4

Structure and shape of polyatomic molecules

Answers to worked examples

WE 4.1 Formal charges in N_2O

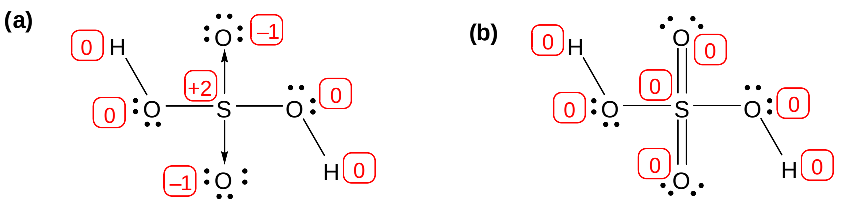
Use formal charges to decide which of the following best represents the structure of sulfuric acid (H_2SO_4).

Strategy

Use Equation 4.1 (p.180) 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 (b) has the lower formal charges so this structure is favoured.



	(a) O	(a) S	(a) O	(b) O	(b) S	(b) O
Number of electrons in the valence shell of a free atom	6	6	6	6	6	6
– Number of bonds to the atom	– 1	– 4	– 1	– 2	– 6	– 2
– Number of unshared electrons	– 6	– 0	– 6	– 4	– 0	– 4
Formal charges	–1	+2	–1	0	0	0

WE 4.3 Using VSEPR theory with ions

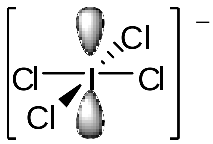
What shape is the ICl_4^- ion based on? Decide the position(s) you would expect any lone pairs to occupy, and thus predict the shape of ICl_4^-.

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 degree angles to work out the best place to locate the more spatially demanding lone pairs.

Solution

In ICl_4^- 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 ICl_4^- 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 degrees. The shape of the ICl_4^- ion is therefore square planar.



WE 4.5 Bonding in BeH_2

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 1*s* 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 1*s* 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.

Answers to boxes

Box 4.3 The fluorinating ability of ClF_3

How would you expect the bond angles in ClF_3 to differ from 90°?

Strategy

Use VSEPR theory to calculate the shape of ClF_3 as shown in Section 4.2 (p.183). Consider the effect that the more spatially demanding lone pairs have on the structure of the trigonal bipyramid.

Solution

ClF_3 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 ClF_3

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 4.5 Ethene and the ripening of fruit

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.

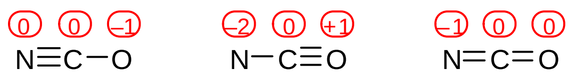
Answers to end of chapter questions

1. 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 A Structure B Structure C

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 oxoanions:
(a) ClO_3^-; (b) ClO_4^-; (c) ClO_2^-; (d) $S_2O_3^{2-}$.

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.

5. Which of the molecules in Question 2 are polar?

Strategy

Any molecule which has a non symmetrical distribution of charge/ligands will be polar.

Solution

All the molecules except BF_3 and SbF_5 have irregular shapes. All the molecules are therefore polar except BF_3 and SbF_5.

7. 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 C is linear, two orbitals are required to form two hybridized orbitals, therefore *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.

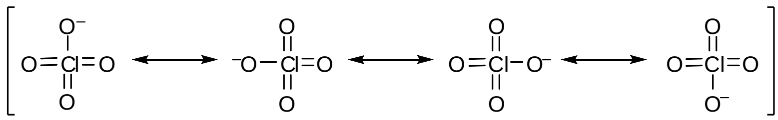
(c) There is a double bond between the nitrogen atoms, so these atoms are both sp^2 hybridized.

9. The four Cl–O bonds in the perchlorate anion (chlorate(VII), 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 $\frac{(-1)+0+0+0}{4} = -\frac{1}{4}$.