
Polyatomic molecules

Answers to worked examples

WE 5.1 Formal charges in N₂O (on p. 221 in *Chemistry*³)

Use formal charges to decide whether oxygen difluoride adopts a structure with a central oxygen atom (FOF) or a central fluorine atom (FFO).

Strategy

Use Equation 5.1 (p.220) to determine the formal charges for the atoms in both structures. The structure with the lower formal charges will be the one adopted.

Solution

The formal charges on the atoms in the two structures are shown below. The structure in (a) has the lower formal charges so this structure is favoured.

	$\begin{array}{c} \text{:}\ddot{\text{F}}\text{---}\ddot{\text{O}}\text{---}\ddot{\text{F}}\text{:} \\ \text{a} \end{array}$	$\begin{array}{c} \text{:}\ddot{\text{F}}\text{---}\ddot{\text{F}}\text{---}\ddot{\text{O}}\text{:} \\ \text{b} \end{array}$
Number of electrons in the valence shell of a free atom	7 6 7	7 7 6
– Number of bonds to the atom	– 1 – 2 – 1	– 1 – 2 – 1
– Number of unshared electrons	– 6 – 4 – 6	– 6 – 4 – 6
Formal charges	0 0 0	0 +1 –1

WE 5.2 The shape of water molecules (on p. 225 in *Chemistry*³)

What is the shape of SiF₄ ?

Strategy

Using VSEPR theory, work out the number of electron pairs around the central silicon atom and use Figure 5.7 (p.223) to work out the shape that the molecule is based on. Next, determine how many of those electron pairs are involved in bonds and how many are lone pairs.

Solution

In SiF₄ there are four electrons from the central silicon atom and one each from the four fluorine atoms. This gives a total of eight electrons, so four electron pairs around the Si atom. All of the electron pairs are bonding pairs, so the shape of SiF₄ is tetrahedral (see Figure 5.7).

WE 5.3 Using VSEPR theory with ions (on p. 226 in *Chemistry*³)

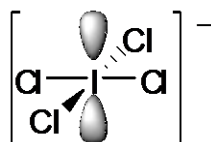
What shape is the ICl₄⁻ ion based on? Decide the position(s) you would expect any lone pairs to occupy, and thus predict the shape of ICl₄⁻.

Strategy

Use VSEPR theory to work out the number of electron pairs around the central iodine atom remembering to add an electron for the negative charge. Then determine how many of those electrons are bond pairs and how many are lone pairs. Consider interactions at 90° angles to work out the best place to locate the more spatially demanding lone pairs.

Solution

In ICl₄⁻ there are seven electrons from the iodine atom, one each from the four chlorine atoms and one from the charge (formal charge on I = -1). This gives a total of twelve electrons around the I atom, so six electron pairs. The shape of ICl₄⁻ is based on an octahedron. There are four bonding pairs and two lone pairs present. The lone pairs are placed opposite each other to avoid positioning the lone pairs at 90° to each other. The shape of the ICl₄⁻ ion is therefore square planar.



WE 5.4 The nitrate ion (on p. 232 in *Chemistry*³)

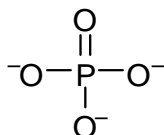
Use VSEPR theory to predict the shape of the phosphate ion (PO_4^{3-}).

Strategy

Draw a Lewis structure for the ion using a combination of single and double bonds. Count up the electrons around the central phosphorus (remember to include the charge on the phosphorus if there is one). Determine the number of electrons pairs and whether they are σ or π electrons (remembering that only the former have an effect on the shape).

Solution

There are five electrons on the central phosphorus atom, two from the double-bonded oxygen atom and one from each of the three singly-bonded oxygen atoms.



This gives a total of ten electrons around P, so five electron pairs. Of these, one is a π -pair and does not contribute to the shape. This leaves four electron pairs, all of which are bonding pairs, so the phosphate ion is tetrahedral. You might expect the tetrahedron to be distorted, with the double bond taking up more space. In reality, the four oxygen atoms are equivalent, and the structure is just one of several equivalent resonance forms (see Section 5.5, p.243).

WE 5.5 Bonding in BeH_2 (on p. 242 in *Chemistry*³)

How does valence bond theory describe the bonding in the trigonal planar molecule BH_3 ?

Strategy

Determine the shape of the BH_3 molecule using VSEPR theory and from this deduce the type of hybridization that is present. Interact the beryllium hybrid orbitals with the hydrogen $1s$ to give the bonding orbitals in BH_3 .

Solution

Using VSEPR theory, BH_3 has six electrons around the central B atom so the shape of the molecule is trigonal planar. The central boron atom is sp^2 hybridized. B has the electronic configuration $1s^2 2s^2 2p^1$, so has three valence electrons, one in each hybrid

orbital. Each of these hybrid orbitals interacts with a H 1s orbital to form a σ -bonding orbital which contains two electrons, one from each atom. The p_z orbital on the boron atom is unhybridized and empty.

WE 5.6 Resonance in the SO_3^{2-} ion (on p. 244 in *Chemistry*³)

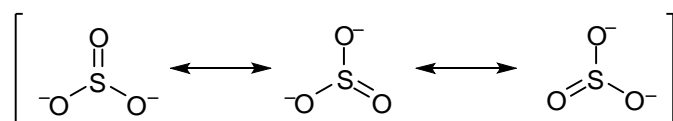
The three bonds in the sulfite ion (sulfate(IV), SO_3^{2-}) are all identical. Draw out the resonance forms for sulfite and determine the average S–O bond order and the average charge on each oxygen atom.

Strategy

Draw a simple Lewis structure of the sulfite ion with two S–O single bonds to negatively charged oxygen atoms and one S=O double bond to a neutral oxygen atom. Draw resonance forms to show that the three bonds are equivalent.

Solution

There are three resonance forms for SO_3^{2-} .



Each S–O bond has a bond order of 1 in two resonance forms, and of 2 in one resonance form. The average bond order is therefore $\frac{1+1+2}{3} = 1\frac{1}{3}$. Each oxygen atom is neutral in one of the resonance forms but carries a -1 charge in the other two. This gives each oxygen atom an average charge of $-\frac{2}{3}$.

Answers to boxes

Box 5.2 N_2O : from laughing gas to dragsters (on p. 221 in *Chemistry*³)

Calculate the percentage by mass of oxygen in N_2O . How does this compare to the percentage of oxygen in air?

Strategy

The air consists of roughly 79% nitrogen and 21% oxygen. Use the relative atomic mass of the nitrogen and oxygen to calculate the percentage of oxygen in N₂O.

Solution

N₂O has a relative molecular mass of 44.013. It contains $\frac{15.999}{44.013} \times 100 = 36.4\%$

oxygen by mass, which is greater than the percentage in air.

Box 5.3 The fluorinating ability of ClF₃ (on p. 229 in *Chemistry*³)

As shown in Figure 5.16, the bond angles for ClF₃ are less than 90°. Explain why the molecule is distorted from a regular geometry in this manner.

Strategy

Use VSEPR theory to calculate the shape of ClF₃ as shown in Section 5.2 (p.223), noting the positions of the lone pairs. Consider the effect that the more spatially demanding lone pairs have on the structure of the trigonal bipyramid.

Solution

ClF₃ is based on the trigonal bipyramid with two lone pairs and three bond pairs. The lone pairs go in the trigonal plane to minimise repulsions. The bond angles in ClF₃ would be expected to be less than 90°. (The actual value is 87.5°.) This reduction from 90° is because the lone pair-bonding pair repulsions are greater than the bonding pair-bonding pair repulsions.

Box 5.4 Nitrates in water (on p. 232 in *Chemistry*³)

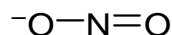
Use VSEPR theory to predict the shape of the nitrite ion.

Strategy

Draw the Lewis structure for the nitrite ion using a combination of double and single bonds, then count up the electrons around the central nitrogen atom (remembering to include the charge on the nitrogen). Decide which electron pairs are in σ bonds (affecting the shape) and which are in π bonds (stereochemically inactive pairs).

Solution

The Lewis structure for NO_2^- is shown below.



Using VSEPR theory, there are five electrons from the nitrogen atom, one from the single bond to O^- and two from the double bond. This gives eight electrons around the central N atom, so four electron pairs. One of the electron pairs is a π -pair which does not affect the shape, leaving three σ -pairs. One of these is a lone pair, so the nitrite ion has a bent structure.

Box 5.5 Ethene and the ripening of fruit (on p. 240 in *Chemistry*³)

The ancient Egyptians cut gashes in figs to speed up the ripening process. How does this work?

Strategy

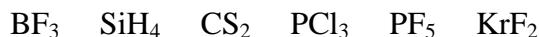
Consider what causes fruits to release ethene and the effect the release has on the ripening process.

Solution

The gashes stress the figs, inducing them to release ethene. The ethene has the effect of speeding up the ripening process.

Answers to end of chapter questions

1. Draw Lewis structures for the following compounds.

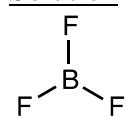


For each molecule, indicate whether the central atom obeys the octet rule, is hypervalent, or is electron poor.

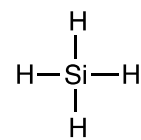
Strategy

Draw a Lewis structure for each molecule, and count the number of electrons around the central atom. If there are eight electrons it obeys the octet rule, less than eight it is electron poor, and more than eight it is hypervalent.

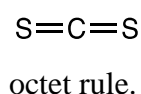
Solution



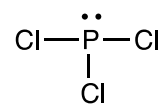
There are 6 electrons around the central boron atom, so BF_3 is electron poor.



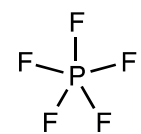
There are 8 electrons around the central silicon atom, so SiH_4 obeys the octet rule.



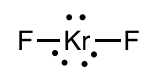
There are 8 electrons around the central carbon atom, so CS_2 obeys the octet rule.



There are 8 electrons around the central phosphorus atom, so PCl_3 obeys the octet rule.



There are 10 electrons around the central phosphorus atom, so PF_5 is hypervalent.

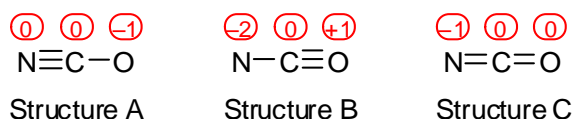


There are 10 electrons around the central krypton atom, so KrF_2 is hypervalent.

2. Three possible resonance forms for the cyanate anion are shown below. Work out the formal charge on each of the atoms in these three structures. Which is the most important resonance form?

Strategy

The most important resonance form will have the lowest formal charges on the atoms. By determining the formal charges it is therefore possible to work out the most important resonance form.

Solution

Structure B is the least important as it has the highest formal charges on the atoms. Structure A is more important than Structure C as the negative charge is placed on the more electronegative oxygen atom.

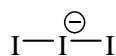
3. Use VSEPR theory to predict shapes for the following molecules and ions: (a) BF_3 ; (b) XeF_5^- ; (c) SbF_5 ; (d) I_3^- ; (e) ICl_4^- ; (f) SF_6 .

Strategy

Count up the number of electrons around the central atom and determine the number of bond pairs and lone pairs, remembering to include the charge for the ions. Use Figure 5.17 (p.230) to work out what geometry the shape is based on. Place lone pairs strategically to avoid them being close to each other.

Solution

- (a) 3 electrons from B and 3 electrons from 3F. 6 electrons around B, so 3 electron pairs. No lone pairs. The shape of the molecule is **trigonal planar**.
- (b) 8 electrons from Xe, 5 electrons from 5F and 1 from the charge. 14 electrons around Xe, so 7 electron pairs. Based on a pentagonal bipyramid with two lone pairs. Lone pairs occupy the axial positions. The shape of the anion is **pentagonal planar**.
- (c) 5 electrons from Sb and 5 electrons from 5F. 10 electrons around Sb, so 5 electron pairs. No lone pairs. The shape of the molecule is **trigonal bipyramidal**.
- (d) One of the iodine atoms is central, with the other two bonded to it. 7 electrons from the central I, 2 electrons from the other 2I and 1 from the charge.

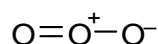


10 electrons around the central I atom, so 5 electron pairs. Based on a trigonal bipyramid with three lone pairs. The shape of the ion is **linear**.

- (e) 7 electrons from I, 4 electrons from 4Cl and 1 from the charge. 12 electrons around I, so 6 electron pairs. Based on an octahedron with two lone pairs. Lone pairs occupy opposite positions to minimise repulsion. The shape of the anion is **square planar**.
- (f) 6 electrons from S and 6 electrons from 6F. 12 electrons around S, so 6 electron pairs. No lone pairs. The shape of the molecule is **octahedral**.

4 Use VSEPR theory to predict shapes for the following molecules: (a) SO₂; (b) SO₃; (c) F₃SN; (d) O₃; (e) XeOF₄; (f) N₂H₂; (g) SeF₄.

- (a) 6 electrons from S and 4 electrons from 2O. 10 electrons around S, so 5 electron pairs, of which 2 are π -pairs and do not contribute to the shape. This leaves 3 σ -pairs. Based on trigonal planar with one lone pair. The shape of the molecule is **bent**.
- (b) 6 electrons from S and 6 electrons from 3O. 12 electrons around S, so 6 electron pairs, of which 3 are π -pairs and do not contribute to the shape. This leaves 3 σ -pairs. No lone pairs. The shape of the molecule is **trigonal planar**.
- (c) 6 electrons from S, 3 electrons from the N atom (triple bond) and 3 electrons from 3F. 12 electrons around S, so 6 electron pairs, of which 2 are π -pairs and do not contribute to the shape. This leaves 4 σ -pairs. Based on tetrahedral with no lone pairs. The molecule has a **distorted tetrahedral** structure because the triple bond takes up more space than a single bond.
- (d) One of the oxygen atoms is central, and the other two bonded to it. One of the bonds is a double bond, and the other is a single bond with the central oxygen atom having a formal charge of +1 and the singly-bonded terminal oxygen atom having a formal charge of -1.



6 electrons from O, 3 electrons from the terminal Os, minus one for the formal charge. 8 electrons around O, so 4 electron pairs of which 1 is a π -pair and does not contribute to the shape. This leaves 3 σ -pairs. Based on trigonal planar with one lone pair. The shape of the molecule is **bent**.

- (e) 8 electrons from Xe, 4 electrons from 4F and 2 electrons from O. 14 electrons around S, so 7 electron pairs, of which 1 is a π -pair and does not contribute to the shape. This leaves 6 σ -pairs of which one is a lone pair. The molecule has a distorted **square pyramidal** structure with the double bond taking up more space than the single bonds
- (f) There are two central atoms in this molecule, though the shape is the same around both of them. For each N, there are 5 electrons from N, 1 electron from F, and 2 electrons from the double bond to the other N. 8 electrons around each N, so 4 electron pairs, of which 1 is a π -pair and does not contribute to the shape. This leaves 3 σ -pairs. The shape around each nitrogen is based on trigonal planar with one lone pair. The geometry around each N is bent.
- (g) 6 electrons from Se and 4 electrons from 4F. 10 electrons around Se, so 5 electron pairs. Based on a trigonal bipyramidal with one lone pair. The molecule has a **disphenoidal** structure, equivalent to that of SF₄ (Fig. 5.14, p.228).

5. Use VSEPR theory to predict shapes for the following oxoanions:

- (a) ClO₃⁻; (b) ClO₄⁻; (c) ClO₂⁻; (d) S₂O₃²⁻.

Strategy

Draw a Lewis structure for the ion using a combination of single and double bonds. Count up the electrons around the central cation (remember to include the charge on the central species). Determine the number of electron pairs and whether they are σ or π electrons (remembering that only the former have an effect on the shape).

Solution

- (a) 7 electrons from Cl, 2 electrons from each of the 2 doubly bonded oxygen atoms and 1 electron from the singly bonded O⁻. 12 electrons around Cl, so 6 electron pairs. 2 of these are π -pairs, leaving 4 σ -pairs. Based on a tetrahedron with one lone pair. The shape of the ion is **trigonal pyramidal**.
- (b) 7 electrons from Cl, 2 electrons from each of the 3 doubly bonded oxygen atoms and 1 electron from the singly bonded O⁻. 14 electrons around Cl, so 7 electron

pairs. 3 of these are π -pairs, leaving 4 σ -pairs. The shape of the ion is **tetrahedral** as there are no lone pairs.

- (c) 7 electrons from Cl, 2 electrons from the doubly bonded oxygen atom and 1 electron from the singly bonded O^- . 10 electrons around Cl, so 5 electron pairs. 1 of these is a π -pair, leaving 4 σ -pairs. Based on a tetrahedron with two lone pairs. The shape of the ion is **bent**.
- (d) 6 electrons from the central S, 2 electrons from the other peripheral S, 2 electrons from the doubly bonded oxygen atom and 1 electrons from each of the singly bonded O^- . 12 electrons around the central S, so 6 electron pairs. 2 of these are π -pairs, leaving 4 σ -pairs. The shape of the ion is **tetrahedral** as there are no lone pairs.

6. Place the following species in order of increasing bond angle: (a) NO_2 ; (b) NO_2^+ and (c) NO_2^- .

Strategy

Use VSEPR theory to determine which geometry shown in Figure 5.7 (p.223) are adopted by these species. Draw a Lewis structure for the ion using a combination of single and double bonds. Count up the electrons around the central cation (remember to include the charge on the central species). Determine the number of electron pairs and whether they are σ or π electrons (remembering that only the former have an effect on the shape). Finally, in identical shapes, consider how the formal charges affect the shape.

Solution

- (a) NO_2 : 5 electrons from N, 2 electron from the doubly bonded oxygen, one from the singly bonded O^- and -1 electron from the $+1$ formal charge. 7 electrons around N, so $3\frac{1}{2}$ electron pairs. 1 of these is a π -pair, leaving $2\frac{1}{2}$ σ -pairs. The shape is based on a trigonal planar with a single electron rather than a lone pair. The shape of the molecule is **bent**.
- (b) NO_2^+ : 5 electrons from N, 4 electrons from 2O and -1 from the charge. 8 electrons around N, so 4 electron pairs. 2 of these are π -pairs, leaving 2 σ -pairs. The shape of the ion is **linear**.

- (c) NO_2^- : 5 electrons from N, 2 electron from the doubly bonded oxygen, one from the singly bonded O^- . 8 electrons total, so 4 electron pairs. 1 of these is a π -pair, leaving 3 σ -pairs. The shape is based on trigonal planar with a lone pair. The shape of the ion is **bent**.
The linear NO_2^+ cation has the largest bond angle (180°). The bond angle in NO_2 is greater than that in NO_2^- as the single electron takes up less space than the lone pair.

7. Which of the molecules and ions in Question 3 have dipoles?

Strategy

Any molecule which has a non-symmetrical distribution of charge/ligands will have a dipole.

Solution

Although in all of the molecules and ions there are polar bonds, in all cases these cancel out and there is no overall dipole in the molecule.

8. Three isomers of difluoroethene ($\text{C}_2\text{H}_2\text{F}_2$) are shown below. Which of these compounds are polar?

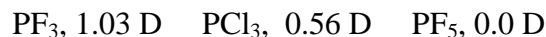
Strategy

Any molecule which has a non-symmetrical distribution of charge/ligands will have a dipole.

Solution

All of the molecules have polar bonds, but in the third structure (*trans*-1,2-difluoroethene) the dipoles cancel, so that the molecule as a whole is non-polar. In the first two examples the dipoles do not cancel out, and the molecules are polar.

9. The dipole moments for some phosphorus halides are given below. Account for the values, and predict the direction of the dipole where present.

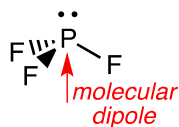


Strategy

Any molecule which has a non-symmetrical distribution of charge/ligands will have a dipole.

Solution

PF_5 has a dipole moment of zero, meaning it is non-polar. The molecule is trigonal bipyramidal, so the dipoles from the individual polar bonds all cancel out. PF_3 and PCl_3 are both trigonal pyramidal, so have a non symmetrical distribution of charge. Both molecules possess a dipole, with the phosphorus δ^+ and the halogens δ^- as shown below. The dipole moment is larger for PF_3 as the electronegativity difference between phosphorus and fluorine is greater than that between phosphorus and chlorine.



10. Identify the type of hybridization present in the non-hydrogen atoms of the following molecules.

Strategy

By examining the geometry at each non-hydrogen atom present, the type of hybridization can be determined. For example if the shape at a carbon atom is linear, two orbitals are required to form two hybridized orbitals, therefore the atom is sp hybridized.

Solution

- (a) The methyl carbon forms four σ -bonds so is sp^3 hybridized. There is a triple bond between the carbon and nitrogen atoms of the nitrile group, so these atoms are both sp hybridized.

- (b) The two methyl carbon atoms are sp^3 hybridized. There is a double bond between the carbon and oxygen atoms of the carbonyl group so these atoms are both sp^2 hybridized.
- (c) There is a double bond between the nitrogen atoms, so these atoms are both sp^2 hybridized.

11. The structure of caffeine is shown in Box 5.1 (p.218). Identify the hybridization present in all of the non-hydrogen atoms in this molecule.

Strategy

By examining the geometry at each non-hydrogen atom present, the type of hybridization can be determined. For example if the shape at a carbon atom is linear, two orbitals are required to form two hybridized orbitals, therefore the atom is sp hybridized.

Solution

The ring carbons all form one double bond so are trigonal planar, so sp^2 hybridized. The methyl carbons are tetrahedral, so sp^3 hybridized. The oxygen atoms each form a double bond so are sp^2 hybridized. The nitrogen atoms bonded to methyl groups have a trigonal pyramidal geometry so are sp^3 hybridized. The remaining nitrogen atom forms a double bond so is sp^2 hybridized.

12. The bond angle in H_2S is 92° , much less than that in H_2O . Suggest a reason for this. Would you expect H_2S to be a stronger or weaker base than H_2O ?

Strategy

Orbitals of similar energies hybridize to give regular geometries about a central atom. Unusual geometries can result if the orbitals do not hybridize as expected.

Solution

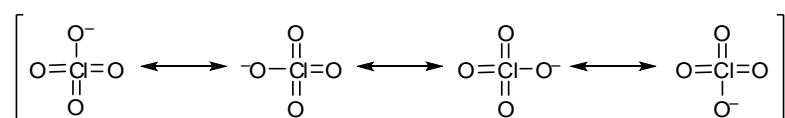
This can be explained by assuming H_2S is not hybridized, and that the bonds are formed through interactions of the sulfur $3p$ orbitals with the hydrogen $1s$ orbitals. H_2S is a weaker base than H_2O as the lone pair is in an unhybridized $3s$ orbital which is less available for donation to a Lewis acid than the lone pair on oxygen in H_2O (see discussion about PH_3 on p.239).

13. The four Cl–O bonds in the perchlorate anion (ClO_4^-) have identical bond lengths. Draw resonance forms to explain this. What is the average charge on each oxygen atom?

Strategy

Draw a simple Lewis structure of the perchlorate anion with one Cl–O single bond to negatively charged oxygen atoms and three Cl=O double bonds to neutral oxygen atoms. Draw resonance forms to show that the four bonds are equivalent and divide the number of charges by the number of bonds to work out the average charge over the four forms.

Solution



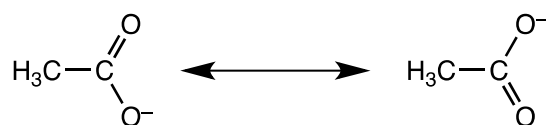
The average charge on each oxygen atom is $\frac{(-1)+0+0+0}{4} = -\frac{1}{4}$.

14. In the ethanoate anion (CH_3CO_2^-) the C–O bonds have been shown experimentally to have the same bond length (125 pm). This differs from ethanoic acid ($\text{CH}_3\text{CO}_2\text{H}$), which contains two different carbon-oxygen distances (122 pm, 132 pm). Draw resonance forms for the ethanoate anion consistent with this observation and determine the average C–O bond order.

Strategy

Draw resonance forms for the ethanoate ion. The average bond order for each C–O bond should be the same, and be between 1 and 2.

Solution



The average bond order for each C–O bond is $\frac{1+2}{2} = 1\frac{1}{2}$.

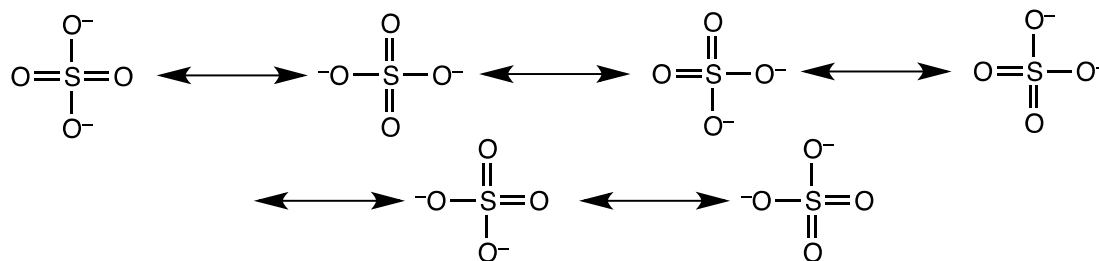
15. In both the sulfate (SO_4^{2-}) and sulfite (SO_3^{2-}) anions, the S–O bond lengths are all the same. Draw resonance forms for the ions to support this. By considering the average S–O bond order in each case, predict which ion has the shorter S–O bond lengths.

Strategy

For each ion, draw all of the resonance forms and calculate the average bond order for the S–O bonds. Since increasing bond order implies decreasing bond length, the ion with the higher average bond order has the shorter S–O bond lengths.

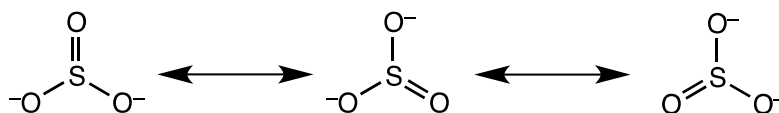
Solution

For sulfate,



The average S–O bond order is $\frac{1+2+2+1+2+1}{6} = 1\frac{1}{2}$.

For sulfite,



The average S–O bond order is $\frac{2+1+1}{3} = 1\frac{1}{3}$.

The average bond order is higher for sulfate, so this has the shorter bonds.

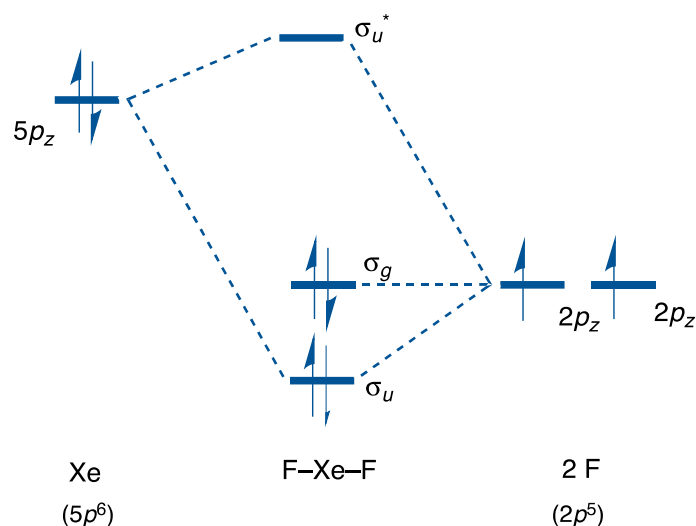
16. The Xe–F bond length in XeF_2 is 198 pm, whereas the equivalent distance in the XeF^+ ion is 187 pm. Rationalize this difference by considering the bonding in the two species.

Strategy

Firstly, determine whether the two species obey the octet rule. If so, the bonding will involve ‘normal’ covalent bonds (*i.e.* 2-electron, 2-centre). If the species is hypervalent, then use a partial MO energy level diagram to explain the bonding, and work out the average bond order.

Solution

XeF^+ obeys the octet rule, with eight electrons around the xenon atom. The bond is a normal covalent bond, with bond order 1. XeF_2 is hypervalent, and can be treated using a partial MO energy level diagram (see Section 5.7, p.249) as shown below.



The bonding in this molecule can be described as a 3-centre 4-electron bond, though 2 of the 4 electrons are non-bonding. This means there is a total bond order of one, spread across two Xe–F contacts. The average bond order for each Xe–F bond is therefore $1/2$. This is lower than the value in XeF^+ , which is consistent with the longer bonds.

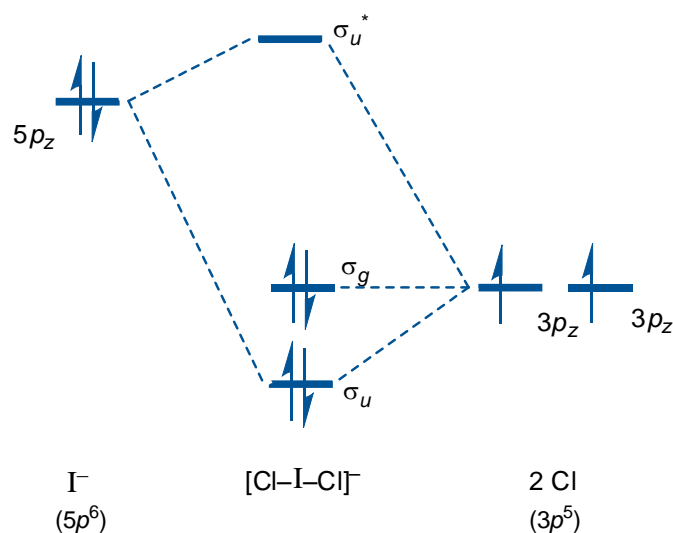
17. For the linear anion ICl_2^- , draw in-phase and out-of-phase combinations of the chlorine p_z orbitals. Determine how these interact with the iodine p_z orbital and use this information to construct a partial MO energy level diagram for ICl_2^- . What is the bond order of each I–Cl bond?

Strategy

First it is necessary to generate the bonding and antibonding combinations of the two p_z orbitals for chlorine. The generated molecular orbitals will be similar to those produced for the element in the second group of the first period. Then by considering the symmetry of these orbitals, work out which of these molecular orbitals can interact with the iodine p_z orbital to form new bonding and antibonding molecular orbitals.

Solution

The combinations of Cl $3p_z$ orbitals are similar to those for the F $2p_z$ orbitals in XeF_2 shown in Figure 5.41 (p.249). The in-phase combination does not have the correct symmetry to interact with the iodine orbital. However, the out-of-phase combination does, and interacts to give a bonding orbital and an antibonding orbital. The partial molecular orbital energy level diagram for ICl_2^- is shown below.



The bonding and non-bonding orbitals are filled and the antibonding orbital is empty, giving a 3-centre 4-electron bond. There is total bond order of one spread over two I-Cl bonds, so the bond order of each bond is $\frac{1}{2}$.