2.2: Chemical Formulas

Learning Objectives

- To describe the composition of a chemical compound.

When chemists synthesize a new compound, they may not yet know its molecular or structural formula. In such cases, they usually begin by determining its **empirical formula**, the *relative* numbers of atoms of the elements in a compound, reduced to the smallest whole numbers. Because the empirical formula is based on experimental measurements of the numbers of atoms in a sample of the compound, it shows only the ratios of the numbers of the elements present. The difference between *empirical* and *molecular* formulas can be illustrated with butane, a covalent compound used as the fuel in disposable lighters. The molecular formula for butane is C_4H_{10}. The ratio of carbon atoms to hydrogen atoms in butane is 4:10, which can be reduced to 2:5. The empirical formula for butane is therefore C_2H_5. The **formula unit** is the *absolute* grouping of atoms or ions represented by the empirical formula of a compound, either ionic or covalent. Butane, for example, has the empirical formula C_2H_5, but it contains two C_2H_5 formula units, giving a molecular formula of C_4H_{10}.

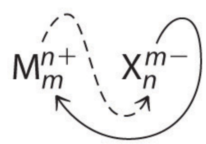
Because ionic compounds do not contain discrete molecules, empirical formulas are used to indicate their compositions. All compounds, whether ionic or covalent, must be electrically neutral. Consequently, the positive and negative charges in a formula unit must exactly cancel each other. If the cation and the anion have charges of equal magnitude, such as Na^+ and $Cl^−$, then the compound must have a 1:1 ratio of cations to anions, and the empirical formula must be NaCl. If the charges are not the same magnitude, then a cation:anion ratio other than 1:1 is needed to produce a neutral compound. In the case of Mg^{2+} and $Cl^−$, for example, two $Cl^−$ ions are needed to balance the two positive charges on each Mg^{2+} ion, giving an empirical formula of $MgCl_2$. Similarly, the formula for the ionic compound that contains Na^+ and $O^{2−}$ ions is Na_2O.

Note the Pattern

Ionic compounds do not contain discrete molecules, so empirical formulas are used to indicate their compositions.

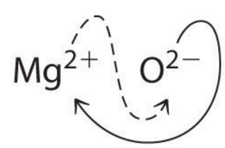
Binary Ionic Compounds

An ionic compound that contains only two elements, one present as a cation and one as an anion, is called a **binary ionic compound**. One example is $MgCl_2$, a coagulant used in the preparation of tofu from soybeans. For binary ionic compounds, the subscripts in the empirical formula can also be obtained by crossing charges: use the absolute value of the charge on one ion as the subscript for the other ion. This method is shown schematically as follows:



Crossing charges. *One method for obtaining subscripts in the empirical formula is by crossing charges.*

When crossing charges, you will sometimes find it necessary to reduce the subscripts to their simplest ratio to write the empirical formula. Consider, for example, the compound formed by Mg^{2+} and $O^{2−}$. Using the absolute values of the charges on the ions as subscripts gives the formula Mg_2O_2:



This simplifies to its correct empirical formula MgO. The empirical formula has one Mg^{2+} ion and one $O^{2−}$ ion.

Example 2.2.1

1. Ga^{3+} and As^{3-}
2. Eu^{3+} and O^{2-}
3. calcium and chlorine

Given: ions or elements

Asked for: empirical formula for binary ionic compound

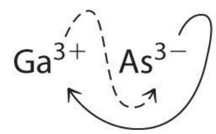
Strategy:

A If not given, determine the ionic charges based on the location of the elements in the periodic table.

B Use the absolute value of the charge on each ion as the subscript for the other ion. Reduce the subscripts to the lowest numbers to write the empirical formula. Check to make sure the empirical formula is electrically neutral.

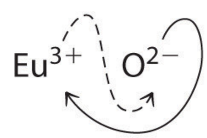
Solution

1. **B** Using the absolute values of the charges on the ions as the subscripts gives Ga_3As_3:



Reducing the subscripts to the smallest whole numbers gives the empirical formula GaAs, which is electrically neutral [+3 + (−3) = 0]. Alternatively, we could recognize that Ga^{3+} and As^{3-} have charges of equal magnitude but opposite signs. One Ga^{3+} ion balances the charge on one As^{3-} ion, and a 1:1 compound will have no net charge. Because we write subscripts only if the number is greater than 1, the empirical formula is GaAs. GaAs is gallium arsenide, which is widely used in the electronics industry in transistors and other devices.

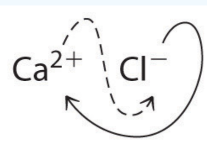
2. **B** Because Eu^{3+} has a charge of +3 and O^{2-} has a charge of −2, a 1:1 compound would have a net charge of +1. We must therefore find multiples of the charges that cancel. We cross charges, using the absolute value of the charge on one ion as the subscript for the other ion:



The subscript for Eu^{3+} is 2 (from O^{2-}), and the subscript for O^{2-} is 3 (from Eu^{3+}), giving Eu_2O_3; the subscripts cannot be reduced further. The empirical formula contains a positive charge of 2(+3) = +6 and a negative charge of 3(−2) = −6, for a net charge of 0. The compound Eu_2O_3 is neutral. Europium oxide is responsible for the red color in television and computer screens.

3. **A** Because the charges on the ions are not given, we must first determine the charges expected for the most common ions derived from calcium and chlorine. Calcium lies in group 2, so it should lose two electrons to form Ca^{2+}. Chlorine lies in group 17, so it should gain one electron to form Cl^{-}.

B Two Cl^{-} ions are needed to balance the charge on one Ca^{2+} ion, which leads to the empirical formula $CaCl_2$. We could also cross charges, using the absolute value of the charge on Ca^{2+} as the subscript for Cl and the absolute value of the charge on Cl^{-} as the subscript for Ca:



The subscripts in $CaCl_2$ cannot be reduced further. The empirical formula is electrically neutral [+2 + 2(−1) = 0]. This compound is calcium chloride, one of the substances used as “salt” to melt ice on roads and sidewalks in winter.

Exercise 2.2.1

Write the empirical formula for the simplest binary ionic compound formed from each ion or element pair.

1. Li^{+} and N^{3-}
2. Al^{3+} and O^{2-}
3. lithium and oxygen

Answer

1. Li_3N
2. Al_2O_3
3. Li_2O

Polyatomic Ions

Polyatomic ions are groups of atoms that bear a net electrical charge, although the atoms in a polyatomic ion are held together by the same covalent bonds that hold atoms together in molecules. Just as there are many more kinds of molecules than simple elements, there are many more kinds of polyatomic ions than monatomic ions. Two examples of polyatomic cations are the ammonium (NH_4^+) and the methylammonium ($CH_3NH_3^+$) ions. Polyatomic anions are much more numerous than polyatomic cations; some common examples are in Table 2.2.1.

Table 2.2.1 Common Polyatomic Ions and Their Names

Formula	Name of Ion
NH_4^+	ammonium
$CH_3NH_3^+$	methylammonium
OH^-	hydroxide
O_2^{2-}	peroxide
CN^-	cyanide
SCN^-	thiocyanate
NO_2^-	nitrite
NO_3^-	nitrate
CO_3^{2-}	carbonate
HCO_3^-	hydrogen carbonate, or bicarbonate
SO_3^{2-}	sulfite
SO_4^{2-}	sulfate
HSO_4^-	hydrogen sulfate, or bisulfate
PO_4^{3-}	phosphate
HPO_4^{2-}	hydrogen phosphate
$H_2PO_4^-$	dihydrogen phosphate
ClO^-	hypochlorite
ClO_2^-	chlorite
ClO_3^-	chlorate
ClO_4^-	perchlorate

Formula	Name of Ion
MnO_4^-	permanganate
CrO_4^{2-}	chromate
$Cr_2O_7^{2-}$	dichromate
$C_2O_4^{2-}$	oxalate
HCO_2^-	formate
$CH_3CO_2^-$	acetate
$C_6H_5CO_2^-$	benzoate

The method we used to predict the empirical formulas for ionic compounds that contain monatomic ions can also be used for compounds that contain polyatomic ions. The overall charge on the cations must balance the overall charge on the anions in the formula unit. Thus K^+ and NO_3^- ions combine in a 1:1 ratio to form KNO_3 (potassium nitrate or saltpeter), a major ingredient in black gunpowder. Similarly, Ca^{2+} and SO_4^{2-} form $CaSO_4$ (calcium sulfate), which combines with varying amounts of water to form gypsum and plaster of Paris. The polyatomic ions NH_4^+ and NO_3^- form NH_4NO_3 (ammonium nitrate), which is a widely used fertilizer and, in the wrong hands, an explosive. One example of a compound in which the ions have charges of different magnitudes is calcium phosphate, which is composed of Ca^{2+} and PO_4^{3-} ions; it is a major component of bones. The compound is electrically neutral because the ions combine in a ratio of three Ca^{2+} ions [3(+2) = +6] for every two ions [2(−3) = −6], giving an empirical formula of $Ca_3(PO_4)_2$; the parentheses around PO_4 in the empirical formula indicate that it is a polyatomic ion. Writing the formula for calcium phosphate as $Ca_3P_2O_8$ gives the correct number of each atom in the formula unit, but it obscures the fact that the compound contains readily identifiable PO_4^{3-} ions.

Example 2.2.1

Write the empirical formula for the compound formed from each ion pair.

1. Na^+ and HPO_4^{2-}
2. potassium cation and cyanide anion
3. calcium cation and hypochlorite anion

Given: ions

Asked for: empirical formula for ionic compound

Strategy:

A If it is not given, determine the charge on a monatomic ion from its location in the periodic table. Use Table 2.4 to find the charge on a polyatomic ion.

B Use the absolute value of the charge on each ion as the subscript for the other ion. Reduce the subscripts to the smallest whole numbers when writing the empirical formula.

Solution

1. **B** Because HPO_4^{2-} has a charge of −2 and Na^+ has a charge of +1, the empirical formula requires two Na^+ ions to balance the charge of the polyatomic ion, giving Na_2HPO_4. The subscripts are reduced to the lowest numbers, so the empirical formula is Na_2HPO_4. This compound is sodium hydrogen phosphate, which is used to provide texture in processed cheese, puddings, and instant breakfasts.
2. **A** The potassium cation is K^+, and the cyanide anion is CN^-. **B** Because the magnitude of the charge on each ion is the same, the empirical formula is KCN. Potassium cyanide is highly toxic, and at one time it was used as rat poison. This use has been discontinued, however, because too many people were being poisoned accidentally.
3. **A** The calcium cation is Ca^{2+}, and the hypochlorite anion is ClO^-. **B** Two ClO^- ions are needed to balance the charge on one Ca^{2+} ion, giving $Ca(ClO)_2$. The subscripts cannot be reduced further, so the empirical formula is $Ca(ClO)_2$. This is calcium hypochlorite, the "chlorine" used to purify water in swimming pools.

Exercise 2.2.1

Write the empirical formula for the compound formed from each ion pair.

1. Ca^{2+} and $H_2PO_4^-$
2. sodium cation and bicarbonate anion
3. ammonium cation and sulfate anion

1. $Ca(H_2PO_4)_2$: calcium dihydrogen phosphate is one of the ingredients in baking powder.
2. $NaHCO_3$: sodium bicarbonate is found in antacids and baking powder; in pure form, it is sold as baking soda.
3. $(NH_4)_2SO_4$: ammonium sulfate is a common source of nitrogen in fertilizers.

Answer

Hydrates

Many ionic compounds occur as **hydrates**, compounds that contain specific ratios of loosely bound water molecules, called **waters of hydration**. Waters of hydration can often be removed simply by heating. For example, calcium dihydrogen phosphate can form a solid that contains one molecule of water per $Ca(H_2PO_4)_2$ unit and is used as a leavening agent in the food industry to cause baked goods to rise. The empirical formula for the solid is $Ca(H_2PO_4)_2 \cdot H_2O$. In contrast, copper sulfate usually forms a blue solid that contains *five* waters of hydration per formula unit, with the empirical formula $CuSO_4 \cdot 5H_2O$. When heated, all five water molecules are lost, giving a white solid with the empirical formula $CuSO_4$ (Figure 2.9).

Loss of Water from a Hydrate with Heating

When blue $CuSO_4 \cdot 5H_2O$ is heated, two molecules of water are lost at 30°C, two more at 110°C, and the last at 250°C to give white $CuSO_4$.

Compounds that differ only in the numbers of waters of hydration can have very different properties. For example, $CaSO_4 \cdot ½H_2O$ is plaster of Paris, which was often used to make sturdy casts for broken arms or legs, whereas $CaSO_4 \cdot 2H_2O$ is the less dense, flakier gypsum, a mineral used in drywall panels for home construction. When a cast would set, a mixture of plaster of Paris and water crystallized to give solid $CaSO_4 \cdot 2H_2O$. Similar processes are used in the setting of cement and concrete.

Summary

An **empirical formula** gives the *relative* numbers of atoms of the elements in a compound, reduced to the lowest whole numbers. The **formula unit** is the *absolute* grouping represented by the empirical formula of a compound, either ionic or covalent. Empirical formulas are particularly useful for describing the composition of ionic compounds, which do not contain readily identifiable molecules. Some ionic compounds occur as **hydrates**, which contain specific ratios of loosely bound water molecules called **waters of hydration**.

KEY TAKEAWAY

- The composition of a compound is represented by an empirical or molecular formula, each consisting of at least one formula unit.

CONCEPTUAL PROBLEMS

1. What are the differences and similarities between a polyatomic ion and a molecule?
2. Classify each compound as ionic or covalent.
    1. $Zn_3(PO_4)_2$
    2. $C_6H_5CO_2H$
    3. $K_2Cr_2O_7$
    4. CH_3CH_2SH
    5. NH_4Br
    6. CCl_2F_2
3. Classify each compound as ionic or covalent. Which are organic compounds and which are inorganic compounds?
    1. $CH_3CH_2CO_2H$
    2. $CaCl_2$
    3. $Y(NO_3)_3$
    4. H_2S
    5. $NaC_2H_3O_2$
4. Generally, one cannot determine the molecular formula directly from an empirical formula. What other information is needed?
5. Give two pieces of information that we obtain from a structural formula that we cannot obtain from an empirical formula.
6. The formulas of alcohols are often written as ROH rather than as empirical formulas. For example, methanol is generally written as CH_3OH rather than CH_4O. Explain why the ROH notation is preferred.
7. The compound dimethyl sulfide has the empirical formula C_2H_6S and the structural formula CH_3SCH_3. What information do we obtain from the structural formula that we do not get from the empirical formula? Write the condensed structural formula for the compound.
8. What is the correct formula for magnesium hydroxide—$MgOH_2$ or $Mg(OH)_2$? Why?
9. Magnesium cyanide is written as $Mg(CN)_2$, not $MgCN_2$. Why?
10. Does a given hydrate always contain the same number of waters of hydration?

Answer

1.
2.
3.
4.
5.
6.
7. The structural formula gives us the connectivity of the atoms in the molecule or ion, as well as a schematic representation of their arrangement in space. Empirical formulas tell us only the ratios of the atoms present. The condensed structural formula of dimethylsulfide is $(CH_3)_2S$.
8.
9.
10.

NUMERICAL PROBLEMS

1. Write the formula for each compound.
    1. magnesium sulfate, which has 1 magnesium atom, 4 oxygen atoms, and 1 sulfur atom
    2. ethylene glycol (antifreeze), which has 6 hydrogen atoms, 2 carbon atoms, and 2 oxygen atoms
    3. acetic acid, which has 2 oxygen atoms, 2 carbon atoms, and 4 hydrogen atoms
    4. potassium chlorate, which has 1 chlorine atom, 1 potassium atom, and 3 oxygen atoms
    5. sodium hypochlorite pentahydrate, which has 1 chlorine atom, 1 sodium atom, 6 oxygen atoms, and 10 hydrogen atoms
2. Write the formula for each compound.

1. cadmium acetate, which has 1 cadmium atom, 4 oxygen atoms, 4 carbon atoms, and 6 hydrogen atoms
2. barium cyanide, which has 1 barium atom, 2 carbon atoms, and 2 nitrogen atoms
3. iron(III) phosphate dihydrate, which has 1 iron atom, 1 phosphorus atom, 6 oxygen atoms, and 4 hydrogen atoms
4. manganese(II) nitrate hexahydrate, which has 1 manganese atom, 12 hydrogen atoms, 12 oxygen atoms, and 2 nitrogen atoms
5. silver phosphate, which has 1 phosphorus atom, 3 silver atoms, and 4 oxygen atoms

3. Complete the following table by filling in the formula for the ionic compound formed by each cation-anion pair.

Ion	K^+	Fe^{3+}	NH_4^+	Ba^{2+}
Cl^-	KCl			
SO_4^{2-}				
PO_4^{3-}				
NO_3^-				
OH^-				

4. Write the empirical formula for the binary compound formed by the most common monatomic ions formed by each pair of elements.
   1. zinc and sulfur
   2. barium and iodine
   3. magnesium and chlorine
   4. silicon and oxygen
   5. sodium and sulfur
5. Write the empirical formula for the binary compound formed by the most common monatomic ions formed by each pair of elements.
   1. lithium and nitrogen
   2. cesium and chlorine
   3. germanium and oxygen
   4. rubidium and sulfur
   5. arsenic and sodium
6. Write the empirical formula for each compound.
   1. $Na_2S_2O_4$
   2. B_2H_6
   3. $C_6H_{12}O_6$
   4. P_4O_{10}
   5. $KMnO_4$
7. Write the empirical formula for each compound.
   1. Al_2Cl_6
   2. $K_2Cr_2O_7$
   3. C_2H_4
   4. $(NH_2)_2CNH$
   5. CH_3COOH

AnswerS

1. 1. $MgSO_4$
   2. $C_2H_6O_2$
   3. $C_2H_4O_2$
   4. $KClO_3$
   5. $NaOCl·5H_2O$
2.

3.

Ion	**K^+**	**Fe^{3+}**	**NH_4^+**	**Ba^{2+}**
Cl^-	**KCl**	$FeCl_3$	NH_4Cl	$BaCl_2$
SO_4^{2-}	K_2SO_4	$Fe_2(SO_4)_3$	$(NH_4)_2SO_4$	$BaSO_4$
PO_4^{3-}	K_3PO_4	$FePO_4$	$(NH_4)_3PO_4$	$Ba_3(PO_4)_2$
NO_3^-	KNO_3	$Fe(NO_3)_3$	NH_4NO_3	$Ba(NO_3)_2$
OH^-	KOH	$Fe(OH)_3$	NH_4OH	$Ba(OH)_2$

4.
5.
    1. Li_3N
    2. CsCl
    3. GeO_2
    4. Rb_2S
    5. Na_3As
6.
7.
    1. $AlCl_3$
    2. $K_2Cr_2O_7$
    3. CH_2
    4. CH_5N_3
    5. CH_2O