

CHAPTER 5 – COVALENT BOND

Introduction

We saw in Chapter 4 that ionic bonds are not directional and that ionic compounds exist as extended networks rather than individual molecules. In this chapter, we begin our study of molecular substances, substances that exist as discrete molecules. Covalent bonds are directional and covalently bound atoms form molecular substances.

5.1 The Covalent Bond

Introduction

Covalent bonds result from the overlap of orbitals and involve a sharing of pairs of electrons. In this lesson, we examine the nature of the covalent bond.

Prerequisites

- 1.8 Electromagnetism and Coulomb's Law (Describe how the energy of interaction between charged particles varies with the distance between them.)
- 1.7 Energy (Predict the direction of energy change for natural processes.)
- 2.6 Orbital Shapes and Sizes

Objectives

- Explain how the energy of two nuclei varies with the distance between them.
- Define bond energy and bond length.

5.1-1. H–H Bond Video

A video or simulation is available online.

5.1-2. H–H Bond

A *covalent bond* results when atoms share one or more pairs of electrons. The electrons that are shared in a covalent bond are called *bonding electrons* or *bonding pairs*.

In Chapters 2 and 3, we discussed the energy of interaction between a nucleus and its electrons, which reduces their potential energy and is responsible for the existence of atoms. However, valence electrons can reduce their energy ever farther by interacting with more than one nucleus. Consider Figure 5.1, which shows the energy of interaction between two hydrogen atoms as a function of their separation, r .

- At a separation of r_1 , the two hydrogen atoms are too far apart to interact; i.e., they have zero energy of interaction, and the electrons are in spherical 1s orbitals.
- At a distance of r_2 , each electron is attracted by the nucleus of the other atom as well as its own. There is also repulsion between the nuclei, but it is much less because the nuclei are still relatively far apart. The greater attractive force between the oppositely charged particles lowers the energy of the system. The electron density begins to concentrate in the region between the nuclei, distorting the orbitals from their spherical shape.
- At r_3 , the atoms are weakly bound together, and the two orbitals overlap one another.
- At r_4 , the energy of the system has reached a minimum as the electron/nuclear attraction just balances the internuclear repulsion. The bonding electrons are in an orbital that concentrates the electron density in the region between the two nuclei. The negative charge of the two electrons holds the positively charged nuclei together in an H–H covalent bond.
- At r_5 , the repulsion between the nuclei is the dominating force, so the energy rises sharply.

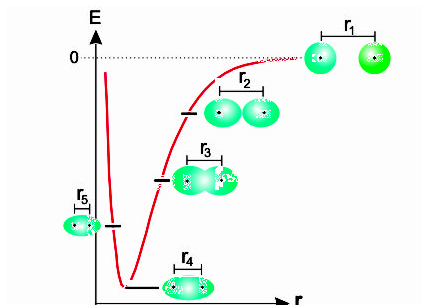


Figure 5.1: H–H Bond Formation and Length Energy of interaction between two H atoms as a function of r , the distance between the nuclei, which are represented by the small dots.

5.1-3. Bond Length and Bond Energy

The bond energy (D) is the energy required to break a mole of bonds in the gas phase.

The bond length is the separation between two bound atoms at the position of minimum energy.

The equilibrium distance between two bound nuclei in a molecule defines the **bond length** of their bond. The H–H bond length, which is 0.74 Å or 74 pm ($p = 1 \times 10^{-12}$), is a very short bond because the two atoms are so small that they must get very close to interact. The I–I bond length, which is 2.7 Å (270 pm), is very long because the two atoms are so large. Most bond lengths lie between 1 and 3 Å (100 and 300 pm).

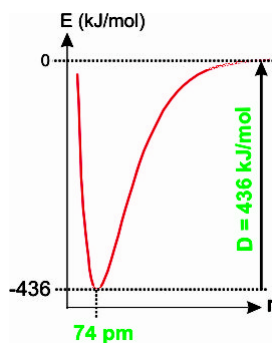


Figure 5.2

The energy of two bound atoms is lower than that of the separated atoms because the bonding electrons on each atom interact with both nuclei. Thus, energy is released when atoms bond. In the case of the H–H bond, 436 kJ is released when two moles of hydrogen atoms combine to form one mole H–H bonds. This means that the minimum energy of two interacting hydrogen atoms is -436 kJ/mol. Separating the two bound atoms requires breaking the bond, which requires an input of the same amount of energy that was released when the bond formed. The energy required to break or dissociate a bond in the gas phase is called the bond or dissociation energy and given the symbol D . The H–H bond energy in H_2 is $D = 436$ kJ/mol and is an average bond energy, as most bond energies lie between 100 and 1000 kJ/mol. The I–I bond is very weak with a bond energy of only 151 kJ/mol.

5.2 Bond Polarity

Introduction

Although the bonding electrons are shared in a covalent bond, electronegativity differences between the bound atoms can result in unequal sharing. Bonds in which the electrons are not shared equally are said to be polar bonds, the topic of this section.

Prerequisites

- 2.7 Electron Configurations
- 2.3 Bohr Model

- 3.6 Electronegativity (Predict the relative electronegativities of two atoms.)

Objectives

- Define the bond dipole and represent it with an arrow.
- Distinguish between *purely covalent*, *polar covalent*, and *ionic* bonds.

5.2-1. Polar vs. Nonpolar Bonds

If the electronegativities of two atoms in a bond are different, then the bond is polar.

A video or simulation is available online.

- The presence of a positive and a negative pole in a covalent bond produces a **bond dipole**.
- A covalent bond with a bond dipole is said to be a **polar covalent bond**.
- A covalent bond with no bond dipole is a **purely covalent bond**.

5.2-2. Polar Bonds and Bond Dipoles

Polar bonds have bond dipoles, which are represented with arrows pointing from the positive pole (less electronegative atom) toward the negative pole (more electronegative atom) with a line through the positive end.

In H_2 the bound atoms have identical electronegativities, so the bonding electrons are shared equally. Such bonds are **purely covalent bonds**. However, if the electronegativities of the bound atoms differ, as in the case of HF, the bonding electrons are not shared equally as the more electronegative fluorine becomes electron rich and the less electronegative hydrogen becomes electron poor. The result is that negative charge is produced on the more electronegative atom and positive charge on the less electronegative atom. The charge that is produced in a covalent bond is only a part of what it would be if the bond were ionic, so it is said to be a partial charge, which is represented with a δ (delta). Thus, a covalent bond involving atoms of different electronegativities has two electrical poles (δ^- and δ^+) and is said to have a **bond dipole** and is called a **polar covalent bond**.

Bond dipoles are frequently represented with arrows pointing from the positive pole toward the negative pole. A line is then drawn through the arrow so as to make a plus sign at the positive end. Although the length of the arrow is normally related to the strength of the dipole, we will use the arrow to show direction only, so relative lengths are not meaningful. No bond dipole exists for nonpolar molecules, so no arrow is used with them.

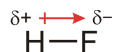


Figure 5.3 The direction of the bond dipole in HF is shown with the red arrow. Note that a line through the arrow makes a plus sign at the positive end of the dipole.

5.2-3. Charge Distribution

Although molecules are neutral, they do contain regions of charge due to the asymmetric charge distribution in polar bonds. We will use the convention of indicating regions of negative charge as red and regions of positive charge as blue. Regions of no charge will be shown as white. Consider the examples below.

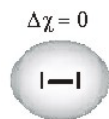


Figure 5.4a: Charge Distribution of an I-I Bond Two iodine atoms have the same electronegativities, so the I-I bond is not polar and there is no asymmetric charge distribution. Consequently, the electron cloud is shown as white.

$$\Delta\chi = 0.5$$



Figure 5.4b: Charge Distribution of an I–H Bond Iodine is more electronegative than hydrogen, so the bonding electrons reside nearer the iodine. The increase in electron density is shown in red. The electrons move away from the hydrogen, giving it a slight positive charge shown in blue. The electronegativity difference is only 0.5, so the intensities of the colors are not very great. The bond dipole points from the positive (blue) region toward the negative (red) region.

$$\Delta\chi = 1.3$$



Figure 5.4c: Charge Distribution of an I–F Bond Iodine is less electronegative than fluorine, so the bonding electrons reside nearer the fluorine. Thus, F carries a partial negative charge, which is represented by the red color. The I atoms carries a partial positive charge as shown by the blue color. $\Delta\chi = 1.3$, so the colors are slightly more intense than in HI.

$$\Delta\chi = 1.8$$



Figure 5.4d: Charge Distribution of an H–F Bond Fluorine is much more electronegative than hydrogen ($\Delta\chi = 1.8$) so the regions are intensely colored.

5.2-4. Bond Type and Electronegativity Differences

Bond types vary continuously from purely covalent to polar covalent to ionic. There is no clear distinction between a polar covalent bond and an ionic one.

The value of δ in $\delta^+X-Y\delta^-$ ranges from 0 to 1 for a compound like H–Cl, depending upon the electronegativity difference between X and Y. As δ increases, the charge separation in the bond increases, and it gains ionic character. When δ is 0, the bond is purely covalent, and when δ is 1, the bond is purely ionic. Thus, we refer to the **percent ionic character** of a bond, which increases as the electronegativity difference between the bound atoms increases. There are no clear lines separating ionic and covalent bonds; they gradually merge into one another as shown in Figure 5.5. However, we will use the following for discussion.

- **covalent bonds:** Bonds with $\Delta\chi \leq 0.4$ have less than 5% ionic character and behave like nonpolar bonds. Consequently, we will refer to them as covalent bonds. The C–H and P–H bonds are covalent bonds.
- **ionic bonds:** Bonds with $\Delta\chi \geq 1.8$ are over 50% ionic, so we will refer to them as ionic bonds. K–Br and Na–Cl are ionic bonds.
- **polar covalent bonds:** Bonds that lie between the covalent and ionic limits given above will be called polar covalent bonds. The P–O and H–Cl bonds are polar covalent bonds.

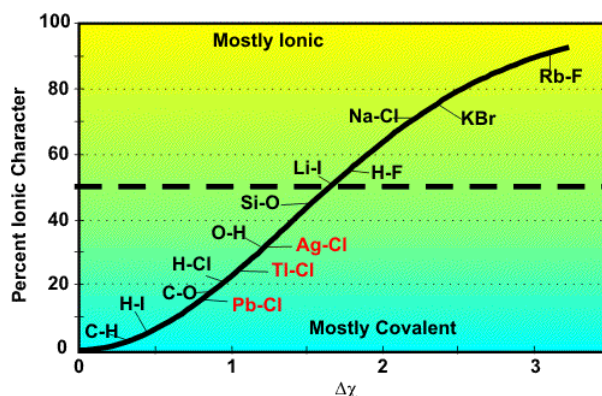


Figure 5.5 Percent Ionic Character of a Bond as a Function of the Electronegativity Difference Between the Bound Atoms

Bond types change continuously from covalent to polar covalent to ionic with no clear boundaries between the bond types. However, ionic bonds are favored by large differences in electronegativity, while covalent bonds are favored by small differences. Consequently, we will use the following generalizations in this course:

- **Ionic bonds form between metals (low χ) and nonmetals (high χ).**
- **Covalent bonds form between nonmetals because they have similar χ s.**

5.2-5. Exceptions

Assume that metal-nonmetal bonds are ionic and nonmetal-nonmetal bonds are covalent, but it is not always true.

The generalization that metal-nonmetal bonds are ionic and nonmetal-nonmetal bonds are covalent will aid our discussions, but it is not a hard and fast rule. As a result, metal-nonmetal bonds are often more covalent than ionic. For example, $\Delta\chi = 1.1$ for the Ag-Cl bond, so it is only about 30% ionic, and $\Delta\chi = 0.7$ for the Pb-Cl bond, so it is less than 15% ionic. Thus, not all metal-nonmetal bonds are ionic. In addition, the H-F bond is between nonmetals, so it will be referred to as covalent, but $\Delta\chi = 1.9$ for the bond, which makes it about 60% ionic. Thus, not all nonmetal-nonmetal bonds are very covalent.

Metal	χ
Ag	1.9
Sn	2.0
Hg	2.0
Tl	2.0
Pb	2.3

Table 5.1

5.2-6. Bond Type Exercises

EXERCISE 5.1:

Use only a Periodic Table to answer the following questions.

Which is the most polar bond?

H-N

H-C

H-O

The C-Cl bond is which of the following?

purely covalent

polar covalent

ionic

The Cl-Cl bond is which of the following?

purely covalent

polar covalent

ionic

Which is the most polar bond?

S-F

O-F

F-F

The Na-Cl bond is which of the following?

purely covalent

polar covalent

ionic

The Sn-Cl bond is which of the following?

purely covalent

polar covalent

ionic

5.3 Naming Binary Covalent Compounds

Introduction

In this lesson, you will learn how to name binary covalent molecules.

Objectives

- Convert between the name and formula of a covalent molecule.

5.3-1. Naming Binary Compounds

Prefixes are used in the names of covalent compounds to indicate the number of each atom present.

Binary compounds are compounds that contain only two different elements. The name of a binary covalent compound consists of the name of the less electronegative element followed by the name of the more electronegative element with its ending changed to -ide. The number of atoms of each element present in a molecule is given by a Greek prefix except that the prefix “mono” is not used for the first atom in the formula. Thus, CO is carbon monoxide (not monocarbon monoxide), but N₂F₄ is dinitrogen tetrafluoride.

Many compounds have common names. For example, H₂O is water, NH₃ is ammonia, and NO is nitric oxide.

By convention, **the less electronegative element is written first in the formula except if one of the elements is hydrogen**. Many hydrogen-containing compounds are acids, and, by convention, hydrogens at the beginning of the formula are considered to be acidic hydrogens. Ammonia is written NH₃ even though hydrogen is the less electronegative element, but dihydrogen sulfide is written as H₂S because it is an acid.

The following Greek prefixes indicate the number of each type of atom that appears in the formula of covalent compounds.

Number	Prefix	Example
1	mono	CO - Carbon monoxide
2	di	CO ₂ - Carbon dioxide
3	tri	SO ₃ - Sulfur trioxide
4	tetra	CCl ₄ - Carbon tetrachloride
5	penta	PF ₅ - Phosphorus pentafluoride
6	hexa	SF ₆ - Sulfur hexafluoride
7	hepta	Cl ₂ O ₇ - Dichlorine heptaoxide*
8	octa	
9	nona	
10	deca	

*An ‘a’ at the end of a prefix is frequently omitted when it is followed by a vowel, so the name may also appear as ‘Dichlorine heptoxide.’

Table 5.2: Prefixes Used in Naming Covalent Compounds

5.3-2. Naming Binary Covalent Compounds Exercise

EXERCISE 5.2:

Name each of the following compounds.

PF₃ _____

IF₅ _____

N₂O₃ _____

CuCl₂ _____

SiCl₄ _____

P₂O₅ _____

NO _____

5.3-3. More Naming Compounds Exercises

EXERCISE 5.3:

Name the following compounds.

N₂F₄ _____

SO₃ _____

PbO₂ _____

CS₂ _____

SF₆ _____

N₂O₄ _____

5.4 Lewis Symbols of the Elements

Introduction

A **Lewis structure** shows the placement of the valence electrons around each of the atoms in a molecule. They are important because they allow us to predict the shapes of molecules, the types and relative strengths of the bonds, and regions of high and low electron density within the molecule. In this section, we introduce Lewis symbols for the elements.

Prerequisites

- Valence Electrons (Determine the number of valence electrons in an atom.)

Objectives

- Write the Lewis symbol for an atom.

5.4-1. Lewis Symbols

The structures of covalently bound molecules and ions depend upon the distribution of the valence electrons. The distribution of valence electrons can be represented by Lewis structures. The **Lewis symbol of an atom shows the valence electrons spread in four different regions and remaining unpaired until each region has at least one electron**. Lewis symbols represent the bonding atom, not the isolated atom. The number of valence electrons for a main group element is simply the element's group number, so the electron distribution given in the Lewis symbols is the same for all atoms in a group.

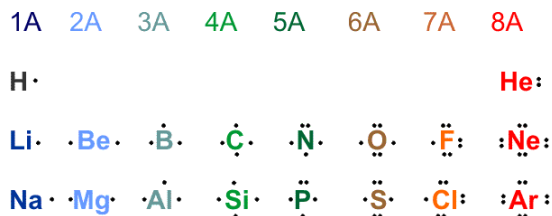


Figure 5.6: Lewis Symbols Lewis Symbol representation of the main group elements.

5.5 Lewis Structures of Diatomic Molecules

Introduction

We use diatomic molecules to introduce Lewis structures of molecules and to introduce some new terms.

Objectives

- Explain the *octet rule*.
- Determine the number of shared pairs in a Lewis formula.
- Distinguish between the bonding pairs and the lone pairs of electrons.
- Define *bond order* and determine the bond order of a bond from a Lewis formula.
- Relate the lengths and strengths of several bonds between the same two elements to the bond orders of the bonds.

5.5-1. Octet Rule

Lewis structures almost always show eight valence electrons around each atom. An exception is hydrogen, which has only two.

Filled or closed shells are very stable and atoms strive toward these configurations when they bond. In Chapter 4, we saw that atoms can attain these configurations by becoming ions: metals lose their valence electrons to obtain

the closed shell configuration of the preceding noble gas, while nonmetals gain electrons to obtain the closed shell configuration of the following noble gas.

Nonmetals can also achieve closed shells by sharing electrons. A closed shell for a nonmetal consists of eight electrons (2 s and 6 p electrons). Thus, nonmetals strive to obtain eight electrons, which is called an **octet**, in their valence shell. This tendency is summarized by the **octet rule**.

- **Lewis structures of molecules formed from nonmetals almost always show eight valence electrons around each atom.**

The octet rule provides a guide to drawing the Lewis structures of compounds.

As indicated by “almost always,” there are some exceptions. The most common exception is the hydrogen atom. A closed shell for hydrogen consists of two, not eight, electrons, so **hydrogen atoms attain only a duet of electrons**. Thus, one and only one bond is drawn to a hydrogen atom. Other exceptions occur, but they are rare and usually result when the molecule has an odd number of electrons or contains an atom of low electronegativity such as boron.

5.5-2. Chlorine

- Chlorine is in Group 7A, so chlorine atoms each have 7 valence electrons. Consequently, chlorine atoms need one more electron to obtain an octet.
- Chlorine atoms react with one another to form Cl_2 molecules.
- The Cl atoms in a Cl_2 molecule each attain an octet by sharing their unpaired electrons.
- There is one bonding pair in Cl_2 , which lies in the region of overlap of the two octet circles.
- Each Cl atom in Cl_2 also has three pairs of electrons that are not involved in the bonding. These nonbonding pairs are called **lone pairs**.
- The two atoms have identical electronegativities, so the Cl–Cl bond is a nonpolar covalent bond.

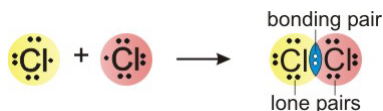


Figure 5.7: Lewis Structure of Cl_2 The yellow and red circles are not part of the Lewis structure and are used here only to distinguish between the two sets of valence electrons and to highlight the bonding pair shown in blue.

5.5-3. Shared Pairs

The number of shared pairs in a molecule can be determined from the number of valence electrons available from the atoms.

The number of shared pairs (bonding pairs) in a molecule is an important property of a molecule because it gives us information about how the atoms bond to one another. Thus, we will have occasion to determine it frequently. The number of electrons that must be shared equals the number of electrons required to satisfy the octet rule for every atom without sharing minus the number of valence electrons that are available. The number of shared pairs is half of the number of shared electrons. Mathematically, the relationship is expressed as

$$\text{SP} = \frac{1}{2}(\text{ER} - \text{VE})$$

- **SP** is the number of shared pairs in the molecule.
- **ER** is the number electrons required to give each atom an octet (or duet for H). It is equal to the number on nonhydrogen atoms times 8 (octet) plus the number of hydrogen atoms times 2 (duet).
- **VE** is the sum of the valence electrons on all of the atoms in the molecule.

EXERCISE 5.4:

Determine the number of shared pairs in each of the following.



ER = _____

ER = _____

ER = _____

VE = _____

VE = _____

VE = _____

SP = _____

SP = _____

SP = _____

5.5-4. Lewis Structures of Three Molecules

Bonding pairs are shown as lines in a Lewis structure, but lone pairs are shown as two dots.

In the previous exercise, we determined the number of shared pairs (SP) in three diatomic molecules (F₂, O₂, and N₂). Each atom obeys the octet rule, so the Lewis structures are drawn by first placing the correct number of shared pairs, then placing enough lone pairs around each atom to assure that each has an octet. In addition, **bonding (shared) pairs of electrons are normally shown as lines rather than dots**. Thus, the Lewis structures of these three diatomic molecules would be represented as follows:

Molecule	F ₂	O ₂	N ₂
SP	1	2	3
Lewis Structure	$\text{:}\ddot{\text{F}}\text{---}\ddot{\text{F}}\text{:}$	$\text{:}\ddot{\text{O}}\text{=}\ddot{\text{O}}\text{:}$	$\text{:}\text{N}\equiv\text{N}\text{:}$

Table 5.3: Lewis Structures of F₂, O₂, and N₂

Thus, each F atom has three lone pairs, each O atom has two, and each N atom has only one lone pair.

5.5-5. Bond Order

The number of bonding pairs in a bond is called its bond order.

The **bond order** of a bond is the number of shared pairs of electrons in the bond (the number of lines). The bond order is frequently given by indicating a single, double, or triple bond.

Bond	Bond Order	Name
F–F	1	single bond
O=O	2	double bond
N≡N	3	triple bond

Table 5.4

5.5-6. Some Bond Lengths and Strengths

Bonds get shorter and stronger as their bond order increases.

The number of electron pairs in a bond dictates the strength and length of the bond. Thus, **increasing the X–Y bond order strengthens and shortens the X–Y bond**. This is evident in the table of average bond energies and bond lengths of bonds involving C, N, and O that is shown below. The bond length also depends on the bound atoms, so **this generalization can be applied only to bonds between the same two atoms**. That is; X–Y bonds can be compared to one another as can X–Z bonds, but X–Y bonds cannot be compared with X–Z bonds.

Bond	Bond Energy (kJ/mol)	Bond Length (Å)	Bond	Bond Energy (kJ/mol)	Bond Length (Å)	Bond	Bond Energy (kJ/mol)	Bond Length (Å)
C–O	358	1.43	C–C	347	1.54	N–N	163	1.47
C=O	799	1.23	C=C	612	1.33	N=N	418	1.24
C≡O	1072	1.13	C≡C	820	1.20	N≡N	941	1.10

Table 5.5: Bond Strength and Length as a Function of Bond Order

5.6 Determining Lewis Structures

Introduction

We now extend the previous lesson to include molecules other than diatomic molecules.

Objectives

- Draw Lewis structures.

5.6-1. Determining Lewis Formulas

To determine the Lewis structure of a molecule:

- 1 Determine the number of shared pairs as before: $SP = \frac{1}{2} (ER - VE)$ where
 - ER = electrons required = 8 times the number of nonhydrogen atoms + 2 times the number of hydrogens.
 - VE = valence electrons = sum of the valence electrons on all of the atoms in the molecule and any charge on an ion. The number of valence electrons is increased by the negative charge of an anion and decreased by positive charge on a cation. VE is the number of electrons that must be shown in the final Lewis structure.
- 2 Draw the skeleton of the molecule (connect all of the atoms with single lines), then determine how many more shared pairs must be added and add them.
- 3 Add lone pairs to atoms to assure that each nonhydrogen atom has an octet.
- 4 Check your structure to be certain that each atom has an octet and that the number of electrons shown in the structure is the same as the number of valence electrons determined above.

Lewis structures should never show double or triple bonds to hydrogen or to a halogen. More than one single bond must be drawn to a halogen when it is the central atom as in ClO_4^{1-} , but a double or triple bond should not be used. We explain why in the section on formal charge.

5.6-2. Determining Shared Pairs and Lone Pairs Exercise

EXERCISE 5.5:

Determine the number of shared pairs (SP) and the number of lone pairs (LP) around the central atom (the atom that appears first in the formula) in each of the following.



ER = _____

VE = _____

SP = _____

LP = _____



ER = _____

VE = _____

SP = _____

LP = _____



ER = _____

VE = _____

SP = _____

LP = _____



ER = _____

VE = _____

SP = _____

LP = _____



ER = _____

VE = _____

SP = _____

LP = _____

5.6-3. Lewis Structure of CO Exercise

EXERCISE 5.6:

Draw the Lewis structure for carbon monoxide, CO.

1. Determine the number of electrons required with no sharing (ER).

2. Determine the number of valence electrons (VE).

3. Determine the number of shared pairs (SP).

4. What is the C–O bond order in CO?

5.6-4. Lewis structure of CO₂ Exercise

EXERCISE 5.7:

Draw the Lewis structure for carbon monoxide, CO₂.

1. Determine the number of electrons required with no sharing (ER).

2. Determine the number of valence electrons (VE).

3. Determine the number of shared pairs (SP).

4. What is the C–O bond order in CO₂?

5.7 Resonance

Introduction

In some instances, more than one Lewis structure can be drawn for a molecule. The different structures are called resonance structures.

Objectives

- Define the term *resonance* and use curved arrows to indicate how the electrons can be moved to convert one resonance form into another.
- Determine the bond order of a bond involved in a resonance structure.

5.7-1. Resonance Structures

Resonance structures are Lewis structures that differ only in the placement of the electron pairs.

Resonance structures are Lewis structures that differ only in the placement of the electron pairs. **Curved arrows** are used to show how the electrons can be moved to convert from one resonance structure into another. We will also use curved arrows in Chapters 12 and 13 to show how acid-base reactions take place, so take a moment to familiarize yourself with their meaning. As shown in the table, they are used in only two ways.

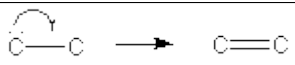
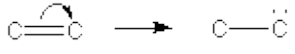
Representation	Direction	Action
	lone pair → bond	the lone pair becomes a bonding pair
	bond → atom	a bonding pair becomes a lone pair

Table 5.6

5.7-2. Resonance forms of CO₂

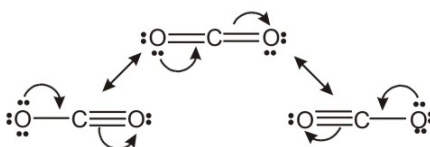


Figure 5.8

View the animation to see how curved arrows are used to explain the electron movement required to attain the three resonance structures of CO₂.

A video or simulation is available online.

5.7-3. The Number of Resonance Structures

The most common form of resonance is one in which a multiple bond can be drawn in any of several positions. Follow these steps to determine the number of such resonance forms that are possible.

Determine the number of shared pairs.

- 1 Determine the number of electrons required with no sharing (ER).
- 2 Determine the number of valence electrons (VE).
- 3 Determine the number of shared pairs (SP).

Resonance structures form when the number of shared pairs exceeds the number of identical bonding regions in which they can be placed. Resonance structures for molecules or ions having a single central atom occur when the number of shared pairs exceeds the number of regions by one. In this case, the number of structures equals the number of bonding regions in which the extra shared pair can be placed. The example of SO₂ is examined in the following exercise.

5.7-4. Resonance in SO₂ Exercise

EXERCISE 5.8:

ER = _____ VE = _____ SP = _____

Based on the bonding regions, how many resonance structures can be drawn for SO₂?

5.7-5. Bond Orders in Bonds Involved in Resonance

When more than one identical resonance structures can be drawn for a molecule, they all contribute equally to the bonding picture. Fractional bond orders result in these cases as one bonding pair is shared in more than one region.

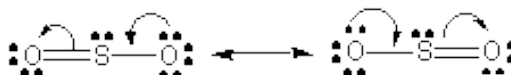


Figure 5.9: Resonance in SO₂ Note that a line with arrows on both ends is used to indicate resonance structures.

When the different resonance forms are equivalent, as is the case in SO₂, each form contributes equally to the bonding. **When more than one resonance form is important in the bonding, then the bonding in the molecule is the average of the resonance forms.** The most common cases of resonance arise when a multiple

bond can be placed in more than one equivalent position. When resonance is important, one bonding pair is shared by (spread over) more than one bond, and the bond order is determined as the following:

$$\text{bond order} = \frac{\text{number of shared pairs}}{\text{number of bonding regions}} \quad (5.1)$$

where only the bonding regions in which the double bond can be placed are considered.

The two resonance structures of SO_2 are equivalent, so the bonding is the average of both forms and the double bond is shared equally by the two S–O bonds. The result is that neither bond is a single bond and neither is a double bond. The two sulfur-oxygen bonds in sulfur dioxide are of equal length, both being shorter than a S–O single bond but longer than a S=O double bond.

EXAMPLE:

The bond order of each of the bonds in SO_2 involved in the resonance is

$$\text{BO} = \frac{(3 \text{ shared pairs})}{(2 \text{ bonds})} = 1.5$$

Bonding electrons that are shared among more than two atoms are sometimes represented by dotted lines in the Lewis structure. The following shows that the two bonds are identical and have bond orders of $3/2$.

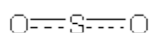


Figure 5.10

5.7-6. Bond Order is a Bond Property, Not a Molecular Property

Bond orders apply to bonds, not molecules.

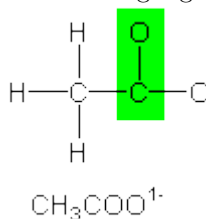
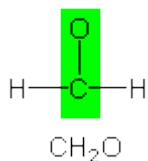
A common misconception among students is that molecules have bond orders. They do not; bonds have bond orders. This misconception arises because all of the bonds are identical in so many of our examples. Thus, it is incorrect to state that the bond order of SO_2 is 1.5; rather, it should be stated that the bond order of each bond in SO_2 is 1.5.

Resonance is important when a multiple bond can be placed in more than one position. In these cases, the bond order of each bond that is affected by the resonance is given by Equation 5.1. However, Equation 5.1 applies only to the bonding regions involved in the resonance. This distinction is the focus of the following exercise.

5.7-7. Bond Order Exercise

EXERCISE 5.9:

The Lewis structure of each of the following skeletal structures requires one more shared pair. Decide how to place the shared pair and then determine the bond order of the highlighted bond.



5.8 Formal Charge and Oxidation State

Introduction

In Chapter 4, we showed how to determine oxidation states of the atoms in a substance without knowledge of the Lewis structure of the substance. However, electron counting can be facilitated with a Lewis structure. By comparing the number of electrons around an atom in a Lewis structure with the number of valence electrons in the unbound atom, we can assign a charge to the atom in a molecule or ion. Oxidation states assign charge by assuming that the bonds are ionic. In this section, we introduce formal charge, which assigns charge by assuming that the bonds are covalent.

Prerequisites

- 3.1 Valence Electrons (Determine the number of valence electrons that an atom has.)

Objectives

- Distinguish between formal charge and oxidation state.
- Predict the formal charge on an atom by counting the number of bonds to the atom.
- Use formal charge to predict the preferred Lewis structure from several resonance forms.
- Determine oxidation states by electron counting.
- Distinguish between the oxidation states determined from Lewis structure and those determined by the oxidation state rules given in Chapter 4.

5.8-1. Regions of Charge in Molecules

The charge on an atom in a molecule lies between its formal charge and its oxidation state. It lies closer to the oxidation state when the bonds are very polar, but closer to the formal charge if they are not.

The charge distribution in bonds is usually asymmetric because the bonds are polar. This asymmetry introduces regions of charge in the molecule. These regions greatly influence both the physical and chemical properties of the molecule. Determining where the charge resides is an important challenge to the chemist. In this section, we show how to determine those regions in the two extremes of purely ionic and purely covalent bonding. The actual situation depends upon the polarity of the bonds and will lie somewhere between the two limits.

The charge that is assigned to an atom in a molecule equals the number of valence electrons in the free atom minus the number of valence electrons assigned to the atom in the molecule. The number of valence electrons in the free atom (VE) is given by the atom's group number. The number of electrons assigned to the atom in the molecule is the number of nonbonding electrons (NB) plus those bonding electrons (BE) that are assigned to it. Thus, the charge on atom A is given as

$$q_A = \text{VE} - (\text{NB} + a\text{BE})$$

where (NB + aBE) is the number of electrons (nonbonding and bonding) that are assigned to the atom. The manner in which *a* is determined and the name of the resulting charge depend upon the type of bonding that is assumed.

- The **formal charge (FC)** on an atom is the charge that the atom would have if the bonds were assumed to be purely covalent, so each atom is assigned half of the bonding electrons. In this case, $a = 1/2$ for each bond. Note that non-zero formal charges are shown within circles to distinguish them from actual charges.
- The **oxidation state (OX)** of an atom is the charge that the atom would have if the bonds were assumed to be ionic, so each atom is assigned all or none of the bonding electrons in each bond. In this case, $a = 0$ for those bonds in which the atom is the less electronegative atom or $a = 1$ for those bonds in which it is the more electronegative.

5.8-2. Oxidation State vs. Formal Charge Videos

A video or simulation is available online.

5.8-3. Formal Charge

Formal charge is the charge an atom would have if the bonds were purely covalent. It can be determined by electron counting.

The **formal charge** is the charge an atom would have if the bonds were purely covalent. This means that one electron from each bonding pair is assigned to each atom in the bond. Consequently, only half of the bonding electrons around an atom are assigned to it. That is, $a = \frac{1}{2}$, and the formal charge on atom A is

$$FC_A = VE - \left(NB + \frac{1}{2} BE \right)$$

Each bond contains two electrons, so one-half of the bonding electrons equals the number of bonds (B). Thus, the formal charge on atom A can also be expressed by

$$FC_A = VE - (NB + B) = VE - NB - B$$

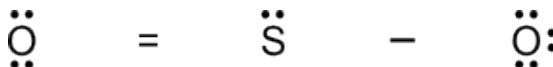
The formal charge on an atom is placed in a circle near the atom. Zero formal charges are not shown. Thus, formal charges of +1, -1, +2, and -2 would be represented by the following.



Figure 5.11

EXERCISE 5.10:

Assign electrons to each of the following and determine their formal charge.



Valence Electrons	_____
Non-Bonding	_____
Bonding	_____
Formal Charge	_____

The Lewis structure of SO₂ that includes the formal charge is shown in the following section.

5.8-4. Lewis Structure of SO₂ with Formal Charge

In the previous exercise, we showed that the sulfur atom in SO₂ has positive formal charge, the oxygen with the single bond had negative formal charge, and the oxygen with the double bond had no formal charge. Thus, the Lewis structures of the two resonance forms that show formal charge are shown in Figure 5.12.



Figure 5.12: Formal Charge in SO₂

5.8-5. Formal Charge and the Number of Bonds

Zero formal charge results when the number of bonds to an atom equals the number of unpaired electrons in its Lewis symbol.

The formal charge of an atom depends upon the number of bonds to the atom—the greater the number of bonds, the more positive the formal charge. Note that when counting bonds, double and triple bonds count as two and three bonds, respectively. The following figures give the formal charge of some common elements as a function of the number of bonds in which it is involved. The number of bonds resulting in zero formal charge is **bolded**.

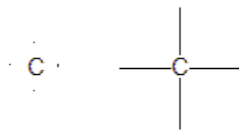


Figure 5.13

Sharing the unpaired electrons in the Lewis symbol results in zero formal charge for an atom. The Lewis symbol of carbon shows four unpaired electrons, so **carbon has zero formal charge when it is involved in four bonds**. Nonzero formal charge is hardly ever assigned to carbon, so a very good rule to use in drawing Lewis structures is that carbon atoms always have four bonds.

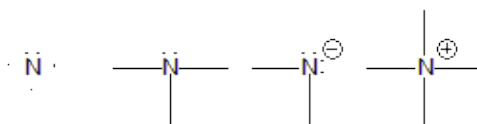


Figure 5.14

The Lewis symbol of nitrogen shows three unpaired electrons, so **nitrogen has zero formal charge when it is involved in three bonds**. Thus, nitrogen usually has three bonds to it, but it is also frequently found with four bonds and positive formal charge, e.g., NH_4^{1+} , the ammonium ion. Occasionally, it has only two bonds, in which case it carries a negative formal charge.

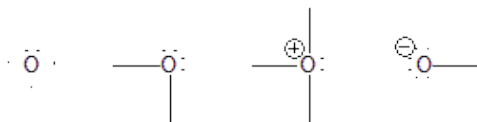


Figure 5.15

The Lewis symbol of oxygen shows two unpaired electrons, so **oxygen has zero formal charge when it is involved in two bonds**. Thus, oxygen usually has two bonds to it, but it is also frequently found with one bond and negative formal charge, e.g., OH^{1-} , the hydroxide ion. Occasionally, it has three bonds (H_3O^{1+}), in which case it carries a positive formal charge.



Figure 5.16

The Lewis symbol of fluorine shows only one unpaired electron, so **fluorine has zero formal charge when it is involved in only one bond**. Adding a second bond to a fluorine atom would produce a positive formal charge, but F is the most electronegative atom, so positive formal charge is never placed on it. Thus, F has one and only one bond in all of its compounds.

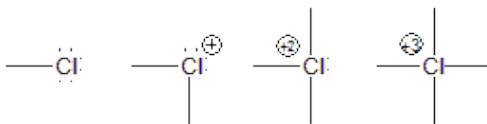


Figure 5.17

The other halogens can have more than one bond in situations where they are bound to a number of more electronegative atoms (O or F). However, a good rule to follow is that **double and triple bonds are not drawn to halogens because they place positive formal charge on these relatively electronegative elements.**

5.8-6. Structure and Formal Charge

Lewis structures that minimize formal charge are preferred.

Formal charge can be used to determine the best Lewis structure in cases where more than one Lewis structure can be drawn because charge separation (creating centers of positive and negative charge) requires energy (Coulomb's law). Thus, Lewis structures with no formal charge are favored over those that do contain formal charge.

The best Lewis structure is the one in which

- all formal charges are closest to zero and
- negative formal charge resides on the more electronegative atoms.



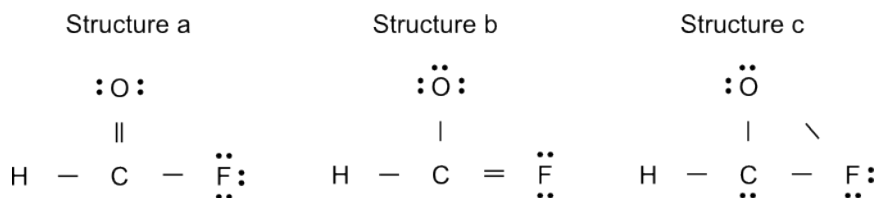
Figure 5.18: Using Formal Charge to Choose between Resonance Structures of CO₂

Although two Lewis structures can be drawn for CO₂, only structure a is important because it contains less formal charge.

5.8-7. Formal Charge Exercise

EXERCISE 5.11:

Determine the formal charges on each atom in the following Lewis structures of FCHO.



Structure a

Structure b

Structure c

O = _____

O = _____

O = _____

H = _____

H = _____

H = _____

C = _____

C = _____

C = _____

F = _____

F = _____

F = _____

Note that the oxygen atom in the last structure has both an C–O and an O–F bond.

Based on the formal charges, the preferred structure is which of the following?

Structure a

Structure b

Structure c

5.8-8. Oxidation States

Oxidation state is the charge the atom would have if the bonds were ionic. It can be determined by electron counting.

The **oxidation state** is the charge the atom would have if the bonds were ionic. This means that **all of the bonding electrons** in each bond are assigned to the more electronegative atom. That is, **a** = 0 or 1, and the oxidation state of atom A is

$$\text{OX}_A = \text{VE} - (\text{NB} + \sum \text{aBE})$$

where the sum is over all of the bonds to atom A and **a** is either 0 or 1 for each bond depending upon whether atom A is less or more electronegative than the other atom in the bond. In the case where the two atoms are identical, neither atom is more electronegative, so **a** = $\frac{1}{2}$ in this special case; i.e., the bond must be assumed to be covalent when the two electronegativities are identical. Thus, the value of a in each bond is determined as follows:

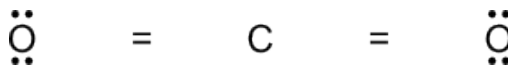
- a = 1 if the atom is the more electronegative atom in the bond.
- a = 0 if the atom is the less electronegative atom in the bond.
- a = $\frac{1}{2}$ if the atoms in the bond are identical, which means that the bond cannot be ionic.

Oxidation states determined with the method outlined above may differ from those determined using the guidelines presented in Section 4.4 because the latter method yields the average oxidation state of all of the atoms if the element being considered, while the method above applies only to the one atom being considered.

5.8-9. Counting Electrons for Oxidation State Exercise

EXERCISE 5.12:

Determine the oxidation state of each atom in CO₂.



Valence Electrons

Non-Bonding

Bonding

Oxidation State

5.8-10. Difference in Oxidation State Methods

The oxidation state of an atom, determined from the rules in Chapter 4, yields the average oxidation states of all the atoms of the element be considered, while the electron counting procedure outlined in this section produces the oxidation states of the individual atom being considered.

The oxidation states determined for the carbon and oxygen atoms in CO₂ are the same whether the method used in Section 4.4 or electron counting is used because the oxidation states of the two oxygen atoms are identical. In cases where the oxidation states of two or more different atoms of the same element are different, the two methods may yield different results because the oxidation state determined by the method given in Section 4.4 is the average of the oxidation states, while that determined by electron counting applies only to the individual atom being considered. Two examples where the two methods differ are given in the following exercise.

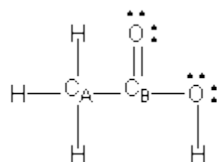
5.8-11. Differences in Oxidation State Methods Exercise

EXERCISE 5.13:

What is the average oxidation state of the C atoms in $C_2H_4O_2$ as determined by the rules outlined in Section 4.4?

$OX_C =$ _____

Use the method described in this chapter to determine the oxidation state of each carbon atom in acetic acid, which has the following Lewis structure:



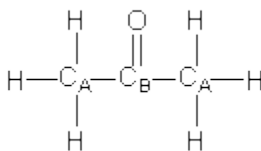
$OX_{CA} =$ _____

$OX_{CB} =$ _____

What is the average oxidation state of the C atoms in C_3H_6O ? Express your answer in decimal form.

$OX_C =$ _____

Use the method described in this chapter to determine the oxidation state of each carbon atom in C_3H_6O , which has the following Lewis structure:



$OX_{CA} =$ _____

$OX_{CB} =$ _____

5.9 Practice with Lewis Structures

Introduction

Practice drawing Lewis structures in this section.

5.9-1. Lewis Structure of SO_3 Exercise

EXERCISE 5.14:

Draw the Lewis structure of SO_3 , and indicate all nonzero formal charge.

ER = _____

VE = _____

SP = _____

How many resonance structures are there?

What is the formal charge on the sulfur atom?

5.9-2. Lewis Structure of SO_3^{2-} Exercise

EXERCISE 5.15:

Draw the Lewis structure of the following molecules and ions. Indicate all nonzero formal charge.

When dealing with ions, remember that negative charge increases the number of valence electrons, while positive charge decreases the number of valence electrons.

ER = _____ VE = _____ SP = _____

What is the formal charge on the sulfur atom?

5.9-3. Lewis Structure of N_3^{1-} Exercise

EXERCISE 5.16:

Draw the Lewis structure of N_3^{1-} , indicating the formal charge on each atom.

ER = _____ VE = _____ SP = _____

What are the formal charges on the central and terminal N atoms?

central _____ terminal _____

5.9-4. Lewis Structure of H_2O Exercise

EXERCISE 5.17:

Draw the Lewis structure of H_2O , indicating the formal charge on each atom.

ER = _____ VE = _____ SP = _____

What is the formal charge on the O atom?

5.9-5. Lewis Structure of SO_2 Exercise

EXERCISE 5.18:

Draw the Lewis structure of SO_2 , indicating the formal charge on each atom.

ER = _____ VE = _____ SP = _____

What is the formal charge on the S atom?

5.9-6. Lewis Structure of NO_3^{1-} Exercise

EXERCISE 5.19:

Draw the Lewis structure of NO_3^{1-} , indicating the formal charge on each atom.

ER = _____ VE = _____ SP = _____

What is the formal charge on the N atom?

5.10 Exercises and Solutions

Links to view either the end-of-chapter exercises or the solutions to the odd exercises are available in the HTML version of the chapter.