

# Chapter 4 – Ionic Bond

## Introduction

Atoms can gain or lose valence electrons to become ions. Ions can be monatomic, such as  $\text{Ca}^{2+}$  and  $\text{Cl}^{1-}$ , or polyatomic, such as  $\text{NH}_4^{1+}$  and  $\text{CO}_3^{2-}$ . An *ionic bond* is the electrostatic (Coulombic) force of attraction between two oppositely charged ions. Ions and how they bond are the topic of this chapter.

## 4.1 Ionic Bonding

### Introduction

Ionic bonds are the electrostatic attraction of oppositely charged ions. The cation is usually a metal, and the anion is usually a nonmetal.

#### 4.1-1. Introduction to Bonding Video

A video or simulation is available online.

#### 4.1-2. Ionic Bonding

An ionic bond is the Coulombic attraction of two oppositely charged ions.

Compounds between metals and nonmetals are ionic.

The unfilled valence orbitals of nonmetals experience large effective nuclear charges, so they are low in energy, which makes nonmetals, such as chlorine, highly electronegative. The valence electrons of metals that lie on the left side of the periodic table experience very low effective nuclear charges, so they are characterized by low ionization energies. Therefore, metals, such as sodium, lose their valence electron easily.

When sodium bonds to chlorine, the high-energy valence electron on sodium is transferred to the low-energy unfilled orbital on chlorine. The loss of an electron by sodium produces a sodium one-plus ion, while the gain of an electron by chlorine produces a chlorine one-minus ion. The resulting ions of opposite charge lower their energy by moving close to one another. The interaction between the two interacting ions is called an ionic bond, and NaCl is an ionic compound. We will assume that all compounds between metals and nonmetals are ionic. However, recall that late metals (those that lie to the right of the periodic table) are fairly electronegative, so they do not give up their valence electrons easily, and their compounds are not very ionic.

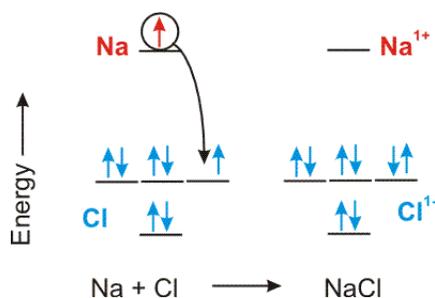


Figure 4.1: Ionic Bond Formation

#### 4.1-3. Ionic Structure

Ionic compounds are arrays of individual ions with no identifiable molecules.

Each ion in a crystal of table salt is surrounded by six identical ions of opposite charge, and all Na–Cl distances are identical. Consequently, there are no pairs of ions that are identifiable as NaCl molecules.

A video or simulation is available online.

## 4.1-4. Ionic Compounds vs. Covalent Compounds

Compounds between nonmetals are covalent.

Covalent compounds are arrays of individual molecules, i.e., they are molecular.

Although covalent bonding is the topic of the following two chapters, a brief introduction is given here to allow us to compare the two different compound types in this chapter. Covalent compounds contain only nonmetals, so the atoms have similar electronegativities. Neither atom in a covalent bond has a very high energy electron that is readily transferred, so the atoms share rather than transfer the bonding electrons. Covalent bonds involve an overlap of atomic orbitals, so they are very directional, while ionic bonds are simply electrostatic interactions between spherical ions with no directionality.

While the distances between adjacent  $\text{Na}^{1+}$  and  $\text{Cl}^{1-}$  ions in a crystal of NaCl are all identical, there are two distinct distances observed between O and H atoms in an ice crystal. The existence of two distinct distances in ice allow us to identify individual water molecules as an oxygen atom and the two hydrogen atoms that are closest to it. The longer distance is then between the oxygen atom on one molecule and a hydrogen atom on an adjacent water molecule in the crystal. Thus, ice consists of individual water molecules that interact to produce the solid, while table salt consists of  $\text{Na}^{1+}$  and  $\text{Cl}^{1-}$  ions with no NaCl molecules.

## 4.1-5. Ionic or Covalent Exercise

### **EXERCISE 4.1:**

Indicate whether each of the following is ionic or covalent.

$\text{CaCl}_2$	$\text{SF}_2$	$\text{KCl}$	$\text{CCl}_4$
ionic	ionic	ionic	ionic
covalent	covalent	covalent	covalent
$\text{Na}_2\text{O}$	$\text{F}_2\text{O}$	$\text{N}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$
ionic	ionic	ionic	ionic
covalent	covalent	covalent	covalent

## 4.2 Naming Ions and Predicting their Charge

### Introduction

Most ionic compounds form between a metal cation and a nonmetal anion. In this section, we examine the electrons that are lost by the metal and the orbitals that are filled by the nonmetal. Once we know which electrons are lost and which orbitals are filled, we can predict the probable charges on the ions and write their electron configurations.

### Prerequisites

- 3.1 Valence Electrons (Write valence electron configurations for atoms.)
- 3.5 Ionization Energy (Predict relative ionization energies of atoms.)
- 3.6 Electronegativity (Predict relative electronegativities of atoms.)

### Objectives

- Predict the cation that a metal is likely to adopt and write its electron configuration.
- Predict the charge on the anion that a nonmetal is likely to adopt and write its electron configuration.
- Determine the orbital occupancy of an ion given the charge on the ion and the occupancy of its atom.

### 4.2-1. Metal Cations

Cations are produced by the loss of valence electrons with those with the highest  $n$  quantum number being lost first. Consequently, first row transition metals lose their 4s electrons before they lose any 3d electrons.

Metals are characterized by low ionization energies, so they lose electrons to become cations, and the charge on the cation is determined by the number of electrons that are lost. While all of the electrons in an atom can be removed, the ionization energy of each successive ionization increases (3.5 Ionization Energy). As a result, no more than three electrons can be removed in chemical processes. In addition, core electrons are very tightly bound and are never removed in chemical processes. Thus, only the valence electrons are lost. While some metals lose all of their valence electrons, others lose only some of them. The following rules help determine which electrons are lost in chemical processes:

- Monatomic cations with charges greater than +3 do not form.
- Electrons from the outermost shell (highest  $n$  quantum number) are lost first. This is important in determining the cations formed by transition metals.
- Within a shell, electrons from the subshell with the highest  $l$  quantum number are lost first. This is important for the heavier metals in Groups 3, 4, and 5.

Group 1A & 2A Metals	Group 3A Metals
Lose their valence electrons to form +1 and +2 ions, respectively.	Lose all of their valence electrons to form +3 ions. Tl forms both +3 and +1 ions, but not a +2 ion. The reason is that the heavier main group elements can lose only a portion of their valence shell. Tl is $6s^26p^1$ . Both valence sublevels are in the same level, so the one with the highest $l$ quantum number is emptied first. Thus, Tl can lose the 6p and not the 6s to form the +1 ion, but it cannot lose the 6s and not the 6p to form a +2 ion.
Group 4A Metals	Transition Metals
+4 monatomic ions do not exist, so the <b>Group 4A metals</b> cannot lose all of their valence electrons. However, the heavier metals in the group (Sn and Pb) can lose the electrons in the sublevel with the highest $l$ quantum number, the outermost p sublevel, to form +2 ions.	Lose electrons in the level with the highest $n$ quantum number. Thus, most transition elements lose their outermost s electrons to form +2 ions. Scandium is an exception because it loses all three valence electrons to form $Sc^{3+}$ (no +2 ion). Silver forms only a +1 ion, and copper forms both +2 and +1 ions. In addition, several transition metals form a +3 ion in addition to a +2 ion.

Table 4.1: Cations Formed by Metals

#### 4.2-2. Nonmetal Anions

Nonmetals form anions by gaining the number of electrons required to fill their valence shell (outermost s and p sublevels).

Nonmetals are electronegative, so they tend to gain electrons to become anions. The number of electrons gained equals the number required to fill their valence shell. A filled valence shell for all nonmetals except hydrogen contains eight electrons (two s and six p electrons). Thus,

$$\text{charge on an anion} = \text{group number} - \text{eight}$$

The resulting electron configuration is the same as that of the next noble gas, i.e., anions are *isoelectronic* with the next noble gas. Each successive electron is more difficult to add due to the Coulombic repulsion between the charge of the electron and that of the anion. Indeed, adding a fourth electron to a  $-3$  anion is so difficult that  $-4$  ions do not form in chemical processes.

7A	6A	5A	4A
-1 ions	-2 ions	-3 ions	Monatomic anions with charges of $-4$ do not exist, so the Group 4A nonmetals do not form anions.

Table 4.2: Anions Formed by Nonmetals

## 4.2-3. Predicting Charge and Electron Configuration Exercise

### EXERCISE 4.2:

Period	1A 2A		d block										3A 4A 5A 6A 7A 8A						
	s block												p block						
1	H	He																	
2	Li	Be											B	C	N	O	F	Ne	
3	Na	Mg	1	2	3	4	5	6	7	8	9	10	Al	Si	P	S	Cl	Ar	
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
7	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt										
			f block																
			1	2	3	4	5	6	7	8	9	10	11	12	13	14			
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu			
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr			

Each atom forms only one monatomic ion. What is the charge on that ion?

S \_\_\_\_\_ Mg \_\_\_\_\_ Sc \_\_\_\_\_

P \_\_\_\_\_ Ag \_\_\_\_\_ Zn \_\_\_\_\_

What are the electron configurations of the following ions? Use noble gas cores.

Sc<sup>3+</sup> \_\_\_\_\_ N<sup>3-</sup> \_\_\_\_\_ Ni<sup>2+</sup> \_\_\_\_\_

Bi<sup>3+</sup> \_\_\_\_\_ K<sup>1+</sup> \_\_\_\_\_ Br<sup>1-</sup> \_\_\_\_\_

## 4.2-4. Orbital Occupancies of Ions Exercise

### **EXERCISE 4.3:**

Substances can gain and/or lose electrons, and we will frequently have to consider the orbital energy diagrams of the resulting species. Consider the following example in which you must identify which ions of substance X (shown with brown background) are represented by Figures a–d.

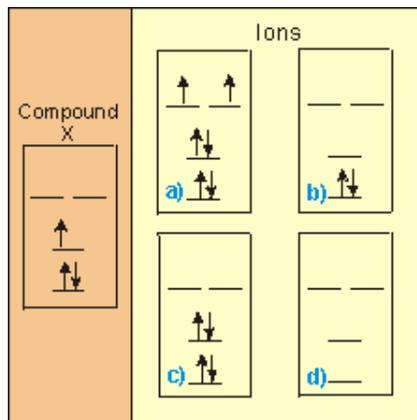


Figure a  
 $X^{4-}$   
 $X^{3-}$   
 $X^{1-}$   
 $X^{1+}$   
 $X^{2+}$   
 $X^{3+}$

Figure b  
 $X^{4-}$   
 $X^{3-}$   
 $X^{1-}$   
 $X^{1+}$   
 $X^{2+}$   
 $X^{3+}$

Figure c  
 $X^{4-}$   
 $X^{3-}$   
 $X^{1-}$   
 $X^{1+}$   
 $X^{2+}$   
 $X^{3+}$

Figure d  
 $X^{4-}$   
 $X^{3-}$   
 $X^{1-}$   
 $X^{1+}$   
 $X^{2+}$   
 $X^{3+}$

## 4.3 Ionic vs. Atomic Size

### Introduction

We saw in the previous chapter that the size of an atom depends upon the size of its outermost orbitals, and ions form when electrons leave or enter those orbitals. Consequently, the sizes of ions are different than those of the atoms. In this section, we compare the sizes of atoms, anions, and cations.

### Prerequisites

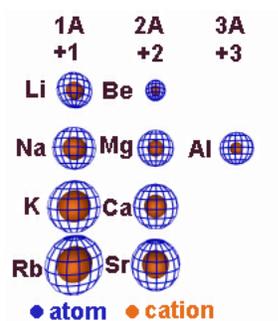
- 3.3 Relative Atomic Size (Predict relative sizes of atoms from their positions in the periodic table.)

### Objectives

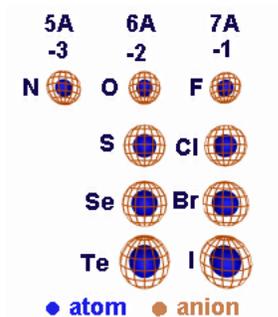
- Explain why cations are smaller than their atoms, but anions are larger.
- Predict the relative sizes of a series of ions.

### 4.3-1. Relative Ion Size

Cations are smaller than their atoms, but anions are larger than their atoms.



**Figure 4.2** Relative Sizes of Cations and Their Atoms: A loss of electrons increases  $Z_{\text{eff}}$  and, if the valence shell is emptied, decreases the  $n$  quantum number. Consequently, cations are smaller than their parent atoms.



**Figure 4.3** Relative Sizes of Anions and Their Atoms: A gain of electrons decreases  $Z_{\text{eff}}$ , so anions are larger than their atoms.

### 4.3-2. Ionic Size Exercise

#### **EXERCISE 4.4:**

Use only a periodic table to determine the **largest** ion in each group.



## 4.4 Oxidation States

### Introduction

Electron counting (keeping track of where the electrons are in a compound) is a valuable aid in predicting the formulas of compounds, balancing certain types of chemical equations, predicting properties, and even predicting reactive centers. In this lesson, we introduce the oxidation state method for counting electrons. We then show how to determine the oxidation states of an atom in a molecule or ion and how to use oxidation states to predict formulas.

### Prerequisites

- 3.4 Relative Orbital Energies (Predict relative valence orbital energies of atoms.)
- 3.5 Ionization Energy (Predict relative valence orbital energies of atoms based on their ionization energies.)
- 3.6 Electronegativity (Predict relative valence orbital energies of atoms based on their electronegativities.)
- 2.3 Bohr Model

## Objectives

- Define the term “oxidation state.”
- Explain how the charge on a species (compound or ion) is related to the oxidation states of its atoms.
- Determine the oxidation states of the atoms in an ion or molecule.
- Predict chemical formulas for binary compounds.

### 4.4-1. Oxidation States from Chemical Formulas Video

A video or simulation is available online.

### 4.4-2. Oxidation State Definition

The oxidation state of an atom in a compound is the charge it would have if its bonds were ionic.

The *oxidation state* of an atom in a compound is the charge the atom would have if its bonds were ionic. However, it is used to account for the electrons in all compounds irrespective of the bond type. **Oxidation states are obtained by assigning all bonding electrons to the more electronegative atom in each bond.** Thus, we can conclude that the oxidation state of an atom is

- negative if it is the more electronegative atom, and
- positive if it is the less electronegative atom.

### 4.4-3. Oxidation States of Hydrogen and Chlorine

The most common oxidation state of Cl is  $-1$  because most of its bonds are to less electronegative elements.

Cl has a zero oxidation state when bound to itself, and it can have positive oxidation states when bound to O or F.

As shown in Figure 4.4, the valence orbitals of hydrogen lie between those of the metals and the nonmetals. Thus, the electrons in a Metal–Hydrogen bond are assigned to the hydrogen, so it adopts a  $-1$  oxidation state. However, in a Nonmetal–Hydrogen bond, the electrons are assigned to the lower energy nonmetal, and the hydrogen adopts a  $+1$  oxidation state. In the H–H bond of  $H_2$ , both orbitals have the same energy, so the electrons must be shared to give each H an oxidation state of 0.

The valence orbitals of chlorine lie below those of all other elements except those of oxygen and fluorine. Consequently, chlorine adopts a  $-1$  oxidation state when bound to most elements. Like hydrogen, it has a zero oxidation state when bound to itself in  $Cl_2$ . However, it can adopt positive oxidation states when bound to O or F. In its binary compounds  $OCl_2$  and  $FCl$ , it is assumed to lose the unpaired electron to adopt a  $+1$  oxidation state, but if it is bound to more than one F or O, the appropriate number of electron pairs are also assigned to the O or F, so Cl can then adopt  $+3$ ,  $+5$ , and  $+7$  oxidation states. See Table 4.3 for some examples.

Ox State of Cl	Examples
$-1$	$CCl_4O$ , $NCl_3$ , $KCl$
0	$Cl_2$
$+1$	$ClF$ , $Cl_2O$ , $ClO^{1-}$
$+3$	$ClF_3$ , $ClO_2^{1-}$
$+5$	$ClO_3^{1-}$
$+7$	$ClO_4^{1-}$

Table 4.3

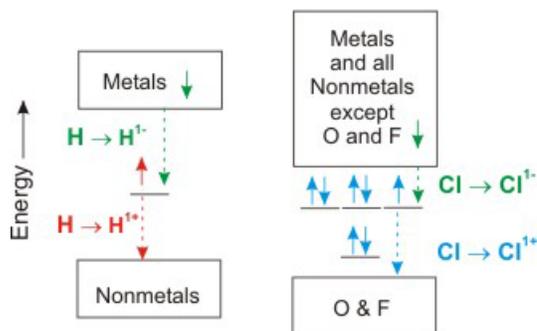


Figure 4.4 Oxidation States of Hydrogen and Chlorine

#### 4.4-4. Oxidation State Sum

The oxidation states of all of the atoms in a chemical species must sum to the charge on the species.

The oxidation states of the atoms in a molecule or ion represent the charge they would have if all of the bonds were ionic. Consequently,

- the oxidation states of all the atoms in an ion must sum to the charge of the ion, and
- the oxidation states of all the atoms in a molecule must sum to zero.

#### EXAMPLE:

For example, let us determine the charge on the carbonate ion ( $\text{CO}_3^x$ ) given that the oxidation states of C and O are +4 and  $-2$ , respectively. The charge on the ion equals the sum of the oxidation states, so we write

$$\text{charge} = (1\text{C})(+4/\text{C}) + (3\text{O})(-2/\text{O}) = 4 - 6 = -2$$

The carbonate ion is the  $\text{CO}_3^{2-}$  ion.

#### 4.4-5. Oxidation State Guidelines

The oxidation state of an atom lies between its group number and its group number minus eight.

The maximum oxidation state of an atom equals the number of electrons that can be lost from its valence shell, which equals its group number. The lowest oxidation state that an atom can achieve is equal to minus the number of electrons required to fill its valence shell, which is  $-(8 - \text{group number})$ .

$$+(\text{group number}) \geq \text{Oxidation State} \geq -(8 - \text{group number})$$

The more electronegative the element, the more likely it is to be found in its lowest (most negative) oxidation state, and the lower its ionization energy, the more likely it is to be found in its highest oxidation state.

The valence orbitals of **metals** are high in energy, so they seldom accept electrons to obtain negative oxidation states. Thus, the metal is always in a positive oxidation state in compounds with nonmetals.

- The Group 1A, 2A, and 3A metals are usually found in their highest oxidation states (+1, +2, and +3) when bound to nonmetals.
- Transition elements tend to adopt oxidation states of +2 and +3, but Ag is +1 and Cu is +1 or +2 in most of their compounds. Some transition elements can achieve oxidation states as high as their group number when surrounded by highly electronegative atoms (usually oxygen). For example, vanadium is +5 in  $\text{VO}_4^{3-}$ , chromium is +6 in  $\text{CrO}_4^{2-}$ , and Mn is +7 in  $\text{MnO}_4^{1-}$ .

The valence orbitals of **nonmetals** are much lower than those of metals, so nonmetals are usually in their lowest oxidation states when bound to metals. The more electronegative a nonmetal is, the more likely it is to assume its lowest oxidation state. However, nonmetals can achieve positive oxidation states when bound to more electronegative elements. They can obtain oxidation states as high as their group number when bound to highly electronegative elements (especially O and F). For example, P is +5 in  $\text{PO}_4^{3-}$  and  $\text{PF}_5$ , S is +6 in  $\text{SO}_3$  and  $\text{SF}_6$ , and Cl is +7 in  $\text{ClO}_4^{1-}$ .

#### 4.4-6. Oxidation State Rules

The oxidation state guidelines give us ranges for the oxidation states of the elements, but many atoms have the same oxidation state in almost all of their compounds. To determine the oxidation state of an atom in a molecule or ion, use the oxidation state rules given in Table 4.4. **The oxidation state rules are listed in order of priority, so they should be used in the order given; that is, a rule takes precedence over any rule below it, or any rule can be violated only to satisfy a rule above it.**

Note that the oxidation state rules merely reflect what we already know about atomic properties: atoms with low ionization energies (Groups 1A and 2A) are generally found in the highest oxidation states, while highly electronegative atoms (F and O) are generally in their lowest oxidation states.

Rule	Reason
The oxidation states of the atoms in an element are all zero.	When the valence orbitals of the two atoms are the same, the bonding electrons are assumed to be shared, not transferred. For example, the oxidation state of Cu in metallic Cu is zero, both F atoms in $\text{F}_2$ are zero (the only time F is not $-1$ ), and all eight sulfur atoms in $\text{S}_8$ are zero.
F is $-1$ .	The valence orbitals of F are lower than the valence orbitals on any other element, i.e., F is the most electronegative element. Consequently, it is always assigned the bonding electrons. There is only one compound in which an F atom is not $-1$ . What is it? Hint: See the only rule that takes priority over this rule.
1A metals are $+1$ , 2A metals are $+2$ , and Al is $+3$ .	The valence orbitals in these metals are very high in energy, i.e., these metals have low ionization energies. They also become iso-electronic with a noble gas when they form the ions.
H is $+1$ .	The $1s$ orbital on H is lower in energy than the valence orbitals of most metals and higher in energy than those of most nonmetals. Therefore, H is $+1$ except when Rule 1 forces it to be 0 or Rule 3 (metals with higher energy valence orbitals) forces it to be $-1$ .
O is $-2$ .	Oxygen is the second most electronegative atom, so it is usually assigned the bonding electrons. However, it is not $-2$ when it is elemental $\text{O}_2$ (Rule 1) or bonds to F (Rule 2). In addition, it can be $-1$ if Rules 3 and 4 force it. Compounds in which the oxidation state of oxygen is $-1$ are called peroxides. Peroxides contain $\text{O}_2^{2-}$ , which has an O–O bond. Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is a common peroxide.
7A elements are $-1$ .	Halogens are electronegative, so they tend to fill their valence shell to attain $-1$ oxidation states. However, they can attain positive oxidation states when bound to more electronegative atoms, such as oxygen, or more electronegative halogens, e.g., Cl is $+7$ in $\text{ClO}_4^{1-}$ , Br is $+5$ in $\text{BrO}_3^{1-}$ , and I is $+3$ in $\text{IF}_3$ .

Table 4.4

## 4.4-7. Oxidation State Exercise

### **EXERCISE 4.5:**

#### **Oxidation State Rules**

- 1 Atoms in elements are zero.
- 2 F is  $-1$ .
- 3 Group 1A metals are  $+1$ , 2A metals are  $+2$ , and Al is  $+3$ .
- 4 H is  $+1$ .
- 5 O is  $-2$ .
- 6 Group 7A elements are  $-1$ .

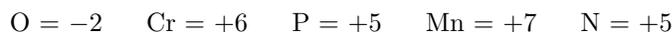
Determine the oxidation state of the first element in each of the following.



## 4.4-8. Using Oxidation States to Determine Charge Exercise

### **EXERCISE 4.6:**

Determine the charge on each ion. Use the following oxidation states.



## 4.4-9. Chemical Formulas from Oxidation States Video

A video or simulation is available online.

## 4.4-10. Predicting Formulas

The likely formula of a compound can be predicted by assigning likely oxidation states to each of the atoms.

Compounds carry no net charge, so the total positive charge must equal the negative of the total negative charge. The total positive charge equals the positive oxidation state ( $OX_{\text{pos}}$ ) times the number of atoms with that oxidation state ( $N_{\text{pos}}$ ), and the total negative oxidation state equals the negative oxidation state ( $OX_{\text{neg}}$ ) times the number of atoms that have that oxidation state ( $N_{\text{neg}}$ ). We can therefore write the following:

$$N_{\text{pos}}OX_{\text{pos}} = -N_{\text{neg}}OX_{\text{neg}}$$

Rearranging, we obtain

$$\frac{N_{\text{pos}}}{N_{\text{neg}}} = \frac{OX_{\text{neg}}}{OX_{\text{pos}}}$$

Thus, the subscripts of the atoms in a chemical formula are inversely proportional to their oxidation state.

To determine the formula of a binary compound (only two elements) follow these steps:

- 1 Assign oxidation states to the two elements. If the elements are not listed in the oxidation state rules, assign +Group number to the less electronegative element and  $-(8 - \text{Group number})$  to the more electronegative element. However, recall that nonmetals can empty only their p sublevel, leaving two s electrons. In this case,  $\text{OX}_{\text{pos}} = \text{Group number} - 2$ .
- 2 Determine the ratio of oxidation states as a ratio of smallest whole numbers.
- 3 The ratio of the subscripts in the formula varies inversely with the ratio of oxidation states, so the whole numbers in step 1 are the subscripts.
- 4 Write the formula, but be sure to always write the less electronegative element first.

#### 4.4-11. Predicting Formulas Exercise

##### **EXERCISE 4.7:**

Predict the formula of the compound formed between each pair of elements below.

oxidation state of 1<sup>st</sup> element

oxidation state of 2<sup>nd</sup> element

Na and O \_\_\_\_\_

Na and O \_\_\_\_\_

Zn and Cl \_\_\_\_\_

Zn and Cl \_\_\_\_\_

Al and S \_\_\_\_\_

Al and S \_\_\_\_\_

C and O \_\_\_\_\_

C and O \_\_\_\_\_

LCM of the two oxidation states

formula of compound

Na and O \_\_\_\_\_

Na and O \_\_\_\_\_

Zn and Cl \_\_\_\_\_

Zn and Cl \_\_\_\_\_

Al and S \_\_\_\_\_

Al and S \_\_\_\_\_

C and O \_\_\_\_\_

C and O \_\_\_\_\_

#### 4.4-12. Writing Formulas of Binary Compounds Exercise

##### **EXERCISE 4.8:**

Use the highest and lowest oxidation states of nonmetals and common oxidation states of metals to predict the formulas of the compounds that would form between each pair of elements.

phosphorus and chlorine

calcium and oxygen

\_\_\_\_\_

\_\_\_\_\_

carbon and fluorine

copper and sulfur

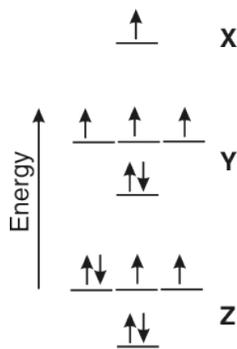
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\_\_\_\_\_

## 4.4-13. Orbital Diagrams and Oxidation State Exercise

### **EXERCISE 4.9:**

Use the energy level diagram for the valence electrons of X, Y, and Z to determine each answer. Always write the more electronegative element last.



oxidation state of X when it bonds to Y or Z \_\_\_\_\_

oxidation state of Y when it bonds to X \_\_\_\_\_

oxidation state of Y when it bonds to Z \_\_\_\_\_

oxidation state of Z when it bonds to Y \_\_\_\_\_

formula of the compound formed between X and Y \_\_\_\_\_

formula of the compound formed between X and Z \_\_\_\_\_

formula of the compound formed between Y and Z \_\_\_\_\_

What are the identities (symbols) of X, Y, and Z if they are all in the second period?

X = \_\_\_\_\_

Y = \_\_\_\_\_

Z = \_\_\_\_\_

## 4.5 Polyatomic Ions

### Introduction

So far, we have considered only monatomic ions (ions composed of a single atom), but many ions consist of several atoms and are called polyatomic ions. The bonds between the atoms in a polyatomic ion are not ionic, but a polyatomic ion does have a net charge and bonds to other ions via an ionic bond.

### Objectives

- Identify the common polyatomic ions.

## 4.5-1. Polyatomic Ions

A number of ionic compounds are composed of polyatomic ions, which are charged groups of covalently bound atoms. While the polyatomic ion forms ionic bonds with oppositely charged ions, the atoms within a polyatomic ion are nonmetals held together by covalent bonds. Many of the polyatomic ions are *oxoanions*, i.e., they are negative ions that contain oxygen atoms covalently bound to another element. In the common polyatomic ions listed in Table 4.5, the only cations are ammonium and hydronium, and the only anions that are not oxoanions are hydroxide and cyanide.

Recall that ionic compounds can be identified as those that contain metals because metals represent almost all of the common monatomic cations. However, ions can also be polyatomic. Ammonium is by far the most common polyatomic cation in compounds. Thus,  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{NO}_3$ , and  $(\text{NH}_4)_2\text{SO}_4$  are also ionic compounds. We conclude that ionic compounds are those that contain either a metal or a polyatomic cation such as ammonium.

Cations			
$\text{NH}_4^{1+}$	ammonium ion	$\text{H}_3\text{O}^{1+}$	hydronium ion
Anions			
$\text{C}_2\text{H}_3\text{O}_2^{1-}$	acetate ion	$\text{OH}^{1-}$	hydroxide ion
$\text{CO}_3^{2-}$	carbonate ion	$\text{NO}_3^{1-}$	nitrate ion
$\text{ClO}_4^{1-}$	perchlorate ion	$\text{NO}_2^{1-}$	nitrite ion
$\text{ClO}_3^{1-}$	chlorate ion	$\text{MnO}_4^{1-}$	permanganate ion
$\text{ClO}_2^{1-}$	chlorite ion	$\text{O}_2^{2-}$	peroxide ion
$\text{ClO}^{1-}$	hypochlorite ion	$\text{PO}_4^{3-}$	phosphate ion
$\text{CrO}_4^{2-}$	chromate ion	$\text{SO}_4^{2-}$	sulfate ion
$\text{Cr}_2\text{O}_7^{2-}$	dichromate ion	$\text{SO}_3^{2-}$	sulfite ion
$\text{CN}^{1-}$	cyanide ion		

Table 4.5: Some Common Polyatomic Ions

## 4.6 Naming Ionic Compounds

### Introduction

Understanding how ionic compounds are named helps you better communicate about chemistry. In this section, we explain how binary ionic compounds and ionic compounds containing polyatomic ions are named.

#### Prerequisites

- 1.11 Dimitri Mendeleev and The Periodic Law

#### Objectives

- Name ions that contain one or more protons.
- Name ionic compounds containing polyatomic ions.

### 4.6-1. Binary Compounds

The oxidation state of the metal is given as a Roman numeral in parentheses when naming inorganic compounds that contain a metal that can attain more than one oxidation state.

The name of a binary ionic compound is simply the name of the cation (name of the metal atom) followed by the name of the anion (name of nonmetal with ending changed to -ide). If the metal has the same oxidation state in all of its compounds, the oxidation state is not indicated. The metals for which the oxidation state is usually omitted are the metals of Groups 1A and 2A, Al, Sc, Zn, Ag, and Cd. The remaining metals have more than one possible oxidation state, and so the oxidation state of the metal is indicated with a Roman numeral in parentheses after the name of the metal. Note that there is no space between the name of the metal and the Roman numeral in parentheses.

Some examples:

- NaCl = sodium chloride (Group 1A are always +1.)
- Mg<sub>3</sub>N<sub>2</sub> = magnesium nitride (Group 2A are always +2.)
- ZnBr<sub>2</sub> = zinc bromide (Zn is always +2.)
- AgF = silver fluoride (Ag is always +1.)
- Sc<sub>2</sub>O<sub>3</sub> = scandium oxide (Sc is always +3.)
- CoO is cobalt(II) oxide to distinguish it from Co<sub>2</sub>O<sub>3</sub>, which is cobalt(III) oxide.
- TlCl is thallium(I) chloride to distinguish it from TlCl<sub>3</sub>, which is thallium(III) chloride.

#### 4.6-2. Naming Exercise

##### **EXERCISE 4.10:**

Name the following compounds.

AlBr<sub>3</sub> \_\_\_\_\_

ZnCl<sub>2</sub> \_\_\_\_\_

Ag<sub>2</sub>O \_\_\_\_\_

FeCl<sub>3</sub> \_\_\_\_\_

CuCl \_\_\_\_\_

PbO<sub>2</sub> \_\_\_\_\_

Hg<sub>2</sub>Cl<sub>2</sub> \_\_\_\_\_

MnO<sub>2</sub> \_\_\_\_\_

ZnBr<sub>2</sub> \_\_\_\_\_

SnO<sub>2</sub> \_\_\_\_\_

CoCl<sub>3</sub> \_\_\_\_\_

K<sub>2</sub>O \_\_\_\_\_

#### 4.6-3. Naming Oxoanions of the Elements of Groups 4, 5, and 6

Suffixes are used to indicate the oxidation state of the central atom in most oxoanions:

- -ate implies that the central atom is in its highest oxidation state (group number).
- -ite tells us that the oxidation state of the central atom is lower than the highest oxidation state by two because the ion has one less oxygen atom than the corresponding ion that ends in -ate.

Removing an oxygen atom from an oxoanion reduces the oxidation state of the central atom by two, but it does not change the charge on the ion. Some examples:

<b>Group 4</b>	CO <sub>3</sub> <sup>2-</sup> is the <b>carbonate</b> ion because Group 4A carbon is in the +4 oxidation state.
<b>Group 5</b>	PO <sub>4</sub> <sup>3-</sup> is the <b>phosphate</b> ion because Group 5A phosphorus is in the +5 oxidation state. However, NO <sub>3</sub> <sup>1-</sup> is the <b>nitrate</b> ion. Removing a single oxygen atom produces NO <sub>2</sub> <sup>1-</sup> , the <b>nitrite</b> ion.
<b>Group 6</b>	SO <sub>4</sub> <sup>2-</sup> is the <b>sulfate</b> ion because Group 6A sulfur is in the +6 oxidation state. Removal of one oxygen atom produces the <b>sulfite</b> ion, SO <sub>3</sub> <sup>2-</sup> .

**Table 4.6**

#### 4.6-4. Naming Oxoanions of Group 7

The oxoanions of the Group 7A elements are an exception because, unlike the others, they each form four oxoanions. Consequently, both prefixes and suffixes must be used (see Table 4.7). In the perchlorate ion ( $\text{ClO}_4^{1-}$ ), the chlorine is in its highest oxidation state (+7). The chlorate ion ( $\text{ClO}_3^{1-}$ ) has one less oxygen, so the oxidation state of Cl is two less, or +5. The chlorite ion ( $\text{ClO}_2^{1-}$ ) has one less oxygen than chlorate, which lowers the oxidation state of Cl to +3. Finally, the hypochlorite ion ( $\text{ClO}^{1-}$ ) has one less oxygen than chlorite, and the oxidation state of the Cl is reduced to +1. Similarly, perbromate is  $\text{BrO}_4^{1-}$ , bromate is  $\text{BrO}_3^{1-}$ , etc. Note, however, that fluorine is the most electronegative element, so it never has a positive oxidation state. Consequently, fluorine forms no oxoanions.

Prefix	Suffix	Oxidation State of Halogen	Formula
Per-	-ate	+7	$\text{XO}_4^{1-}$
	-ate	+5	$\text{XO}_3^{1-}$
	-ite	+3	$\text{XO}_2^{1-}$
Hypo-	-ite	+1	$\text{XO}^{1-}$

Table 4.7: Prefixes and Suffixes of the Oxoanions Formed by the Halogens

#### 4.6-5. Protonated Ions

Ions that have charges of  $-2$  and  $-3$  pick up protons to produce protonated anions, which are named by placing hydrogen (or dihydrogen) and a space in front of the name of the ion. An older, but still common, method for naming some of these ions is to replace the “hydrogen and a space” with simply “bi” with no space. Thus,  $\text{HS}^{1-}$  is either the hydrogen sulfide ion or the bisulfide ion.

$\text{HCO}_3^{1-}$	hydrogen carbonate or bicarbonate ion
$\text{HPO}_4^{2-}$	hydrogen phosphate ion
$\text{H}_2\text{PO}_4^{1-}$	dihydrogen phosphate ion
$\text{HSO}_4^{1-}$	hydrogen sulfate or bisulfate ion
$\text{HSO}_3^{1-}$	hydrogen sulfite or bisulfite ion

Table 4.8: Common Protonated Oxoanions

#### 4.6-6. Writing Formulas for Compounds with Polyatomic Ions Exercise

##### **EXERCISE 4.11:**

Use the fact that *the names of the polyatomic ions are used without change when naming compounds that contain one or more polyatomic ions* to write formulas for the following compounds.

ammonium bromide \_\_\_\_\_

potassium chlorate \_\_\_\_\_

cobalt(III) nitrate \_\_\_\_\_

scandium phosphate \_\_\_\_\_

ammonium sulfate \_\_\_\_\_

calcium cyanide \_\_\_\_\_

### 4.7 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.