Tetrahedral	CH_4, NH_3, H_2O, NH_4^+

Sample Exercise 9.6 Describing σ and π Bonds in a Molecule

Continued

The O atom also has three electron domains around it, and so we assume it has sp^2 hybridization as well. One of these hybrid orbitals participates in the C — O σ bond, while the other two hold the two nonbonding electron pairs of the O atom. Like the C atom, therefore, the O atom has an unhybridized 2*p* orbital that is perpendicular to the plane of the molecule. These two orbitals overlap to form a C — O π bond (Figure 9.25)

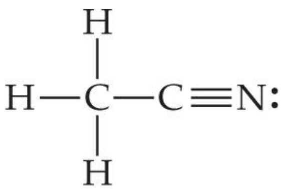


Sample Exercise 9.6 Describing σ and π Bonds in a Molecule

Continued

Practice Exercise

(a) Predict the bond angles around each carbon atom in acetonitrile:



(b) Describe the hybridization at each carbon atom, and (c) determine the number of σ and π bonds in the molecule.

Answers: (a) approximately 109° around the left C and 180° around the right C; (b) sp^3, sp; (c) five σ bonds and two π bonds

Sample Exercise 9.7 Delocalized Bonding

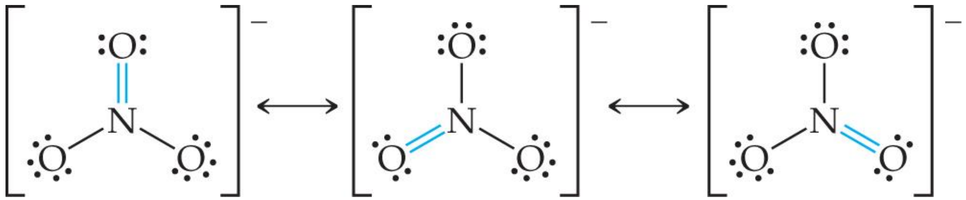
Describe the bonding in the nitrate ion, NO_3^-. Does this ion have delocalized π bonds?

Solution

Analyze Given the chemical formula for a polyatomic anion, we are asked to describe the bonding and determine whether the ion has delocalized π bonds.

Plan Our first step is to draw Lewis structures. Multiple resonance structures involving the placement of the double bonds in different locations suggest that the π component of the double bonds is delocalized.

Solve In Section 8.6 we saw that NO_3^- has three resonance structures:

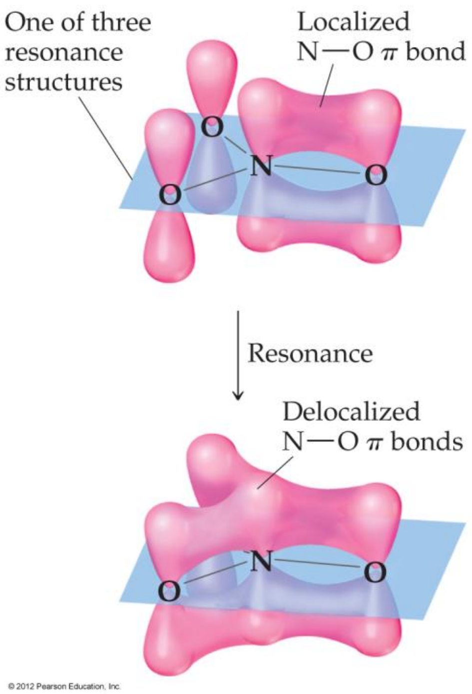


In each structure, the electron-domain geometry at nitrogen is trigonal planar, which implies *sp*^{2} hybridization of the N atom. The *sp*^{2} hybrid orbitals are used to construct the three N — O σ bonds present in each resonance structure.

Sample Exercise 9.7 Delocalized Bonding

Continued

The unhybridized 2*p* orbital on the N atom can be used to make π bonds. For any one of the three resonance structures shown, we might imagine a single localized N — O π bond formed by the overlap of the unhybridized 2*p* orbital on N and a 2*p* orbital on one of the O atoms, as shown in Figure 9.28. Because each resonance structure contributes equally to the observed structure of NO_3–however, we represent the π bonding as delocalized over the N — O three bonds, as shown in the figure.



Practice Exercise

Which of these species have delocalized bonding: SO_3, SO_3^{2-} ,H_2CO, O_3, NH_4^+?

Answer: SO_3 and O_3, as indicated by the presence of two or more resonance structures involving π bonding for each of these molecules

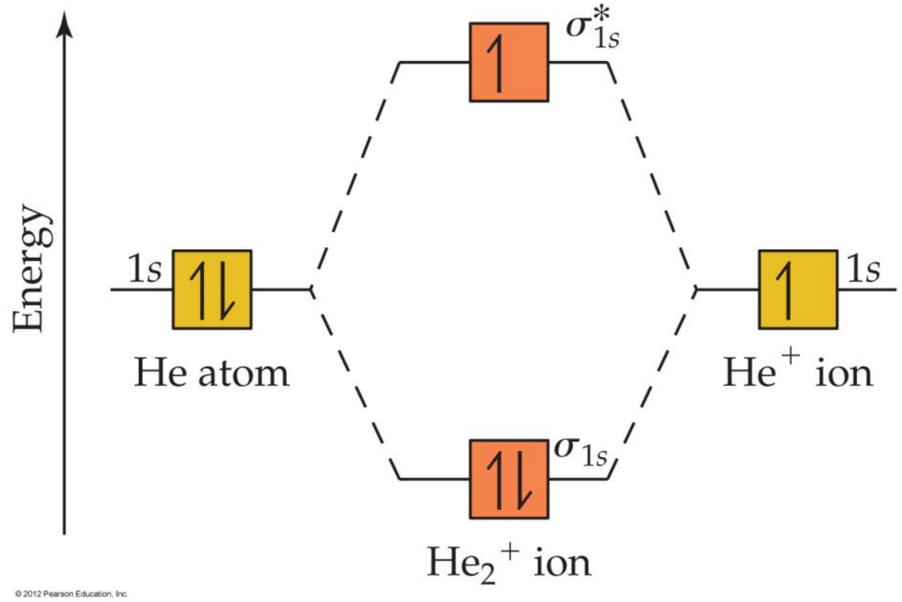
Sample Exercise 9.8 Bond Order

What is the bond order of the He_2^+ ion? Would you expect this ion to be stable relative to the separated He atom and He^+ ion?

Solution

Analyze We will determine the bond order for the He_2^+ ion and use it to predict whether the ion is stable.

Plan To determine the bond order, we must determine the number of electrons in the molecule and how these electrons populate the available MOs. The valence electrons of He are in the 1*s* orbital, and the 1*s* orbitals combine to give an MO diagram like that for H_2 or He_2 (Figure 9.33). If the bond order is greater than 0, we expect a bond to exist, and the ion is stable.



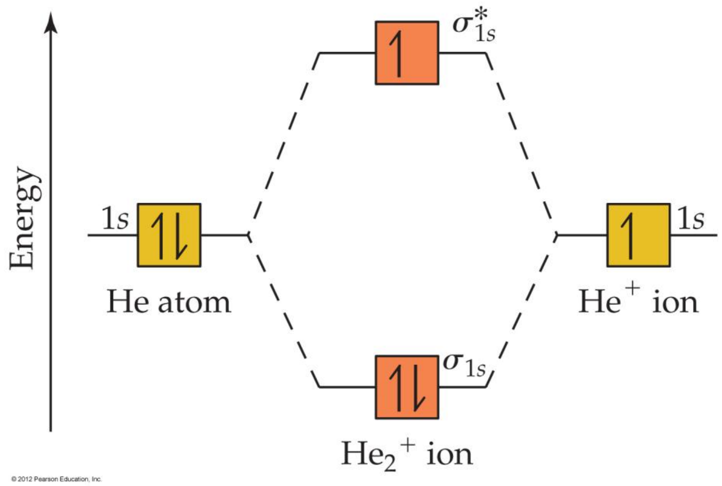
Sample Exercise 9.8 Bond Order

Continued

Solve The energy-level diagram for the He_2^+ ion is shown in Figure 9.34. This ion has three electrons. Two are placed in the bonding orbital and the third in the antibonding orbital. Thus, the bond order is

$$\text{Bond order} = \frac{1}{2}(2 - 1) = \frac{1}{2}$$

Because the bond order is greater than 0, we predict the He_2^+ ion to be stable relative to the separated He and the He^+. Formation of He_2^+ in the gas phase has been demonstrated in laboratory experiments.



Practice Exercise

Determine the bond order of the H_2^- ion.
Answer: $\frac{1}{2}$

Sample Exercise 9.9 Molecular Orbitals of a Period 2 Diatomic Ion

For the O_2^+ ion, predict (a) number of unpaired electrons, (b) bond order, (c) bond enthalpy and bond length.

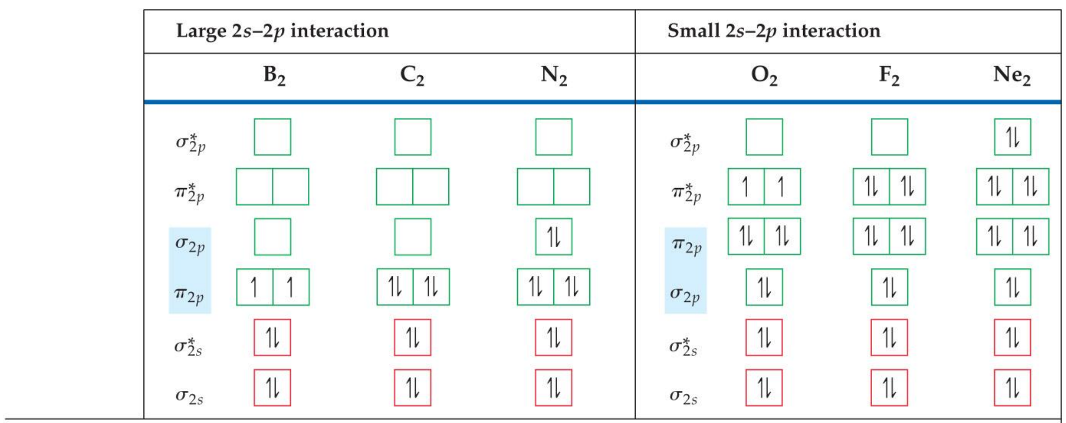
Solution

Analyze Our task is to predict several properties of the cation O_2^+.

Plan We will use the MO description of O_2^+ to determine the desired properties. We must first determine the number of electrons in O_2^+ and then draw its MO energy diagram. The unpaired electrons are those without a partner of opposite spin. The bond order is one-half the difference between the number of bonding and antibonding electrons. After calculating the bond order, we can use Figure 9.43 to estimate the bond enthalpy and bond length.

Solve

(a) The O_2^+ ion has 11 valence electrons, one fewer than O_2. The electron removed from O_2 to form O_2^+ is one of the two unpaired π^*_{2p} electrons (Figure 9.43). Therefore, O_2^+ has one unpaired electron.



	B_2	C_2	N_2	O_2	F_2	Ne_2
Bond order	1	2	3	2	1	0
Bond enthalpy (kJ/mol)	290	620	941	495	155	—
Bond length (Å)	1.59	1.31	1.10	1.21	1.43	—
Magnetic behavior	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic	—

Sample Exercise 9.9 Molecular Orbitals of a Period 2 Diatomic Ion

Continued

(b) The molecule has eight bonding electrons (the same as O_2) and three antibonding electrons (one fewer than O_2). Thus, its bond order is

$$\frac{1}{2}(8 - 3) = 2\frac{1}{2}$$

(c) The bond order of O_2^+ is between that for O_2 (bond order 2) and N_2 (bond order 3). Thus, the bond enthalpy and bond length should be about midway between those for O_2 and N_2, approximately 700 kJ/mol and 1.15 Å. (The experimentally measured values are and 1.123 Å.)

Practice Exercise

Predict the magnetic properties and bond orders of (a) the peroxide ion, O_2^{2-} (b) the acetylide ion, C_2^{2-} .
Answers: (a) diamagnetic, 1; (b) diamagnetic, 3