Formula Weights

Calculation of Formula Weights

The formula weight (sometimes called the molecular weight) of a compound or ion is the sum of the atomic weights of all elements in the compound or ion, with each element's atomic weight being multiplied by the number of atoms of that element occurring in the formula.

Moles of Compounds

The mole was defined as 6.02 X 1023 items. In that section, we talked about moles of atoms and you learned that one mole of a particular element has a mass in grams equal to the element's atomic weight. We can also have moles of compounds or of ions. One mole of a compound or an ion will have a mass in grams equal to the formula weight of that compound or ion. In Example 6.8 we calculated the formula weight of sulfuric acid to be 98.09 amu thus it follows that one mole of sulfuric acid has a mass of 98.09 g. The formula of a compound also tells how many moles of a particular element are contained in one mole of the comp und For example, one mole of sulfuric acid contains:

2 mol hydrogen atoms, weighing 2(1.008 g) or 2.016 g

1 mol sulfur atoms, weighing 1(32.07 g) or 32.07 g

4 mol oxygen atoms, weighing 4(16.00 g) or 64.00 g

Note that these individual masses add up t our calculated formula weight for the acid. This relationship between mass and moles of a compound is often used as a conversion factor in solving problems.

Example:

How many atoms of xygen are in 0.262 g carbon dioxide, CO_2?

Wanted: ? atoms oxygen

Given: 0.262 g arbon dioxide

Conversion factors
The formula weight of carbon dioxide is:

carbon 1x12.01 = 12.01
Oxygen 2x16.00 = 32.00
Total: 44.01 amu (for CO_2)

Equation

$$? \text{ atoms O} = 0.262 \text{ g } CO_2 \times \frac{1 \text{ mol } CO_2}{44.01 \text{ g } CO_2} \times \frac{2 \text{ mol}}{1 \text{ m}}$$

$$\times \frac{6.02 \times 10^{23} \text{ atoms}}{1 \text{ mol atoms}}$$

Answer: 7.17×10^{23} atoms O

In this example , notice that each factor involving a mole states the chemical composition of the mole: "1 mol CO2" and "2 mol O atoms." As problems become incr asi gly complex, this bookkeeping habit becomes especially important. Notice also that t e example deals with atoms of oxygen; we are not concerned here with the fact that oxygen exists in nature as a diatomic molecule, O2.

Percent Composition

Percent means parts per hundred. The percent composition of a compound is the number of grams of each element or group of elements in 100 g of the compound, expressed as a percent.

$$\text{Percent element} = \frac{\text{g element}}{\text{g compound}} \text{ X } 100\%$$

For example, the percent c mpos tion of potassium chloride, KCl, can be calculated from the atomic weights of potassium and chlorine and the formula weight of KCl.

Formula weight of KCl: 39.10 g + 35.45 g = 74.55 g

$$\text{Perc nt potassium: } \frac{39.10 \text{ g K}}{74.55 \text{ g KCl}} \text{ X } 100\% = 52.45\% \text{ potassium}$$

Percent chlorine: $\frac{35.45 \text{ g Cl}}{74.55 \text{ g KCl}}$ X 100% = 47.55% chlorine

Example:

Calculate the percent composition of carbon tetrachloride, CCl_4

Solution
The formula weight of carbon tetrachloride is:

carbon	12.01 x 1 =	12.01
chlorine	35.45 x 4 =	141.8
		153.8 amu

$$\text{Percent C} \quad \frac{12.01 \text{ g C}}{153.8 \text{ g } CCl_4} \text{ x100\% = 7.81\%C}$$

$$\text{Percent Cl} \quad \frac{141.8 \text{ g Cl}}{153.8 \text{ g } CCl_4} \text{ x100\% = 92 19\%Cl}$$

It is always wise to check these percent calculations by assuring yourself that they add up to 100% as they do here.

Percent Composition

The empirical formula of a compound expresses a ratio between the numbers of atoms of different elements present in a mole ule of the compound. This ratio is a mole ratio as well as a ratio between numbers of atoms. From the formula it is possible to calculate the percent composition of a compound. Going in the opposite direction from the composition of a compound, it is possible to calculate its empirical formula. Consider the compound chloroform. The percent composition of chloroform is 10.06% carbon, 0.85% hydrogen, and 89.09% chlorine. We know then that 100 g chloroform contain 10.06 g carbon, 0.85 g hydrogen, and 89.09 g chlorine. This weight relationship can be converted to a mole ratio by the following calculations:

$$\text{carbon} \quad 10.06 \text{ g C X } \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 0.8376 \text{ mol C}$$

$$\text{hydrogen} \quad 0.85 \text{ g H X } \frac{1 \text{ mol H}}{} = 0.84 \text{ mol H}$$

$$\text{chlorine} \quad 89.09 \text{ g Cl} \times \frac{1 \text{ mol Cl}}{35.45 \text{ g Cl}} = 2.513 \text{ mol Cl}$$

These calculations show that the mole ratio between the elements in chloroform is 0.84 mol C to 0.84 mol H to 2.51 mol Cl. This ratio can be expressed by the formula:

$C_{0.8376}H_{0.84}Cl_{2.513}$

However, formulas by definition can contain only whole numbers of atoms. The ratio can be changed to whole numbers by dividing each subscript by the smallest subscript, giving the formula of chloroform as:

$C_{0.8376/0.8376}H_{0.84/0.8376}Cl_{2.513/0.8376}$ or $CHCl_3$

Empirical versus Molecular Formulas

The formulas we have calculated in the preceding section express the simplest atomic ratio between the elements in the compound. Such formulas are called empirical formulas. An empirical formula does not necessarily represent the actual numbers of atoms present in a molecule of a compound; it represents only the ratio between those numbers. The actual numbers of atoms of each element that occur in the smallest freely existing unit or molecule of the compound is expressed by the molecular formula of the compound. The molecular formula of a compound may be the empirical formula, or it may be a multiple of the empirical formula. For example, the molecular formula of butene, C4H8, shows that each freely existing molecule of butene contains four atoms of carbon and eight atoms of hydrogen. Its empirical formula is CH2. One molecule of ethylene (molecular formula C2H4) contains two atoms of carbon and four atoms of hydrogen. Its empirical formula is CH2. Both have the same empirical formula, yet they are different compounds with different molecular formulas. Butene is C4H8, or four times the empirical formula; ethylene is C2H4, or twice the empirical formula.

Table below shows three groups of compounds. Within each group, the compounds have the same empirical formula and percent composition but different molecular formulas. That they are different compounds is shown by their different boiling points.

Compounds with the same empirical formula but different molecular formulas			
Empirical formula	**Compound**	**Molecular formula**	**Boiling point, °C**

CH (92.2% C; 7.8% H)	acetylene	C_2H_2	-84
	benzene	C_6H_6	80
CH_2 (85.6% C; 14.4% H)	ethylene	C_2H_4	-103
	butene	C_4H_8	-6.3
	cyclohexane	C_6H_{12}	80.7
CH_2O (40.0% C; 6.7% H; 53.3% O)	formaldehyde	CH_2O	-21
	acetic acid	C_2H_4O	117
	glyceraldehyde	$C_3H_6O_3$	140

The molecular formula of a compound can be determined from the empirical formula if the formula weight, or molecular weight, is known.

wo kinds of data are needed to determine the molecular formula of a compound: (1) its composition, from which we can calculate its empirical formula, and (2) its molecular weight. The molecular weight will be a multiple of the empirical formula weight. The molecular formula is the same multiple of the empirical formula.

The Chemical Bond

The atoms of a compound are held together by chemical bonds formed by the interaction of electrons from each atom. According to the octet rule Section 5.7C1, atoms bond together to form molecules in such a way that each atom participating in a chemical bond acquires an electron configuration resembling hat of the noble gas nearest it in the periodic table. Thus the outer shell of each bonded atom wi l ontain eight electrons (or two electrons for hydrogen and lithium).

The simplest chemical bond i that formed between two hydrogen atoms. Each hydrogen atom has one electron. As the two atoms approach each other, the nucleus of one atom attracts the electron of the oth r. Eventually the two orbitals overlap, becoming a single orbital containing two electrons (se Figure below).

This orbital en ompasses space around both nuclei. Although the electrons may be in any part of this orbital, we can predict that they are most likely to be in the space between the nuclei, shi lding one nucleus from the other and being attracted by both. In the resulting molecule, both toms have two electrons and a filled outer (valence) shell. These shared electrons form a bond betw en the two atoms. This chemical bond is a covalent bond, a pair of electrons shared between two atoms. When this bond forms, energy is released. This release of energy shows that the molecule of hydrogen is more stable than the separate atoms.

Covalent, Polar covalent, and Ionic Bonds

Because the hydrogen molecule contains two identical atoms, it can be assumed that the bonding

electrons in this covalent bond are shared equally by these atoms.

Most chemical bonds are not between like atoms but form between atoms of different elements. These bonds are slightly different from that in a hydrogen molecule. Consider the bond between hydrogen and chlorine: Again both atoms require one more electron to satisfy the octet rule. As the atoms come together, their orbitals overlap and the two atoms share a pair of electrons.

However, the hydrogen-chlorine bond differs from the hydrogen-hydrogen bond because the electrons are not shared equally between hydrogen and chlorine but are more strongly a trac ed to the chlorine. They are more apt to be found close to the chlorine than close to the hydrogen. Because of this unequal sharing, the chlorine atom assumes a slightly negative character and the hydrogen atom a slightly positive character. We say that the bond is polar covalen meaning that the bond consists of electrons shared between two atoms (therefore covalent but shared unequally, thus giving the bond a positive and a negative end, a condition described by the term polar. We can also say that the bond is a dipole or has a dipole moment meaning that the bond has a positive end (the hydrogen) and a negative end (the chlorine) The more negative atom in a bond is often shown with the symbol and the more positive atom is shown with the symbol. The bond between hydrogen atoms is nonpolar (has no positive and negative ends) covalent (electrons are shared).

An ionic bond is the extreme case of a polar covalen bond. In an ionic bond, the bonding atoms differ so markedly in their attraction for electrons tha one or more electrons are essentially transferred from one atom to the other. The sodium-chlorine bond is an example of an ionic bond. The attraction of the chlorine atom for ele trons is so much greater than that of a sodium atom that the 3s electron of sodium is said to be completely transferred from sodium to chlorine.

In summary, then, the three types of bonds are:

(1) a covalent bond, in which the el ctrons are shared equally;
(2) a polar covalent bond, in which he electrons are shared unequally; and
(3) an ionic bond, in which electrons are transferred from one atom to the other.

Predicting Bond Typ ; Electronegativity
It is possible to predict he type of bond that will form between two elements. The farther apart (left to right) he two elements are in the periodic table, the more ionic and the less covalent will be the bond between them. Thus, metals react with nonmetals to form ions joined predominantly by ionic bonds. Bonds with the highest degree of ionic character are formed by the reaction of alkali or alka ine earth metals with the halogens, particularly with fluorine or chlorine. Nonmet ls react together to form covalent bonds. If the bond is between two neighbors in the table, the bond will be less polar than if the nonmetals are separated by other element. For example, carbon and nitrogen are in neighboring columns, and carbon and fluorine are in Groups 4 and 7, respectively. A carbon-nitrogen bond will be less polar than a carbon-fluorine bond. Finally, if the two atoms are of the same element, as in a hydrogen molecule or a chlorine molecule, the bond will be essentially nonpolar.

The concepts in the previous paragraph have been quantified by the concept of electronegativity.

The electronegativity (EN) of an element measures its attraction for the electrons in a chemical bond.

One scale of electronegativity was developed by the American chemist Linus Pauling (b. 1901). On this scale, fluorine, the most electronegative element, has an electro negativity of 4.0. Carbon has an electro negativity of 2.5, hydrogen, 2.1, and sodium 0.9. Figure below shows the electro negativities of the elements with which we deal most often.

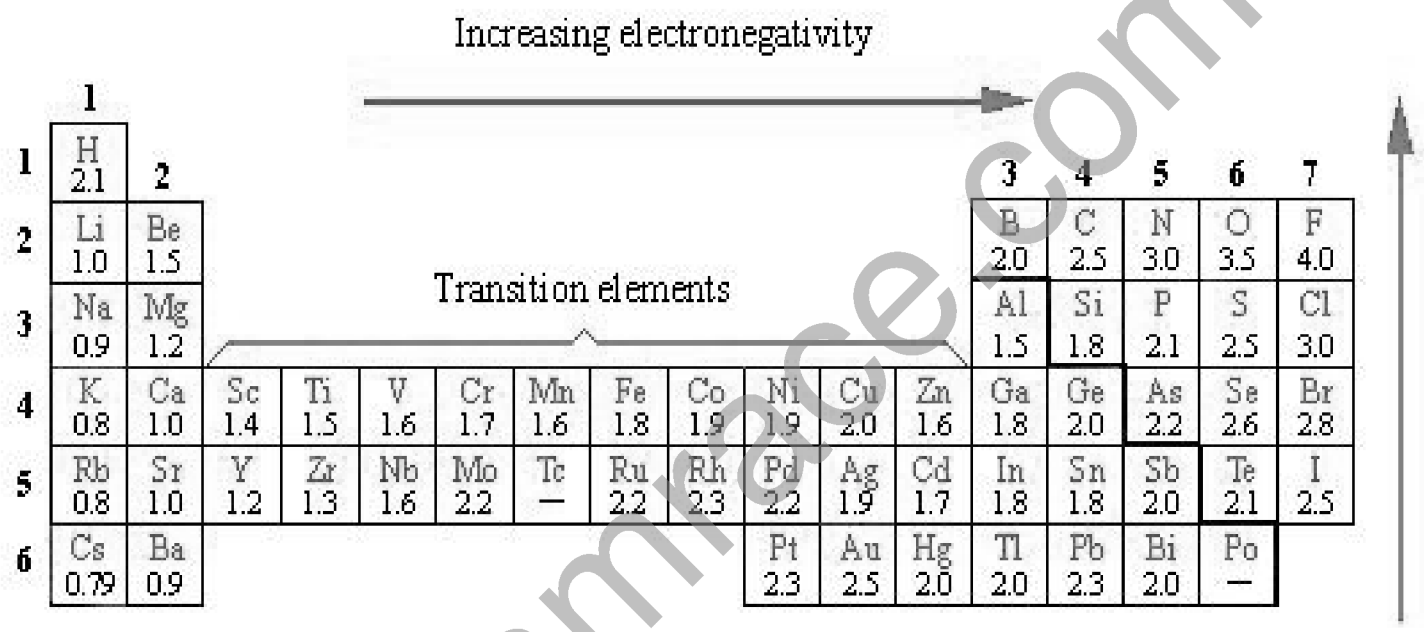


FIGURE 7.3 Electronegativities of some elements (Pauling scale).

Notice that the electronegativit of most metals is close to 1.0 and that the electronegativity of a nonmetal, although dependent on its location in the table, is always greater than 1.0. In general, electronegativity increases from bottom to top in a column and from left to right across a period.

Note that the noble gases, Group 8, do not appear in this table. Electronegativity measures the relative attraction of atoms for electrons in chemical bonds. The noble gases react differently from the h log ns and other nonmetals. The concepts of electronegativity do not apply to them.

When two at ms combine, the nature of the bond between them is determined by the difference betw en their electronegativities (denoted EN). If the atoms forming the bond differ in electronegativity by more than 1.7 units, the bond will be at least 50% ionic (referred to as percent ionic character); we treat such a bond as wholly ionic. If the values differ by less than 0.4 units, we consider the bond to be wholly nonpolar. If the difference is between 0.4 and 1.7 electronegativity units, the bond is considered to be polar covalent. Remember that electronegativities have been calculated from fairly imprecise data for particular bonding situations.

Electronegativity is useful in predicting the nature of a bond and for comparing bond types, but

the prediction is only an approximation. Remember too that no sharp distinction exists between ionic, polar covalent, and nonpolar bonds; rather, they form a continuum. Even the most ionic bond (between cesium and fluorine) has some covalent character, and only bonds between atoms of the same element have no ionic character.

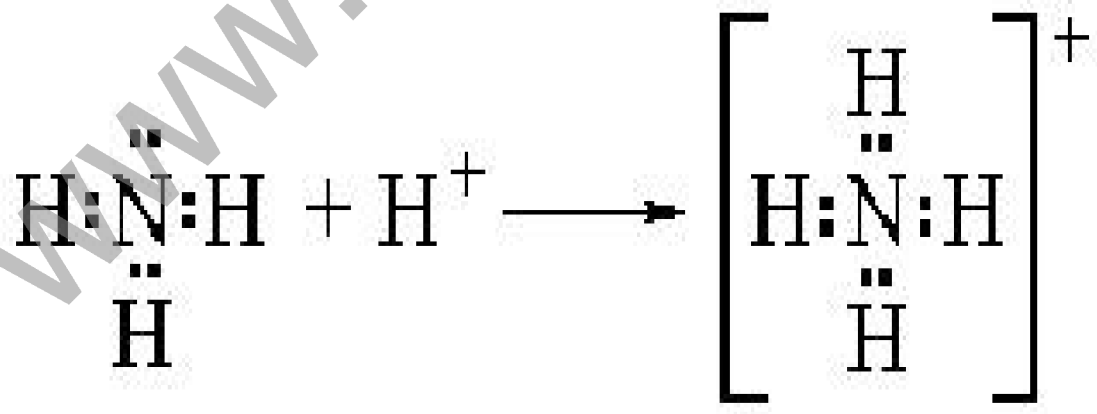
In these bonds, the atom with the higher electronegativity will be the negative end of the bond and, in extreme situations, will become the negative ion. To show these partial charges on a polar covalent bond, we mark the positive end of the bond with a and the negative end of the bond with a. Table given below summarizes these data.

TABLE : Guidelines for predicting bond type from electronegativity data.

Difference in electronegativity (EN)	**Type of bond predominant**	**Example**	**EN**	**More positive atom**
> 1.7	ionic	NaCl	2.1	sodium
0.4 - 1.7	polar covalent	C-Cl	1.5	carbon
< 0.4	covalent	H-H	0.0	neither
		C - H	0.4	n ither

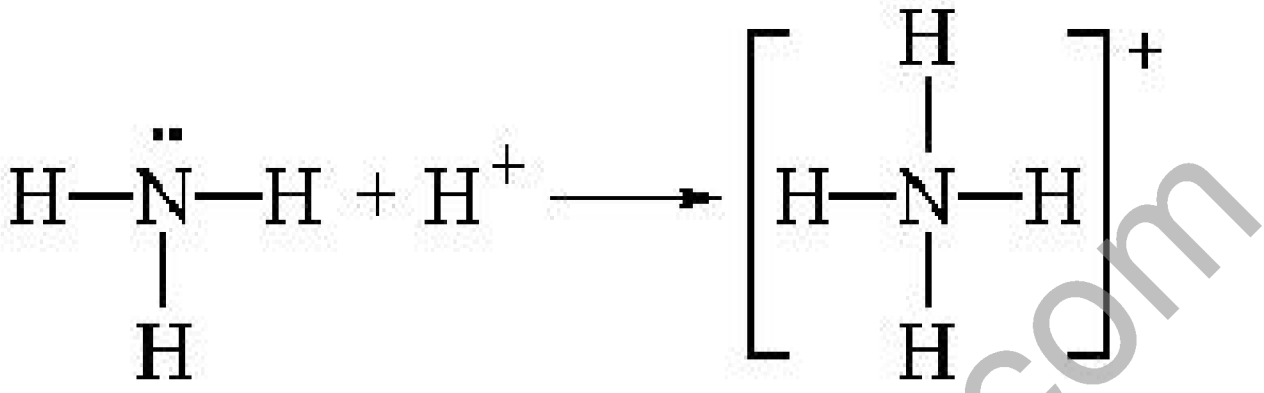
\ Single, Double, and Triple Bonds

A covalent bond represents the sharing of electrons between two atoms. Single bonds result from the sharing of a single pair of elect ons. The covalent bonds shown in Figure 7.2 are single bonds. Usually, as in the hydrogen molecule, each atom forming the bond contributes one electron to the bond. Some imes, as in the reaction of ammonia, NH3, with a hydrogen ion, H+, to form the ammonium ion, NH4+, both electrons come from the same atom:



It is common practice to use a dash to represent a pair of electrons. In this text we will use dashes for shared electrons and dots for unshared (lone-pair) electrons. With this notation, the above

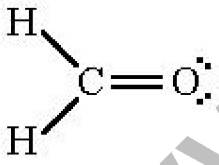
equation is written:



In the ammonia molecule, the nitrogen shares a pair of electrons with each of the three hydrogen. In each bond, one electron comes from nitrogen and one from hydrogen. The nitrogen still has an unshared pair of electrons. A hydrogen ion has no electrons; the single hydrogen electron was lost when the atom became an ion and gained a positive charg . When the hydrogen ion bonds to the ammonia molecule, both electrons of the bond come from the nit ogen.

A bond in which one atom has donated both electron is often referred to as a coordinate covalent bond. It is most important to realize that the different name refers only to the method of formation. Once the ammonium ion is formed, all hydrogen-nitrogen bonds in the ion are equivalent. Notice, too, that the entire ammonium ion now carries a positive charge, denoted by placing brackets around the ion and writing superscript +.

In addition to single bonds, there are double bonds and triple bonds. A double bond represents the sharing of four electrons by two atoms. The bond between carbon and oxygen is often a double bond, as in formaldehyde, CH_2O.



Here carbon is singly bonded to each of the hydrogens and doubly bonded to oxygen. Of this double bond two electrons have come from carbon and two from oxygen. The single carbon-hydrog n bonds are nonpolar (EN = 0.4); the double carbon-oxygen bond is polar covalent (EN = 1 0). Note that each atom in the diagram of formaldehyde now follows the octet rule. Each hydrogen has two electrons; the carbon and the oxygen have eight electrons each. Notice too that the oxygen has two pairs of unshared electrons. Such an unshared pair is sometimes known as a lone pair. We will see that the negative end of a polar bond often holds unshared electron pairs.

A triple bond is formed when two atoms share six electrons (three pairs). The nitrogen molecule contains a triple bond. Its structure is

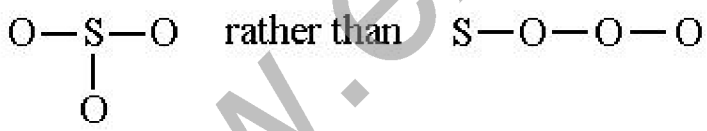
Each nitrogen donates three electrons to the bond and retains a lone pair.

Lewis Structures

A compound contains two or more atoms of different elements joined by chemical bonds. The properties of the compound depend on the arrangement of atoms in the compound and the types of bonds between them. To help in gaining this information for covalently bonded molecules, we draw structures for the molecules such as for hydrogen, ammonia, formaldehyde, and ni rogen. These structures are called Lewis structures. A Lewis structure shows each atom in the molecule or ion and its relationship to the other atoms. It also shows all bonding elect ons as well as those valence electrons that are nonbonding.

The Arrangement of Atoms

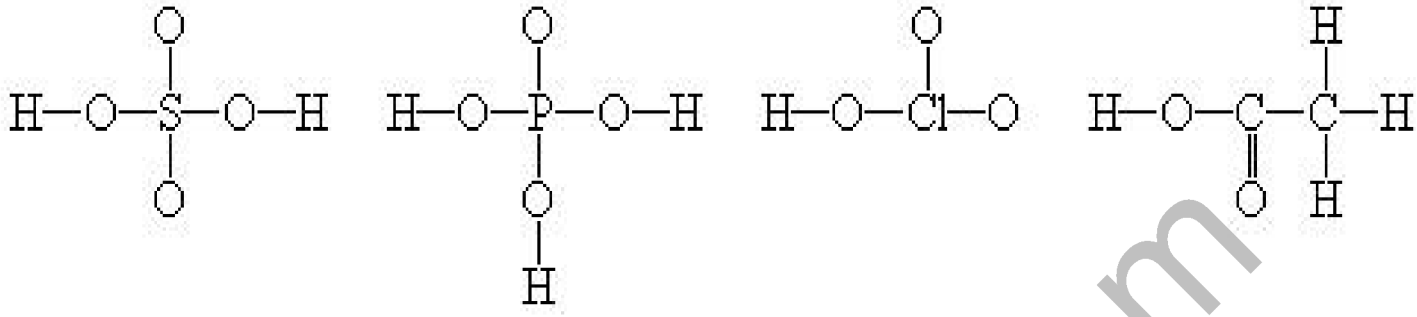
Most often the formula of a compound is written in a way that predicts the arrangement of its atoms. Each covalently bonded molecule or ion has one c ntral tom or a chain of central atoms. The central atom or chain of atoms will be the least elec roneg tive element in the structure. This chain is often of carbon atoms, although it may be of nitrogen or some other nonmetal. Methane, CH_4, has one central carbon atom. Butane, C_4H_{10} has a chain of four carbon atoms. The element symbols that directly follow the central atom in the f rmula indicate that these atoms are bonded to the central atom(s). Thus, methane, CH_4 has four hydrogen atoms bonded to its central carbon atom. Butane, C4H10, has ten hydrogen atoms bonded to the four carbon atoms. Formaldehyde, whose formula is written CH2O or HCHO, has two hydrogen atoms and one oxygen atom bonded to the central carbon atom. Methyl amine, CH3NH2, has three hydrogen atoms bonded to the carbon atom. The carbon atom is also bonded to a nitrogen atom, and two more hydrogen atoms are also bonded to the nitrogen atom.



If more than one arrangement of atoms seems possible, we choose the one with the most symmetry. In carbon dioxide, CO2, the atoms are arranged O - C - O, a more symmetrical arrangement than C - O - O. Similarly, sulfur trioxide, SO3 is written as

In showing the arrangement of atoms, keep in mind two things. Hydrogen rarely bonds to more than one atom. Halogens are usually bonded to only one atom. Only in polyatomic ions or molecules, such as bromate ion, BrO3-, or chloric acid, HClO3, are halogens the central atom and thus bonded to more than one other atom.

Oxyacids like H_2SO_4, H_3PO_4, $HClO_3$, and acetic acid are a little different. The acid hydrogens, those that are written at the beginning of the formula, are not bonded to the central atom but are bonded to oxygen. Therefore, these compounds have the atomic arrangements:



The Number and Placement of Electrons in Lewis Structures

The Lewis structure of a molecule or ion shows the arrangement of atoms and the distribution of electrons in that molecule or ion. In Section 7.2A, we showed how to predict the arrangement of atoms; in this section we show how to predict the number and distribution of electrons. Some of these electrons will be shared; some will be unshared. The number in each category can be determined using the following steps. Notice that in these examples all the atoms follow the octet rule. We will illustrate each step of this process using a molecule of formaldehyde, CH_2O.

1. Each atom in the molecule except hydrogen is assumed to require eight electrons; hydrogen will require only two. (See Section 5.7C1 on the octet rule exceptions.) Formaldehyde, CH_2O, will require electrons to fill 20 spaces.

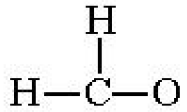
2(2)	+ 8	+ 8	= 20 spaces to fill
hydrogen	carbon	oxygen	

2. Each atom contributes its valence electrons toward filling these spaces. (Valence electrons were defined in Section 5.5D.) Formaldehyde has 12 available valence electrons:

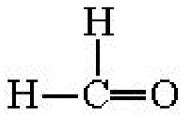
2(1)	+ 4	+ 6	= 12 valence electrons available
hydrogen	carbon	oxygen	

3. The difference between these numbers is the number of bonding electrons shared by two atoms. Formaldehyde will contain eight shared electrons: 20 - 12 = 8 shared electrons

4. The number of unshared electrons is the difference between the number of valence electrons available and the number of shared or bonding electrons. Formaldehyde will have 12 - 8 = 4 unshared electrons. Now we draw the Lewis structure. Having determined the arrangement of atoms, we place a pair of electrons between each set of neighboring atoms. For formaldehyde, we write

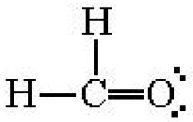


which uses six electrons and leaves two more electrons to be shared. These electrons will group with another pair to form a double bond. Carbon-hydrogen bonds are always single; therefore, the double bond will be between carbon and oxygen, giving the structure



Lewis Structures

5. The unshared electrons are then added where needed to give an octet. In the strucure for formaldehyde, we have four unshared electrons. Oxygen still does not have an octet, so the unshared electrons are added to the oxgygen, giving



This structure is the complete Lewis structure of formaldehyde.

Rules for drawing Lewis structures of molecules:

1. Draw skeleton of molecule.

   Least electronegative atom will be at center. Hydrogen and halogens will be at perimeter.

2. Calculate the following.

   Number of spaces to fill if each atom obeys octet rule (A)

   Total number of valence electrons available (V)

   Number of bonding electrons (B): B=A-V

   Number of nonbonding (unshared) electrons (N): N=V-B

3. Assign two bonding electrons to each bond. Assign any bonding electrons remaining to double or triple bonds between appropriate atoms (not hydrogen or halogen).

4. Assign nonbonding electrons (N) where needed to complete octets.

Lewis Structures of Ions

To draw the Lewis structure of an ion, we follow the same steps as for drawing the Lewis structure of a molecule with one exception: In calculating the number of valence electrons available, one additional electron i add d for each negative charge on the ion or one electron is subtracted for each positive charge on the ion. The entire structure is enclosed in brackets, and the charge is shown as a superscrip outside the brackets. This structure is the complete Lewis structure of formaldehyde

Resonance

As chemists began o w rk with Lewis structures, it became more and more obvious that, for a great many molecules and ions, no single Lewis structure provided a truly accurate representa on For example, a Lewis structure for the carbonate ion, CO32-, shows carbon bonded to three oxygen atoms by a combination of one double bond and two single bonds. Three possibl Lewis structures for CO32- are shown in Figure below. Each implies that one carbon oxygen bond is different from the other two. However, this difference in bonding is not the case; rather it has been shown that all three bonds are identical.

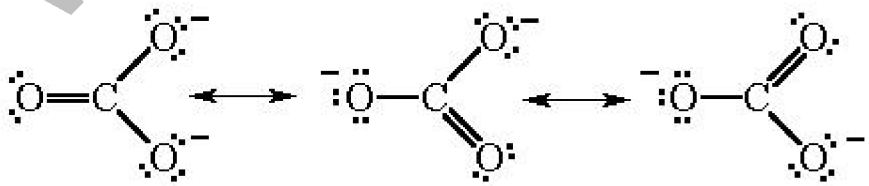


FIGURE : Three possible Lewis structures for the carbonate ion, CO3-2

To describe molecules and ions, like the carbonate ion, for which no single Lewis structure is adequate, the theory of resonance was developed by Linus Pauling in the 1930s. According to resonance theory, many molecules and ions are best described by drawing two or more Lewis structures and considering the real molecule or ion as a hybrid (composite) of these structures. The individual Lewis structures are called contributing structures. We show that the real structure is a hybrid of the various contributing structures by connecting them with double-headed arrows as in Figure below.

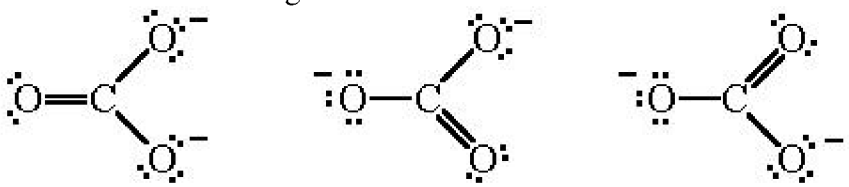


FIGURE : The carbonate ion can be represented as its three possibl contributing structures connected with double-headed arrows to imply resonance.

Remember that the carbonate ion, or any other compound we d scribe in this way, has one and only one real structure. The problem is that our systems of representation are not adequate to describe the real structures of molecules and ions. The res nance method is a particularly useful way to describe the structure of these compounds for it retains the use of Lewis structures with electron-pair bonds. We fully realize that the carbonate ion is not accurately represented by any single contributing structure

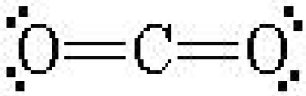
Bonding and Geometry

Bond Angles and the Shapes of Molecules

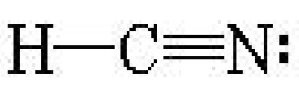
In the previous section a shared pair of electrons was presented as the fundamental unit of the covalent bond, and Lewis s uctu es were drawn for several small molecules and ions containing various combinations of single, double, and triple bonds. In this section, we use the valence-shell electron-pair repulsion (VSEPR) model to predict the geometry of these and other covalently bonded molecules and ns. The VSEPR model can be explained in the following way. We know that an atom has an outer shell of valence electrons. These valence electrons may be involved in the format on of single, double, or triple bonds, or they may be unshared. Each set of electrons, whether unshared or in a bond, creates a negatively charged region of space. We have already learned that l ke charges repel each other. The VSEPR model states that the various regions containing electrons or electron clouds around an atom spread out so that each region is as far fr m the others as possible.

Linear Molecules

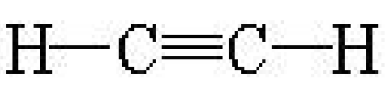
If a molecule contains only two atoms, those two atoms are in a straight line and thus form a linear molecule. Some three-atom molecules also have straight-line geometry. For example:



carbon dioxide



hydrogen cyanide

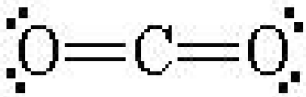


acetylene

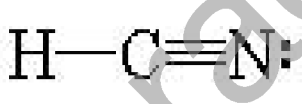
Notice that, in the Lewis structure of these molecules, the central atom(s) bonds with only two other atoms and has no unshared electrons. Only two electron clouds emerge from that central atom. For these two clouds to be as far away from each other as possible, they must be on opposite sides of the central atom, forming a bond angle of 180° with each other. An angle of 180° gives a straight line. The VSEPR theory says, then, that the geometry around a atom that has only two bonds and no unshared electrons is a straight line.

Structures with Three Regions of High Electron Density around the Central Atom

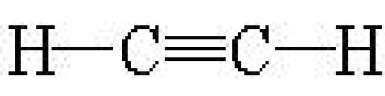
Look at the following Lewis structures:



carbon dioxide



hydrogen cyanide

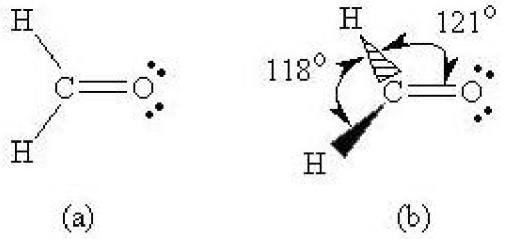


acetylene

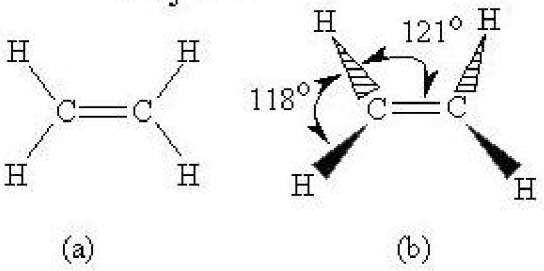
In these molecules, each central atom has three electron clouds emanating from it. In sulfur dioxide, the sulfur atom is bonded to two oxygen atoms and has one unshared pair of electrons. In formaldehyde and ethylene, each carbon atom has two single bonds to hydrogen, a double bond to another atom, and no unshared pair. The sulfur atom in sulfur dioxide and the carbon atom in ethylene and formaldehyde is surrounded by three clouds of high electron density. For these clouds to be as far as possible from one another, they will form a plane containing the central atom and will emanate from the central atom at angles of 120° to each other. The structure will be trigonal planar. The central atom will be in the center of the triangle, and the ends of the electron clouds at the corners of the triangle. If you experiment with a marshmallow as the central atom and three toothpicks as electron clouds, you can prove to yourself that the toothpicks are farthest apart when using a trigonal planar structure.

Note that the angles are not exactly 120° but are remarkably close to that predicted value.

Formaldehyde



Ethylene

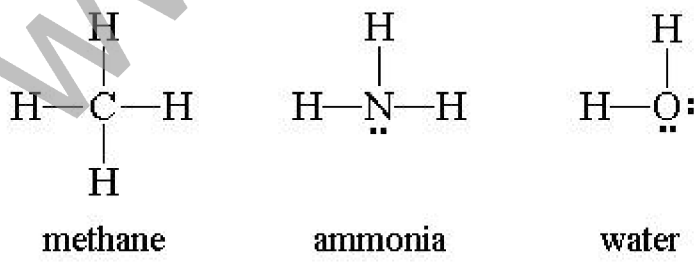


Although the electron clouds of these molecules give a trigonal planar shape around each carbon atom, one describes the geometry of a molecule only on the basis of the relationships between its atoms. A formaldehyde molecule is trigonal planar because it has an atom at the end of each electron cloud. The ethylene molecule has trigonal planar geometry around each of its carbon atoms. The whole molecule is planar, and its shape resembles two triangles joined point to point. In sulfur dioxide, there are three electron clouds around the sulfur. Only two of these connect two atoms. In the molecule, the oxygen-sulfur-oxygen atoms make a 120° angle. The molecule is bent.

A central atom surrounded by three clouds of high electron density will have trigonal planar geometry if it is bonded to three atoms. Its geometry will be called bent if it is bonded to two atoms and also has an unshared pair of electron.

Structures with Four Regions of High Electron Density around the Central Atom

The following Lewis structures show three molecules whose central atom is surrounded by four clouds of high electron density:



These molecules are alike in that each central atom is surrounded by four pairs of electrons, but

they differ in the number of unshared electron pairs on the central atom. Remember that, although we have drawn them in a plane, the molecules are three-dimensional and atoms may be in front of or behind the plane of the paper. What geometry does the VSEPR theory predict for these molecules?

Let us predict the shape of methane, CH4. The Lewis structure of methane shows a central atom surrounded by four separate regions of high electron density. Each region consists of a pair of electrons bonding the carbon atom to a hydrogen atom. According to the VSEPR model the e regions of high electron density spread out from the central carbon atom in such a way th t they are as far from one another as possible.

You can predict the resulting shape using a styrofoam ball or marshmallow and four toothpicks. Poke the toothpicks into the ball, making sure that the free ends of the toothpicks are as far from one another as possible. If you have positioned them correctly, the ngle between any two toothpicks will be 109.5°. If you now cover this model with four tria gular pieces of paper, you will have built a four-sided figure called a regular tetrahedron

According to the VSEPR model, the H - C - H bond angle in methane should be 109.5°. This angle has been measured experimentally and found t be 109.5°. Thus, the bond angle predicted by the VSEPR model is identical to that observ d. We s y that methane is a tetrahedral molecule. The carbon atom is at the center of a tetrahedron Each hydrogen is at one of the corners of the tetrahedron.

Structures with Four Regions of High Electron Density around the Central Atom

We can predict the shape of the ammonia molecule in exactly the same manner. The Lewis structure of NH3 shows a entral nitrogen atom surrounded by four separate regions of high electron density. Three of the e regions consist of a single pair of electrons forming a covalent bond with a hydrogen atom the fourth region contains an unshared pair of electrons. According to the VSEPR model, the four regions of high electron density around the nitrogen are arranged in a tetrahedral manner, so we predict that each H - N - H bond angle should be 109.5°. The observed bond angle is 107.3°. This small difference between the predicted angle and the observed angle can be explained by proposing that the unshared pair of electrons on nitrogen rep ls the adjacent bonding pairs more strongly than the bonding pairs repel each other.

Ammonia is not a tetrahedral molecule. The atoms of ammonia form a pyramidal molecule with nitrogen at the peak and the hydrogen atoms at the corners of a triangular base. Just as the unshared pair of electrons in sulfur dioxide contribute to the geometry of the molecule but are not included in the description of its geometry, the unshared pair of electrons in ammonia gives it a tetrahedral shape but its geometry is based only on the arrangement of atoms, which is pyramidal. Figure 7.10 shows the Lewis structure of the water molecule. In H2O, a central

oxygen atom is surrounded by four separate regions of high electron density. Two of these regions contain a pair of electrons forming a covalent bond between oxygen and hydrogen; the other two regions contain an unshared electron pair. The four regions of high electron density in water are arranged in a tetrahedral manner around oxygen. Based on the VSEPR model, we predict an H - O - H bond angle of 109.5°. Experimental measurements show that the actual bond angle is 104.5°. The difference between the predicted and observed bond angles can be explained by proposing, as we did for NH3, that unshared pairs of electrons repel adjacent bonding pairs more strongly than the bonding pairs repel each other. Note that the varia ion from 109.5° is greatest in H2O, which has two unshared pairs of electrons; it is smaller in NH3 which has one unshared pair; and there is no variation in CH4.

To describe the geometry of the water molecule, remember that the geometry of a molecule describes only the geometric relationships between its atoms. The three atoms of a water molecule are in a bent line like those of sulfur dioxide. We say the water molecule is bent.

A general prediction emerges from our discussions of the shapes of methane, ammonia, and water: Whenever four separate regions of high electron density s rround a central atom, we can accurately predict a tetrahedral distribution of electron clouds and bond angles of approximately 109.5°.

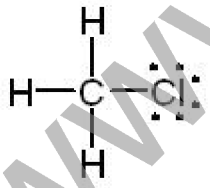
Example

Predict all bond angles in the following m lecules.

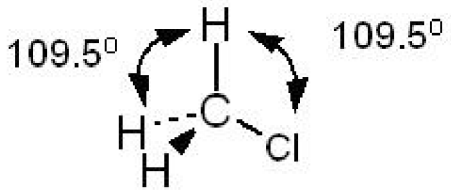
a. CH_3Cl b. CH_3CNl c. CH_3COOH

Solution

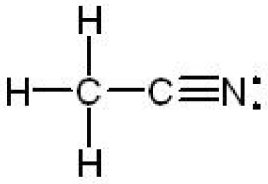
a. The Lewis structure of methyl chloride is:



In the Lewis structure of CH_3Cl carbon is surrounded by four regions of high electron density, each of which forms a single bond. Based on the VSEPR model, we predict a tetrahedral distribution of electron clouds around carbon, H - C - H and H - C - Cl bond angles of 109.5°, and a tetrahedral shape for the molecule. Note the use of doted lines to represent a bond projecting behind the plane of the paper and a solid wedge to represent a bond projecting forward from the plane of the paper.

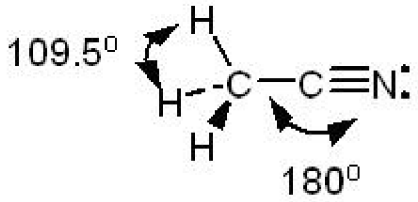


b. The Lewis structure of acetonitrile, CH_3CN is:

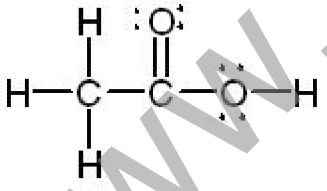


Example Continued

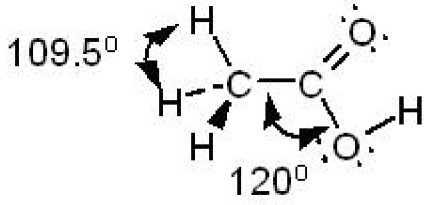
The methyl group, CH_3-, is tetrahedral. The carbon of the -CN group is in the middle of a straight line stretching from the carbon of the methyl gr up through the nitrogen.



c. The Lewis structure of acetic acid is:



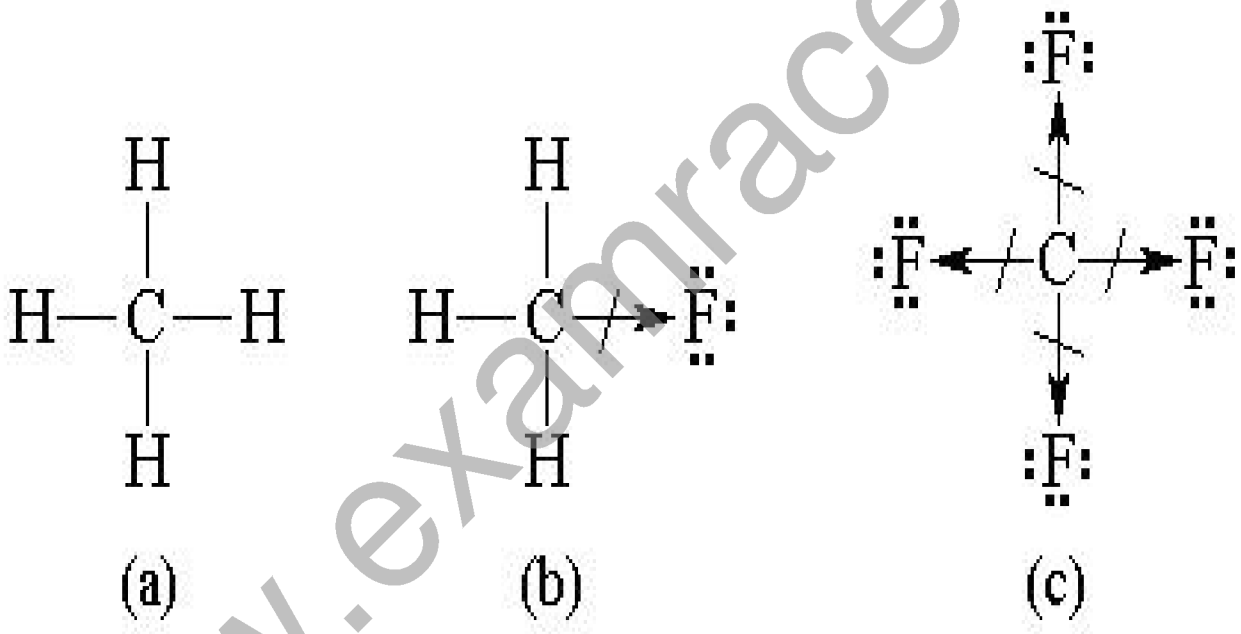
Bo h th carbon bonded to three hydrogens and the oxygen bonded to carbon and hydrogen are centers of tetrahedral structures. The central carbon will have 120 7deg bond angles.



The geometry around the first carbon is tetrahedral, around the second carbon atom is trigonal planar, and around the oxygen is bent.

The Polarity of Molecules

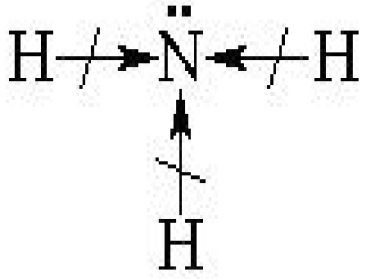
Some molecules contain only nonpolar bonds - for example, methane, CH4. Such molecules are nonpolar molecules. Other molecules contain polar bonds - that is, bonds between atoms whos electronegativities differ by more than 0.4 units. Whether these latter molecules are polar o nonpolar depends on the arrangement in space of these bonds and the resulting geometry of th molecules. If we picture the geometry of a molecule and show its polar bonds with an arrow () aimed at the more electronegative atom, we can usually obtain a picture of the molecule that indicates whether or not it is polar. Figure given below illustrates this method for several molecules.



Methane, which con ains no polar bonds, is clearly nonpolar. Methyl fluoride contains one polar bond between carbon (EN = 2.5) and fluorine (EN = 4.0). Methyl fluoride is a polar molecule; the negative nd of the dipole is at the fluoride atom. Now look at carbon tetrafluoride. It cont ins four polar carbon-fluorine bonds but they counteract one another, so the molecule itself is nonpolar. If the guy wires are correctly balanced against one another, the tower stays erect. (Compare the balanced pull of the carbon-fluorine bonds in carbon tetrafluoride.) If the guy wires are not balanced, the tower topples. (Compare the unbalanced pull of the carbon-fluorine bond in methyl fluoride.)

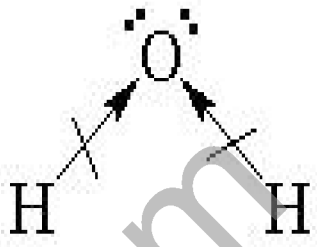
Notice that both ammonia and water have unshared electrons on the atom at the negative end of the dipole. These unshared electrons enhance the polarity of the bond to make these molecules

very polar.



(a)

(b)



(c)