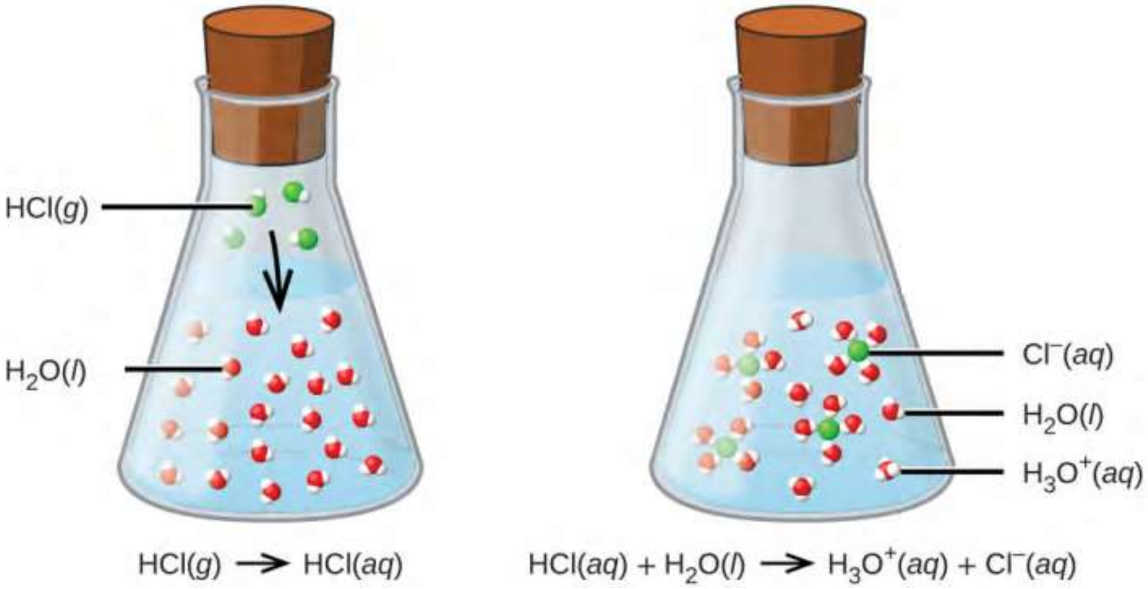
ZABKOVSKA O., SHAFOROST Yu.

INORGANIC CHEMISTRY

PART 1

GENERAL CHEMISTRY



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Lecture notes

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Lecture notes prepared for first-year students of the E3 Chemistry major at the bachelor's level.

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Lecture notes were prepared according to the work program of the discipline "General and Inorganic Chemistry". This work briefly presents the main topics related to the study of general chemistry, namely, the periodic table, the structure of the atom, and the kinetics and thermodynamics of chemical reactions. The types and mechanisms of chemical bonds, as well as the properties and pH of solutions, are also described. Some chapters are devoted to electrochemical processes in chemistry (electroplating and electrolysis).

Lecture notes can be useful for students in Chemistry, Secondary Education (Chemistry), Biology, and Chemistry.

The data in the prepared lecture notes are taken from the corresponding books and sites, which are set out in English and are given at the end of this edition.

Table of context

Preface

Chemistry is designed for the one-semester general chemistry course. As such, this textbook provides an important opportunity for students to learn the core concepts of chemistry and understand how those concepts apply to their lives and the world around them. The context has been developed to meet the scope and sequence of most general chemistry courses. At the same time, the book includes several innovative features designed to enhance student learning.

A strength of these lecture notes is that the sections indicate links to the practical part of the topic (virtual laboratory “PhET”).

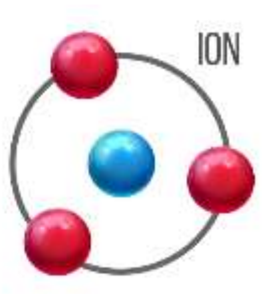
Chemistry in everyday life ties chemistry concepts to everyday issues and real-world applications of science that students encounter in their lives.

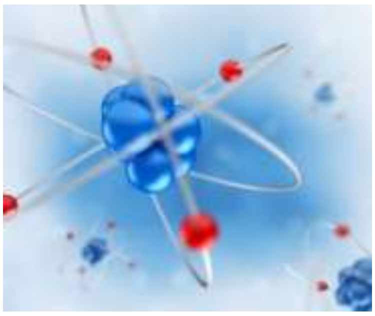
The content of these notes has been developed and arranged to provide a logical progression from fundamental to more advanced concepts of chemical science. Topics are introduced within the context of familiar experiences whenever possible to satisfy the learner.

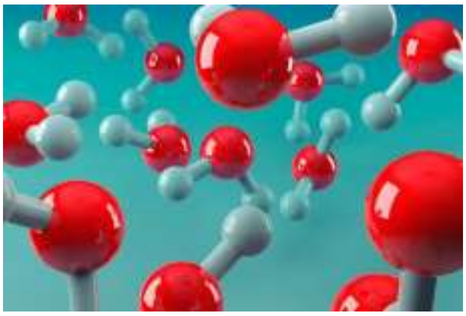
The developed lectures are designed to enhance students’ understanding of concepts through clear, effective illustrations, diagrams, and photographs.

CHAPTER 1

ATOMS, MOLECULES, AND IONS







Chapter Outline

1.1 Chemical formulas
1.2 The Periodic Table
1.3 Molecular and Ionic Compounds

1.1.Chemical formulas

A molecular formula represents a molecule that uses chemical symbols to indicate the types of atoms, followed by subscripts to show the number of atoms of each type in the molecule. (A subscript is used only when more than one atom of a given type is present.) Molecular formulas are also used as abbreviations for the names of compounds.

The structural formula for a compound gives the same information as its molecular formula (the types and numbers of atoms in the molecule), but also shows how the atoms are connected in the molecule. The structural formula for methane contains symbols for one N atom and three H atoms, indicating the number of atoms in the molecule (Figure 1.1). The lines represent bonds that hold the atoms together. (A chemical bond is an attraction between atoms or ions that holds them together in a molecule or a crystal.) We will discuss chemical bonds and see how to predict the arrangement of atoms in a molecule later. For now, know that the lines indicate how the atoms are connected in a molecule. A ball-and-stick model shows the geometric arrangement of the atoms with atomic sizes not to scale, and a space-filling model shows the relative sizes of the atoms.

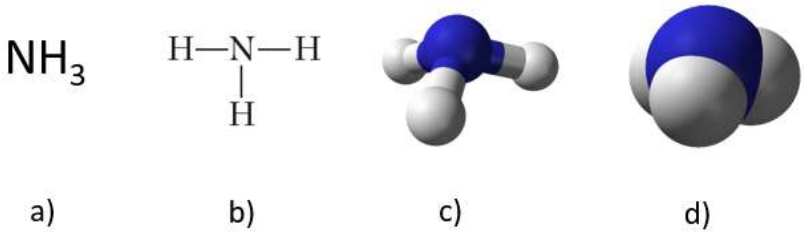


Figure 1.1 A methane molecule can be represented as (a) a molecular formula, (b) a structural formula, (c) a ball-and-stick model, and (d) a space-filling model. Nitrogen and hydrogen atoms are represented by blue and white spheres, respectively.

Although many elements consist of discrete, individual atoms, some exist as molecules made up of two or more atoms of the element chemically bonded together. For example, most samples of the elements hydrogen, oxygen, and nitrogen are composed of molecules that contain two atoms each (called diatomic molecules) and thus have the molecular formulas H_2, O_2, and N_2, respectively. Other elements commonly found as diatomic molecules are fluorine (F_2), chlorine (Cl_2), bromine (Br_2), and iodine (I_2). The most common form of the element sulfur is composed of molecules that consist of eight atoms of sulfur; its molecular formula is S_8 (Figure 1.2).

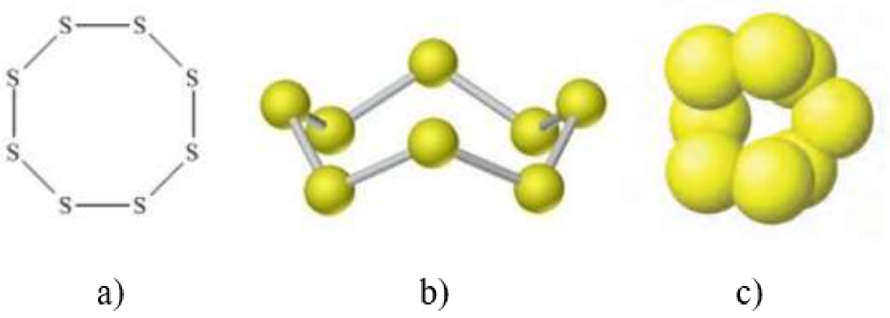


Figure 1.2 A molecule of sulfur is composed of eight sulfur atoms and is therefore written as S8. It can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. Sulfur atoms are represented by yellow spheres.

It is important to note that a subscript following a symbol and a number in front of a symbol do not represent the same thing; for example, H_2 and 2H represent distinctly different species. H2 is a molecular formula; it represents a diatomic molecule of hydrogen, consisting of two atoms of the element that are chemically bonded together. The expression 2H, on the other hand, indicates two separate hydrogen atoms that are not combined as a unit. The expression $2H_2$ represents two molecules of diatomic hydrogen (Figure 1.3).

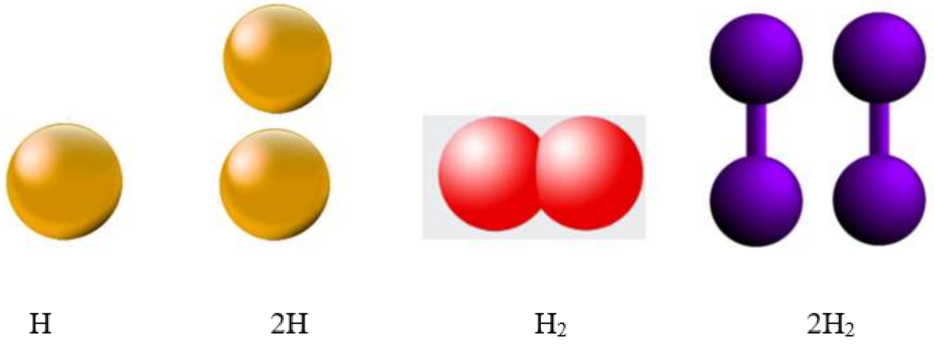
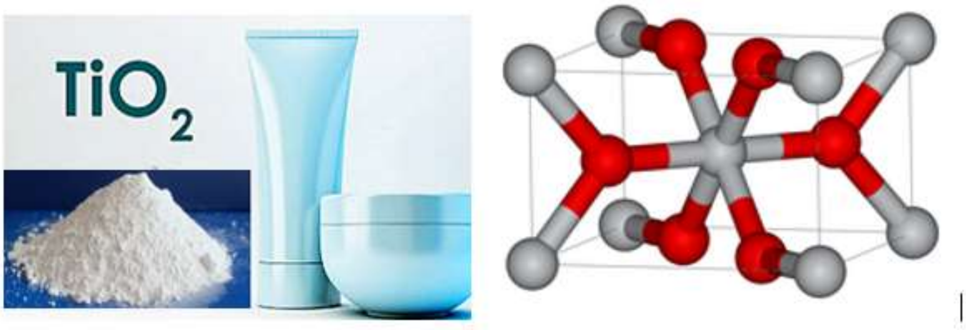


Figure 1.3 The symbols H, 2H, H_2, and $2H_2$ represent very different entities.

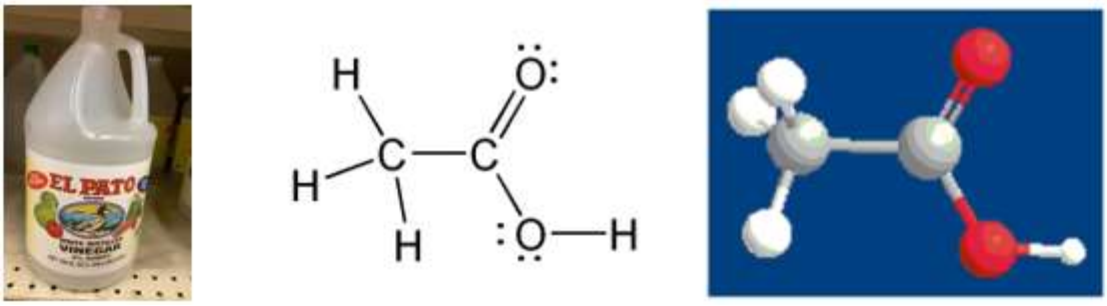
Compounds are formed when two or more elements chemically combine, resulting in the formation of bonds. For example, hydrogen and oxygen can react to form water, and sodium and chlorine can react to form table salt. We sometimes describe the composition of these compounds with an empirical formula, which indicates the types of atoms present and the simplest whole-number ratio of the number of atoms (or ions) in the compound. For example, titanium dioxide (used as a pigment in white paint and in the thick, white, blocking type of sunscreen) has an empirical formula of TiO_2. This identifies the elements titanium (Ti) and oxygen (O) as the constituents of titanium dioxide and indicates the presence of twice as many atoms of the element oxygen as atoms of the element titanium (Figure 1.4).



a) b)

Figure 1.4 (a) The white compound titanium dioxide provides effective protection from the sun. (b) A crystal of titanium dioxide, TiO_2, contains titanium and oxygen in a ratio of 1: 2. The titanium atoms are gray and the oxygen atoms are red.

If we know a compound's formula, we can easily determine the empirical formula. (This is somewhat of an academic exercise; the reverse chronology is generally followed in actual practice.) For example, the molecular formula for acetic acid, the component that gives vinegar its sharp taste, is $C_2H_4O_2$. This formula indicates that a molecule of acetic acid (Figure 1.5) contains two carbon atoms, four hydrogen atoms, and two oxygen atoms. The ratio of atoms is 2:4:2. Dividing by the lowest common denominator (2) gives the simplest, whole-number ratio of atoms, 1:2:1, so the empirical formula is CH_2O. Note that a molecular formula is always a whole-number multiple of an empirical formula.



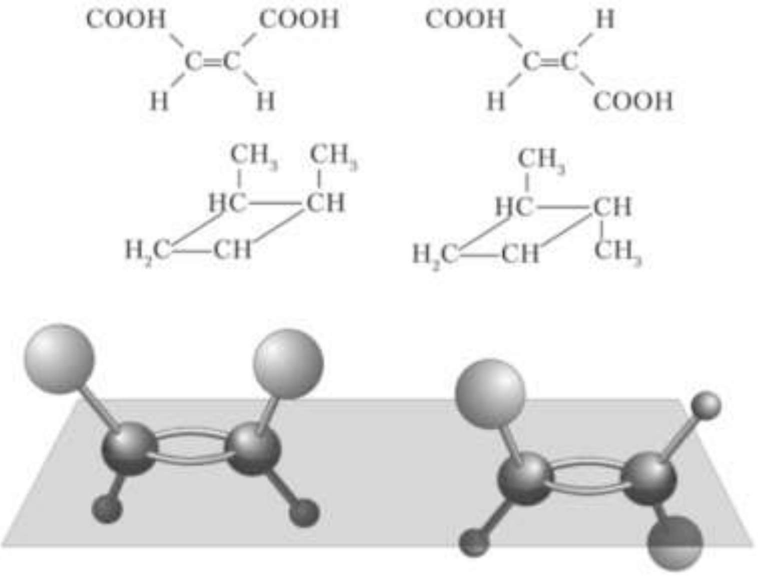
a) b) c)

Figure 1.5 (a) Vinegar contains acetic acid, $C_2H_4O_2$, which has an empirical formula of CH_2O. It can be represented as (b) a structural formula and (c) a ball-and-stick model.

Link to Learning

You can explore molecule building (http://openstaxcollege.org/l/16molbuilding) using an online simulation.

Many types of isomers exist (Figure 1.6). Acetic acid and methyl formate are structural isomers, compounds in which the molecules differ in how the atoms are connected. There are also various types of spatial isomers, in which the relative orientations of the atoms in space can be different.



a) *b)*

Figure 1.6 Molecules are spatial isomers; they only differ in the relative orientations of the atoms in space (*a)* cis isomer; *b)* trans isomer)

1.2 The Periodic Table

That various elements could be grouped by their similar chemical behaviors. One such grouping includes lithium (Li), sodium (Na), and potassium (K): These elements all are shiny, conduct heat and electricity well, and have similar chemical properties. A second grouping includes calcium (Ca), strontium (Sr), and barium (Ba), which are also shiny, good conductors of heat and electricity, and have chemical properties in common. However, the specific properties of these two groupings are notably different from each other. For example, Li, Na, and K are much more reactive than Ca, Sr, and Ba; Li, Na, and K form compounds with oxygen in a ratio of two of their atoms to one oxygen atom, whereas Ca, Sr, and Ba form compounds with one of their atoms to one oxygen atom. Fluorine (F), chlorine (Cl), bromine (Br), and iodine (I) also exhibit similar properties to each other, but these properties are drastically different from those of any of the elements above.

By the twentieth century, it became apparent that the periodic relationship involved atomic numbers rather than atomic masses. The modern statement of this relationship, the periodic law, is as follows: the properties of the elements are periodic functions of their atomic numbers. A modern periodic table arranges the elements in increasing order of their atomic numbers and groups atoms with similar properties in the same vertical column (Figure 1.7).

Each box represents an element and contains its atomic number, symbol, average atomic mass, and (sometimes) name. The elements are arranged in seven horizontal rows, called periods or series, and 18 vertical columns, called groups. Groups are labeled at the top of each column. In the United States, the labels traditionally were numerals with capital letters. However, IUPAC recommends that the numbers 1 through 18 be used, and these labels are more common. For the table to fit on a single page, parts of two of the rows, a total of 14 columns, are usually written below the main body of the table.

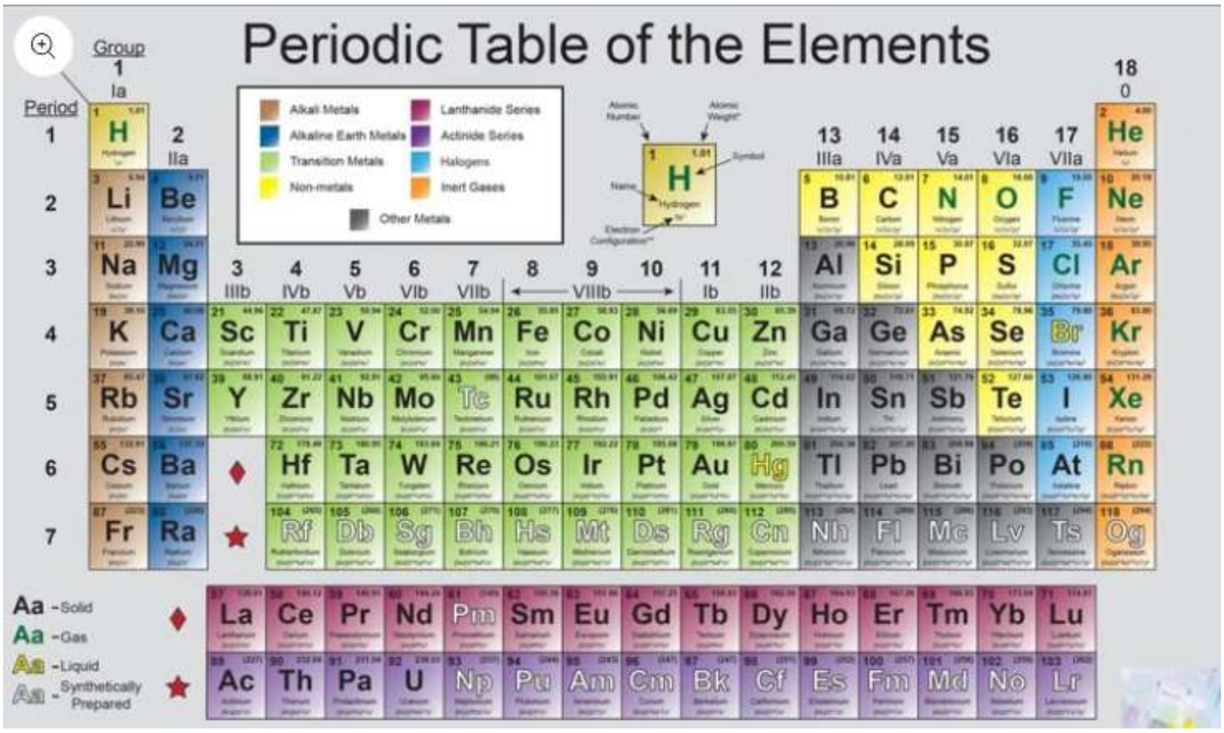


Figure 1.7 Elements in the periodic table are organized according to their properties.

We can sort the elements into large classes with common properties: **metals** (elements that are shiny, malleable, good conductors of heat and electricity—shaded the dark colors – blue, brown); **nonmetals** (elements that appear dull, poor conductors of heat and electricity—shaded yellow); and **metalloids** elements that conduct heat and electricity moderately well and possess some properties of metals and some properties of nonmetals) (https://pubchem.ncbi.nlm.nih.gov/periodic-table/) .

The elements can also be classified into **the main-group elements** (**or representative elements**) in the columns labeled 1, 2, and 13–18; **the transition metals** in the columns labeled 3–12; and **inner transition metals** in the two rows at the bottom of the table (the top-row elements are called **lanthanides** and the bottom-row elements are **actinides**; Figure 1.8). The elements can be subdivided further by more specific properties, such as the composition of the compounds they form. For example, the elements in group 1 (the first column) form compounds that consist of one atom of the element and one atom of hydrogen. These elements (except hydrogen) are known as alkali metals, and they all have similar chemical properties. The elements in group 2 (the second column) form compounds consisting of one atom of the element and two atoms of hydrogen: These are called **alkaline earth metals**, with similar properties among members of that group. Other groups with specific names are **the pnictogens** (group 15), **chalcogens** (group 16), **halogens** (group 17), and **noble gases** (group 18, also known as inert gases). The groups can also be referred to by the first element of the group: For example, the chalcogens can be called the oxygen group or oxygen family. Hydrogen is a unique, nonmetallic element with properties similar to both group 1A and group 7A elements. For that reason, hydrogen may be shown at the top of both groups or by itself.

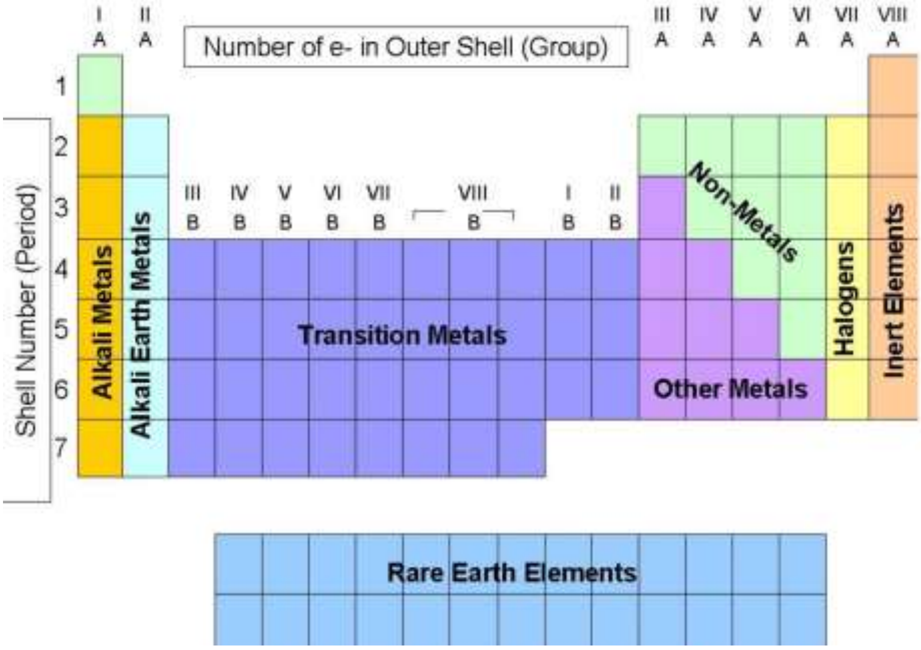


Figure 1.8 The periodic table organizes elements with similar properties into groups.

Link to Learning

Click on this link (http://surl.li/ihinhy) for an interactive periodic table, which you can use to explore the properties of the elements (includes podcasts and videos of each element) / http://surl.li/lsnxcf

In studying the periodic table, you might have noticed something about the atomic masses of some of the elements. Element 43 (technetium), element 61 (promethium), and most of the elements with atomic number 84 (polonium)and higher have their atomic mass given in square brackets. This is done for elements that consist entirely of unstable, radioactive isotopes (you will learn more about radioactivity in the nuclear chemistry chapter). An average atomic weight cannot be determined for these elements because their radioisotopes may vary significantly in relative abundance, depending on the source, or may not even exist in nature. The number in square brackets is the atomic mass number (and approximate atomic mass) of the most stable isotope of that element.

1.3 Molecular and Ionic Compounds

You can use the periodic table to predict whether an atom will form an anion or a cation, and you can often predict the charge of the resulting ion. Atoms of many main-group metals lose enough electrons to leave them with the same number of electrons as an atom of the preceding noble gas. To illustrate, an atom of an alkali metal (group 1) loses one electron and forms a cation with a 1+ charge; an alkaline earth metal (group 2) loses two electrons and forms a cation with a 2+ charge, and so on. For example, a neutral magnesium atom, with 12 protons and 12 electrons, readily loses two electrons. This results in a cation with 12 protons, 10 electrons, and a 2+ charge. It has the same number of electrons as atoms of the preceding noble gas, neon, and is symbolized by Mg^{2+}. The name of a metal ion is the same as the name of the metal atom from which it forms, so Mg^{2+} is called a magnesium ion.

When atoms of nonmetal elements form ions, they generally gain enough electrons to give them the same number of electrons as an atom of the next noble gas in the periodic table. Atoms of group 17 gain one electron and form anions with a 1− charge; atoms of group 16 gain two electrons and form ions with a 2− charge, and so on. For example, the neutral chlorine, with 17 protons and 17 electrons, can gain one electron to provide it with 18 electrons. This results in an anion with 17 protons, 18 electrons, and a 1^{-} charge. It has the same number of electrons as atoms of the next noble gas, argon, and is symbolized by Cl^{-}.

Note the usefulness of the periodic table in predicting likely ion formation and charge (Figure 1.9). Though we can see that transition metals form positive ions, and some transition metals have set charges, most transition metals are extremely variable, and depending on what element they bond with, they can become one of many different ions. Why does this happen? Because it is a lot easier for transition metals to lose electrons compared to the alkaline earth metals (groups one and two). This is because transition metals have 5 d-orbitals. D-orbitals have a variety of oxidation states, whereas the s-orbitals in alkaline earth metals cause these metals to have set oxidation states. For example, in $CoBr_2$, we see that Cobalt is +2 because Bromine is a +1 ion, and two Bromines create a charge of +2.

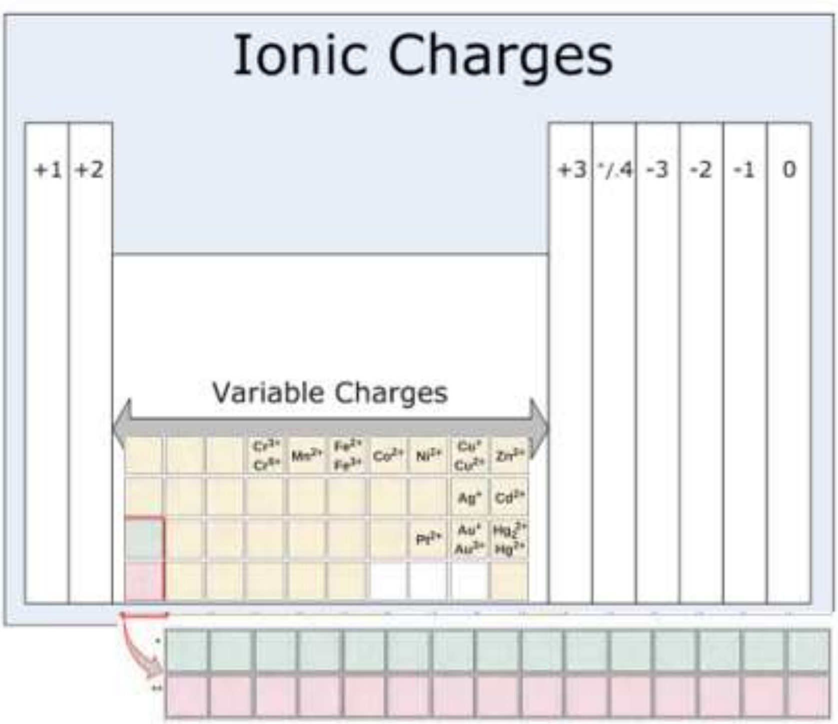
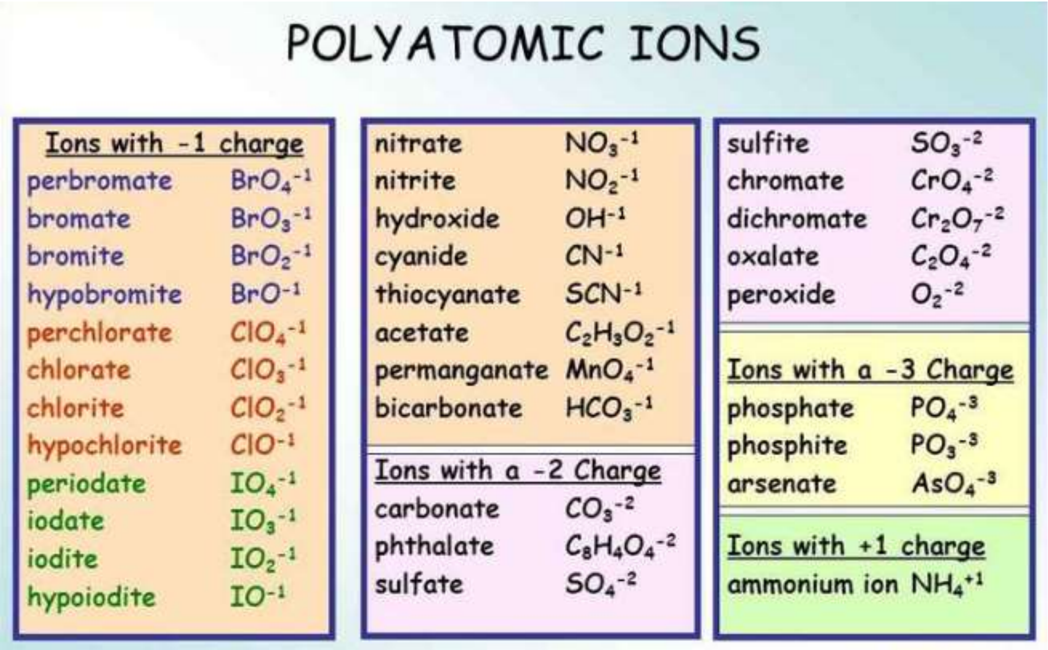


Figure 1.9 Some elements exhibit a regular pattern of ionic charge when they form ions.

The monatomic ions are ions formed from only one atom. We also find many polyatomic ions. These ions, which act as discrete units, are electrically charged molecules (a group of bonded atoms with an overall charge). Some of the more important polyatomic ions are listed in Table 1.1. Oxyanions are polyatomic ions that contain one or more oxygen atoms. You should memorize the names, formulas, and charges of the most common polyatomic ions. Because you will use them repeatedly, they will soon become familiar.



POLYATOMIC IONS

Ions with -1 charge	
perbromate	BrO_4^{-1}
bromate	BrO_3^{-1}
bromite	BrO_2^{-1}
hypobromite	BrO^{-1}
perchlorate	ClO_4^{-1}
chlorate	ClO_3^{-1}
chlorite	ClO_2^{-1}
hypochlorite	ClO^{-1}
periodate	IO_4^{-1}
iodate	IO_3^{-1}
iodite	IO_2^{-1}
hypoiodite	IO^{-1}
nitrate	NO_3^{-1}
nitrite	NO_2^{-1}
hydroxide	OH^{-1}
cyanide	CN^{-1}
thiocyanate	SCN^{-1}
acetate	$C_2H_3O_2^{-1}$
permanganate	MnO_4^{-1}
bicarbonate	HCO_3^{-1}

Ions with a -2 Charge	
carbonate	CO_3^{-2}
phthalate	$C_8H_4O_4^{-2}$
sulfate	SO_4^{-2}
sulfite	SO_3^{-2}
chromate	CrO_4^{-2}
dichromate	$Cr_2O_7^{-2}$
oxalate	$C_2O_4^{-2}$
peroxide	O_2^{-2}

Ions with a -3 Charge	
phosphate	PO_4^{-3}
phosphite	PO_3^{-3}
arsenate	AsO_4^{-3}

Ions with +1 charge	
ammonium ion	NH_4^{+1}

Table 1.1 Examples of the important polyatomic ions.

Note that there is a system for naming some polyatomic ions; -ate and -ite are suffixed, designating polyatomic ions containing more or fewer oxygen atoms. Per- (short for "hyper") and hypo (meaning "under") are prefixes meaning more oxygen atoms than -ate and fewer oxygen atoms than -ite, respectively. For example, perchlorate is ClO_4^-, chlorate is ClO_3^-, chlorite is ClO_2^-, and hypochlorite is ClO^-. Unfortunately, the number of oxygen atoms corresponding to a given suffix or prefix is not consistent; for example, nitrate is NO_3^-, while sulfate is SO_4^{2-}. This will be covered in more detail in the next module on nomenclature. The nature of the attractive forces that hold atoms or ions together within a compound is the basis for classifying chemical bonding. When electrons are transferred and ions form, ionic bonds result. Ionic bonds are electrostatic forces of attraction, that is, the attractive forces experienced between objects of opposite electrical charge (in this case, cations and anions). When electrons are "shared" and molecules form, covalent bonds result. Covalent bonds are the attractive forces between the positively charged nuclei of the bonded atoms and one or more pairs of electrons that are located between the atoms. Compounds are classified as ionic or molecular (covalent) based on the bonds present in them.

Ionic compounds

When an element composed of atoms that readily lose electrons (a metal) reacts with an element composed of atoms that readily gain electrons (a nonmetal), a transfer of electrons usually occurs, producing ions. The compound formed by this transfer is stabilized by the electrostatic attractions (ionic bonds) between the ions of opposite charge present in the compound. For example, when each sodium atom in a sample of sodium metal (group 1) gives up one electron to form a potassium cation, K^+, and each chlorine atom in a sample of chlorine gas (group 17) accepts one electron to form a bromine anion, Br^-, the resulting compound, KBr, is composed of potassium ions and bromine ions in the ratio of one K^+ ion for each Br^- ion. Similarly, each magnesium atom (group 2) can give up two electrons and transfer one to each of two bromine atoms to form $MgBr_2$, which is composed of Mg^{2+} and Br^- ions in the ratio of one Mg^{2+} ions to two Br^- ions.

A compound that contains ions and is held together by ionic bonds is called **an ionic compound**. The periodic table can help us recognize many of the ionic compounds: When a metal is combined with one or more nonmetals, the compound is usually ionic. However, it is not always true (for example, aluminum chloride, $AlCl_3$, is not ionic).

You can often recognize ionic compounds because of their properties. Ionic compounds are solids that typically melt at high temperatures and boil at even higher temperatures. For example, sodium chloride melts at 801°C and boils at 1413°C. (As a comparison, the molecular compound water melts at 0 °C and boils at 100 °C.) In solid form, an ionic compound is not electrically conductive because its ions are unable to flow ("electricity" is the flow of charged particles). When molten, however, it can conduct electricity because its ions can move freely through the liquid (Figure 1.10).

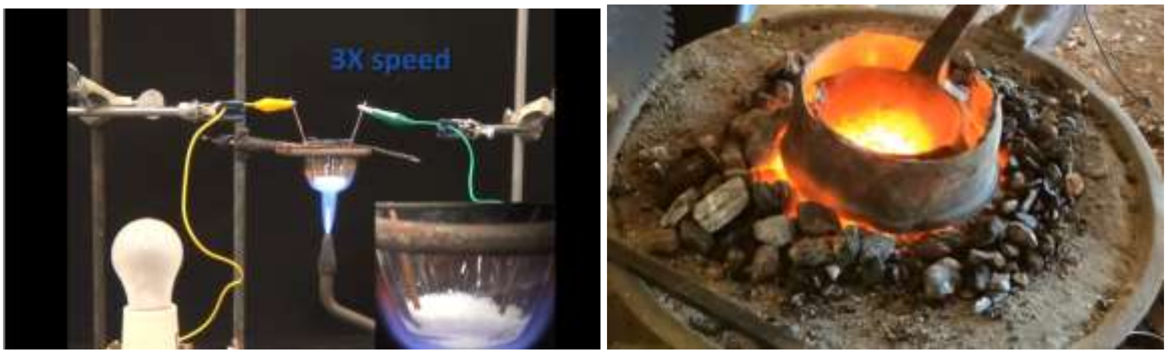


Figure 1.10 Sodium chloride melts at 801°C and conducts electricity when molten.

Link to Learning

Watch this video https://u.to/8sy8Hw to see the salts melt and conduct electricity.

Molecular Compounds

Many compounds do not contain ions but instead consist solely of neutral molecules. These molecular compounds (covalent compounds) result when atoms share, rather than transfer (gain or lose), electrons. We can often identify molecular compounds based on their physical properties. Under normal conditions, molecular compounds often exist as gases, low-boiling liquids, and low-melting solids, although many important exceptions exist. Whereas ionic compounds are usually formed when a metal and a nonmetal combine, covalent compounds are usually formed by a combination of nonmetals. Thus, the periodic table can help us recognize many of the covalent compounds. We can use the positions of a compound's elements in the periodic table to predict whether it is ionic or covalent.

CHAPTER 2

COMPOSITION OF SUBSTANCES AND SOLUTIONS

Chapter Outline
2.1 Formula mass and mole
2.2 Determining Empirical and Molecular Formulas
2.3 Molarity
2.4 Other units for concentrations of the solution

2.1 Formula mass and mole

In an earlier chapter, we described the development of the atomic mass unit, the concept of average atomic masses, and the use of chemical formulas to represent the elemental makeup of substances. These ideas can be extended to calculate **the formula mass** of a substance by summing the average atomic masses of all the atoms represented in the substance's formula.

If we talk about the covalent compounds, the formula represents the numbers and types of atoms composing a single molecule of the substance; therefore, the formula mass may be correctly referred to as a molecular mass. The molecular formula of carbon dioxide indicates that a single molecule contains one carbon atom and two oxygen atoms. The average molecular mass of a molecule is therefore equal to the sum of the average atomic masses of these atoms, which is 44 amu.

Ionic compounds are composed of discrete cations and anions combined in ratios to yield electrically neutral bulk matter. The formula mass for an ionic compound is calculated in the same way as the formula mass for covalent compounds: by summing the average atomic masses of all the atoms in the compound's formula. Keep in mind, however, that the formula for an ionic compound does not represent the composition of a discrete molecule, so it may not correctly be referred to as the "molecular mass." As an example, consider potassium chloride, KCl, the chemical name for common table salt. Sodium chloride is an ionic compound composed of potassium cations, K^+, and chloride anions, Cl^-, combined in a 1:1 ratio. The formula mass for this compound is computed as 74.44 amu.

A mole is an amount unit similar to familiar units like pair, dozen, gross, etc. It provides a specific measure of the number of atoms or molecules in a bulk sample of matter. A mole is defined as the amount of substance containing the same number of discrete entities (such as atoms, molecules, and ions) as the number of atoms in a sample of pure ^{12}C weighing exactly 12 g. One Latin connotation for the word "mole" is "large mass" or "bulk," which is consistent with its use as the name for this unit. The mole provides a link between an easily measured macroscopic property, bulk mass, and an extremely important fundamental property, the number of atoms, molecules, and so forth.

The number of entities composing a mole has been experimentally determined to be $6.02214179 \times 10^{23}$, a fundamental constant named **Avogadro's number** (N_A). This constant is properly reported with an explicit unit of "per mole," a conveniently rounded version being 6.022×10^{23}/mol (https://www.youtube.com/watch?v=zX918pF1HO0).

Consistent with its definition as an amount unit, 1 mole of any element contains the same number of atoms as 1 mole of any other element. The masses of 1 mole of different elements, however, are different, since the masses of the individual atoms are drastically different. The molar mass of an element (or compound) is the mass in grams of 1 mole of that substance, a property expressed in units of grams per mole (g/mol).

The relationships between formula mass, the mole, and Avogadro's number can be applied to compute various quantities that describe the composition of substances and compounds. For example, if we know the mass and chemical composition of a substance, we can determine the number of moles and calculate the number of atoms or molecules in the sample. Likewise, if we know the number of moles of a substance, we can derive the number of atoms or molecules and calculate the substance's mass.

2.2 Determining Empirical and Molecular Formulas

Percent Composition

The elemental makeup of a compound defines its chemical identity, and chemical formulas are the most succinct way of representing this elemental makeup. When a compound's formula is unknown, measuring the mass of each of its constituent elements is often the first step in the process of determining the formula experimentally. The results of these measurements permit the calculation of the compound's percent composition, defined as the percentage by mass of each element in the compound. For example, consider a gaseous compound composed solely of nitrogen and hydrogen. The percent composition of this compound could be represented as follows:

$$\%\ \mathrm{H} = \text{mass H} \times 100\% \,/\, \text{mass compound}$$
$$\%\ \mathrm{C} = \text{mass C} \times 100\% \,/\, \text{mass compound}$$

Determination of Empirical Formulas

As previously mentioned, the most common approach to determining a compound's chemical formula is to first measure the masses of its constituent elements. However, we must keep in mind that chemical formulas represent the relative numbers, not masses, of atoms in the substance. Therefore, any experimentally derived data involving mass must be used to derive the corresponding numbers of atoms in the compound. To accomplish this, we can use molar masses to convert the mass of each element to many moles. We then consider the moles of each element relative to each other, converting these numbers into a whole-number ratio that can be used to derive the empirical formula of the substance (https://u.to/1ibAHw).

Link to Learning

From the Molecular Formula to the Empirical Formula (https://u.to/JijAHw).

Derivation of Molecular Formulas

Recall that empirical formulas are symbols representing the relative numbers of a compound's elements. Determining the absolute numbers of atoms that compose a single molecule of a covalent compound requires knowledge of both its empirical formula and its molecular mass or molar mass. These quantities may be determined experimentally by various measurement techniques. Molecular mass, for example, is often derived from the mass spectrum of the compound (see discussion of this technique in the previous chapter on atoms and molecules). Molar mass can be measured by many experimental methods, many of which will be introduced in later chapters of this text. Molecular formulas are derived by comparing the compound's molecular or molar mass to its empirical formula mass. As the name suggests, an empirical formula mass is the sum of the average atomic masses of all the atoms represented in an empirical formula. If we know the molecular (or molar) mass of the substance, we can divide this by the empirical formula mass to identify the number of empirical formula units per molecule, which we designate as n:

$$\frac{\text{molecular or molar mass}\left(\text{amu or }\frac{\text{g}}{\text{mol}}\right)}{\text{empirical formula mass}\left(\text{amu or }\frac{\text{g}}{\text{mol}}\right)} = n\text{ formula units/molecule}$$

The molecular formula is then obtained by multiplying each subscript in the empirical formula by n, as shown by the generic empirical formula A_xB_y:

$$(A_xB_y)_n = A_{nx}B_{nx}$$

2.3 Molarity

Solutions

We have previously defined solutions as homogeneous mixtures, meaning that the composition of the mixture (and therefore its properties) is uniform throughout its entire volume. Solutions occur frequently in nature and have also been implemented in many forms of manmade technology. We will explore a more thorough treatment of solution properties in the chapter on solutions and colloids, but here we will introduce some of the basic properties of solutions.

The relative amount of a given solution component is known as its **concentration**. Often, though not always, a solution contains one component with a concentration that is significantly greater than that of all other components.

This component is called the solvent and may be viewed as the medium in which the other components are dispersed or **dissolved**. Solutions in which water is the solvent are, of course, very common on our planet. A solution in which water is **the solvent** is called **an aqueous solution**. A solute is a component of a solution that is typically present at a much lower concentration than the solvent.

Solute concentrations are often described with qualitative terms such as **dilute** (of relatively low concentration) and **concentrated** (of relatively high concentration). Concentrations may be quantitatively assessed using a wide variety of measurement units, each convenient for particular applications. **Molarity (M)** is a useful concentration unit for many applications in chemistry. Molarity is defined as the number of moles of solute in exactly 1 liter (1 L) of the solution:

$$M = \text{mol solute/ L solution}$$

Dilution of Solutions

Dilution is the process whereby the concentration of a solution is lessened by the addition of solvent. For example, we might say that a glass of iced tea becomes increasingly diluted as the ice melts. The water from the melting ice increases the volume of the solvent (water) and the overall volume of the solution (iced tea), thereby reducing the relative concentrations of the solutes that give the beverage its taste (Figure 2.1).

Figure 2.1 Both solutions contain the same mass of potassium permanganate. The solution on the left side is more dilute because the potassium permanganate is dissolved in more solvent.

Dilution is also a common means of preparing solutions of a desired concentration. By adding solvent to a measured portion of a more concentrated stock solution, we can achieve a particular concentration.

A simple mathematical relationship can be used to relate the volumes and concentrations of a solution before and after the dilution process. According to the definition of molarity, the molar amount of solute in a solution is equal to the product of the solution's molarity and its volume in liters:

$$n = ML$$

Expressions like these may be written for a solution before and after it is diluted:

$$n_1 = M_1L_1$$

$$n_2 = M_2L_2$$

where the subscripts "1" and "2" refer to the solution before and after the dilution, respectively. Since the dilution process does not change the amount of solute in the solution, $n1 = n2$. Thus, these two equations may be set equal:

$$M_1L_1 = M_2L_2$$

This relation is commonly referred to as the dilution equation. Although we derived this equation using molarity as the unit of concentration and liters as the unit of volume, other units of concentration and volume may be used, so long as the units properly cancel per the factor-label method. Reflecting this versatility, the dilution equation is often written in the more general form:

$$C_1V_1 = C_2V_2$$

where C and V are concentration and volume, respectively.

Link to Learning

Use the simulation (http://surl.li/ikklox) to explore the relations between solute amount, solution volume, and concentration and to confirm the dilution equation.

2.4 Other units for concentrations of the solution

Mass Percentage

Earlier, we introduced percent composition as a measure of the relative amount of a given element in a compound. Percentages are also commonly used to express the composition of mixtures, including solutions. The mass percentage of a solution component is defined as the ratio of the component's mass to the solution's mass, expressed as a percentage:

$$\textit{mass percentage} = \textit{mass of the component} \times 100\% / \textit{mass of solution}$$

We are generally most interested in the mass percentages of solutes, but it is also possible to compute the mass percentage of solvents.

The mass percentage is also referred to by similar names such as percent mass, percent weight, weight/weight percent, and other variations on this theme. The most common symbol for mass percentage is simply the percent sign, %, although more detailed symbols are often used, including % mass, % weight, and (w/w) %.

Volume Percentage

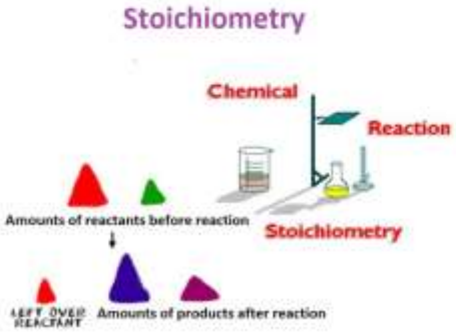
Liquid volumes over a wide range of magnitudes are conveniently measured using common and relatively inexpensive laboratory equipment. The concentration of a solution formed by dissolving a liquid solute in a liquid solvent is therefore often expressed as a volume percentage, %vol or (v/v) %:

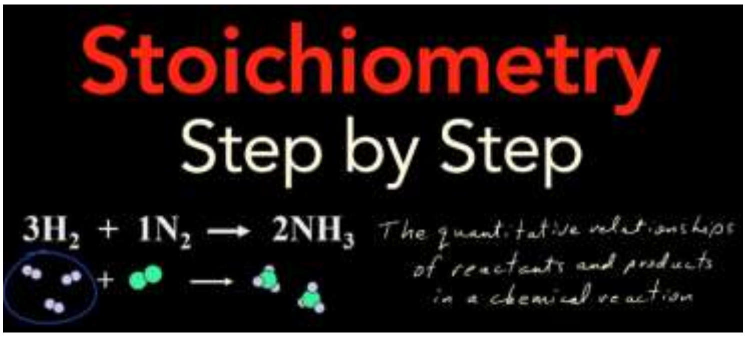
$$\textit{volume percentage} = \textit{volume solute} \times 100\% / \textit{volume solution}$$

In addition to molarity, several other solution concentration units are used in various applications. Percentage concentrations based on the solution components' masses, volumes, or both are useful for expressing relatively high concentrations, whereas lower concentrations are conveniently expressed using ppm or ppb units. These units are popular in environmental, medical, and other fields where mole-based units such as molarity are not as commonly used.

CHAPTER 3

STOICHIOMETRY OF CHEMICAL REACTIONS





Chapter Outline

3.1 Writing and Balancing Chemical Equations
3.2 Classifying Chemical Reactions
3.3 Reaction Stoichiometry
3.4 Reaction Yields

3.1 Writing and balancing chemical equations

When atoms gain or lose electrons to yield ions or combine with other atoms to form molecules, their symbols are modified or combined to generate chemical formulas that appropriately represent these species. Extending this symbolism to represent both the identities and the relative quantities of substances undergoing a chemical (or physical) change involves writing and balancing a chemical equation. Consider, as an example, the reaction between one methane molecule (CH_4) and two diatomic oxygen molecules (O_2) to produce one carbon dioxide molecule (CO_2) and two water molecules (H_2O). The chemical equation representing this process is provided in Figure 3.1.

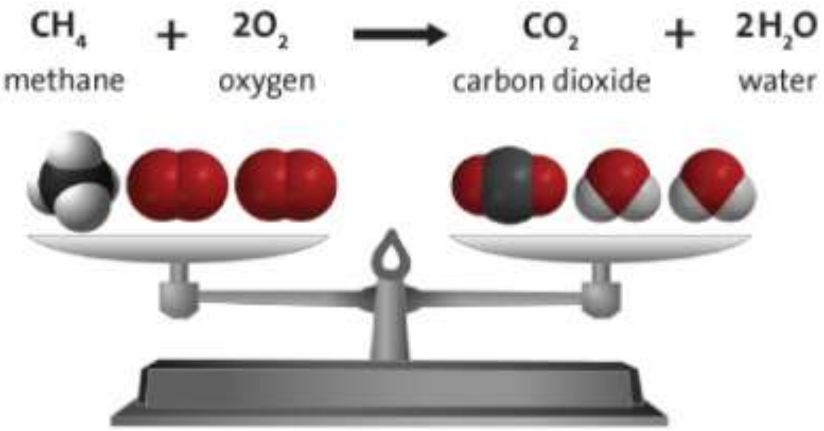


Figure 3.1 The reaction between methane and oxygen to yield carbon dioxide in water.

In the reaction, the bonds in the methane and oxygen come apart, the atoms rearrange, and then re-bond to form water and carbon dioxide.

The little number written at the lower right after an atom (subscript) tells how many of those atoms are in the molecule.

The big number written in front of a molecule (coefficient) shows how many of that molecule there are.

All the atoms in the products come from the atoms in the reactants.

This example illustrates the fundamental aspects of any chemical equation:

In the reaction, the bonds in the methane and oxygen come apart, and the atoms rearrange and then re-bond to form water and carbon dioxide.

- *The little number written at the lower right after an atom (subscript) tells how many of those atoms are in the molecule.*
- *The big number written in front of a molecule (coefficient) shows how many of that molecule there are.*
- *All the atoms in the products come from the atoms in the reactants.*

Likewise, these coefficients may be interpreted concerning any amount (number) unit, and so this equation may be correctly read in many ways, including:

One methane molecule and two oxygen molecules react to yield one carbon dioxide molecule and two water molecules.

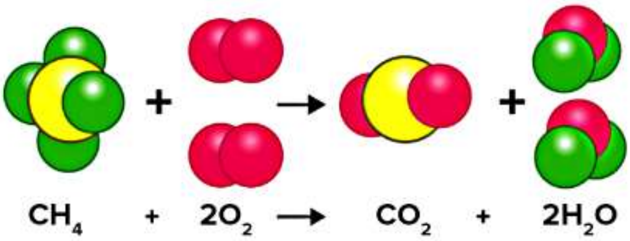
- One dozen methane molecules and two dozen oxygen molecules react to yield one dozen carbon dioxide molecules and two dozen water molecules.
- One mole of methane molecules and 2 moles of oxygen molecules react to yield 1 mole of carbon dioxide molecules and 2 moles of water molecules.

Balancing equations

The chemical equation is balanced, meaning that equal numbers of atoms for each element involved in the reaction are represented on the reactant and product sides. This is a requirement that the equation must satisfy to be consistent with the law of conservation of matter. It may be confirmed by simply summing the numbers of atoms on either side of the arrow and comparing these sums to ensure they are equal. Note that the number of atoms for a given element is calculated by multiplying the coefficient of any formula containing that element by the element's subscript in the formula. If an element appears in more than one formula on a given side of the equation, the number of atoms represented in each must be computed and then added together. For example, both product species in the example reaction, CO_2 and H_2O, contain the element oxygen, and so the number of oxygen atoms on the product side of the equation is.

$$\left(1\ \mathrm{CO_2\ molecule} \times \frac{2\ \mathrm{O\ atoms}}{\mathrm{CO_2\ molecule}}\right) + \left(2\ \mathrm{H_2O\ molecule} \times \frac{1\ \mathrm{O\ atom}}{\mathrm{H_2O\ molecule}}\right) = 4\ \mathrm{O\ atoms}$$

The equation for the reaction between methane and oxygen to yield carbon dioxide and water is confirmed to be balanced per this approach, as shown here:



A balanced chemical equation often may be derived from a qualitative description of some chemical reaction by a fairly simple approach known as balancing by inspection.

The equation for the reaction between molecular nitrogen and molecular hydrogen to produce ammonia is, indeed, balanced.

$$3N_2 + 9H_2 \longrightarrow 6NH_3$$

The coefficients are not the smallest possible integers representing the relative numbers of reactant and product molecules. Dividing each coefficient by the greatest common factor, 3, gives the preferred equation:

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

Molecular and Ionic Equations

When carbon dioxide is dissolved in an aqueous solution of sodium hydroxide, the mixture reacts to yield aqueous sodium carbonate and liquid water. Write balanced molecular, complete ionic, and net ionic equations for this process.

Solution

Begin by identifying formulas for the reactants and products and arranging them properly in chemical equation form:

$CO_2(aq) + NaOH(aq) \longrightarrow Na_2CO_3(aq) + H_2O$ (l) (unbalanced)

Balance is achieved easily in this case by changing the coefficient for NaOH to 2, resulting in the molecular equation for this reaction:

$CO_2(aq) + 2NaOH(aq) \longrightarrow Na_2CO_3(aq) + H_2O$ (l)

The two dissolved ionic compounds, NaOH and Na2CO3, can be represented as dissociated ions to yield the complete ionic equation:

$CO_2(aq) + 2Na^+(aq) + 2OH^-(aq) \longrightarrow 2Na^+(aq) + CO_3^{2-}(aq) + H_2O$ (l)

Finally, identify the spectator ion(s), in this case, $Na^+(aq)$, and remove it from each side of the equation to generate the net ionic equation:

$CO_2(aq) + \cancel{2Na^+(aq)} + 2OH^-(aq) \longrightarrow \cancel{2Na^+(aq)} + CO_3^{2-}(aq) + H_2O$ (l)

$CO_2\ (aq) + 2OH^-(aq) \longrightarrow CO_3^{2-}(aq) + H_2O$ (l)

Link to Learning

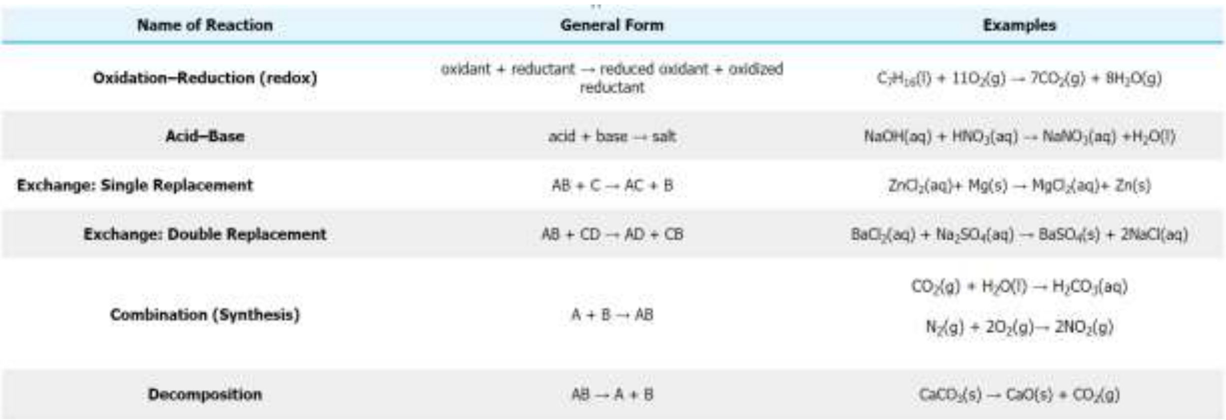
Use this interactive tutorial (http://openstaxcollege.org/l/16BalanceEq) for additional practice balancing equations.

3.2 Classifying Chemical Reactions

Most chemical reactions can be classified into one or more of five basic types: acid-base reactions, exchange reactions, condensation reactions (and the reverse, cleavage reactions), and oxidation-reduction reactions. The general forms of these five kinds of reactions are summarized in Table 3.1 along with examples of each. It is important to note, however, that many reactions can be assigned to more than one classification, as you will see in our discussion.

Table 3.1

Basic types of chemical reactions.



Name of Reaction	General Form	Examples
Oxidation–Reduction (redox)	oxidant + reductant → reduced oxidant + oxidized reductant	$C_7H_{16}(l) + 11O_2(g) \rightarrow 7CO_2(g) + 8H_2O(g)$
Acid–Base	acid + base → salt	$NaOH(aq) + HNO_3(aq) \rightarrow NaNO_3(aq) + H_2O(l)$
Exchange: Single Replacement	AB + C → AC + B	$ZnCl_2(aq) + Mg(s) \rightarrow MgCl_2(aq) + Zn(s)$
Exchange: Double Replacement	AB + CD → AD + CB	$BaCl_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaCl(aq)$
Combination (Synthesis)	A + B → AB	$CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$ $N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$
Decomposition	AB → A + B	$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

The classification scheme is only for convenience; the same reaction can be classified in different ways, depending on which of its characteristics is most important. Oxidation-reduction reactions, in which there is a net transfer of electrons from one atom to another, and condensation reactions will be discussed. Acid-base reactions are one kind of exchange reaction—the formation of an insoluble salt, for instance, such as barium sulfate, when solutions of two soluble salts are mixed.

Combination reactions

A **combination reaction** is a reaction in which two or more substances combine to form a single new substance. Combination reactions can also be called synthesis reactions. The general form of a combination reaction is:

$$A+B \rightarrow AB$$

One combination reaction is two elements combining to form a compound. Solid sodium metal reacts with chlorine gas to produce solid sodium chloride.

$$2Na_{(s)}+Cl_{2(g)} \rightarrow 2NaCl_{(s)}$$

Notice that to write and balance the equation correctly, it is important to remember the seven elements that exist in nature as diatomic molecules ($2H_2$, N_2, O_2, F_2, Cl_2, Br_2, and I_2).

One type of combination reaction that occurs frequently is the reaction of an element with oxygen to form an oxide. Metals and nonmetals both react readily with oxygen under most conditions. Magnesium reacts rapidly and dramatically when ignited, combining with oxygen from the air to produce a fine powder of magnesium oxide:

$$2Mg_{(s)}+O_{2(g)} \rightarrow 2MgO_{(s)}$$

Transition metals are capable of adopting multiple positive charges within their ionic compounds. Therefore, most transition metals are capable of forming different products in a combination reaction. Iron reacts with oxygen to form both iron (II) oxide and iron (III) oxide:

$$2Fe_{(s)}+O_{2(g)}\rightarrow 2FeO_{(s)}$$

$$4Fe_{(s)}+3O_{2(g)}\rightarrow 2Fe_2O_{3(s)}$$

Combination reactions can also take place when an element reacts with a compound to form a new compound composed of a larger number of atoms. Carbon monoxide reacts with oxygen to form carbon dioxide according to the equation:

$$2CO_{(g)}+O_{2(g)}\rightarrow 2CO_{2(g)}$$

Two compounds may also react to form a more complex compound. A very common example is the reactions of oxides with water. Calcium oxide reacts readily with water to produce an aqueous solution of calcium hydroxide:

$$CaO(s)+H_2O_{(l)}\rightarrow Ca(OH)_{2(aq)}$$

Sulfur trioxide gas reacts with water to form sulfuric acid. This is an unfortunately common reaction that occurs in the atmosphere in some places where oxides of sulfur are present as pollutants. The acid formed in the reaction falls to the ground as acid rain (Figure 3.2).

$$SO_{3(g)}+H_2O_{(l)}\rightarrow H_2SO_{4(aq)}$$

Figure 3.2 Acid rain has severe consequences on both natural and manmade objects. Acid rain degrades marble statues like the one on the left (A). The trees in the forest on the right (B) have been killed by acid rain.

Decomposition Reactions

A **decomposition reaction** is a reaction in which a compound breaks down into two or more simpler substances. The general form of a decomposition reaction is:

$$AB\rightarrow A+B$$

Most decomposition reactions require an input of energy in the form of heat, light, or electricity.

Binary compounds are compounds composed of just two elements. The simplest kind of decomposition reaction is when a binary compound decomposes into its elements. Mercury (II) oxide, a red solid, decomposes when heated to produce mercury and oxygen gas (http://surl.li/oovewg):

$$2HgO_{(s)}\rightarrow 2Hg_{(s)}+O_{2(g)}$$

A reaction is also considered to be a decomposition reaction even when one or more of the products are still compounds. A metal carbonate decomposes into a metal oxide and carbon dioxide gas. For example, calcium carbonate decomposes into calcium oxide and carbon dioxide:

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$$

Single Replacement Reactions

A third type of reaction is the single replacement reaction, in which one element replaces a similar element in a compound. The general form of a single-replacement (also called single-displacement) reaction is:

$$A + BC \rightarrow AC + B$$

In this general reaction, element A is a metal and replaces element BB, also a metal, in the compound. When the element that is doing the replacing is a nonmetal, it must replace another nonmetal in a compound, and the general equation becomes:

$$Y + XZ \rightarrow XY + Z$$

where Y is a nonmetal and replaces the nonmetal Z in the compound with X.

Metal replacement

Magnesium is a more reactive metal than copper. When a strip of magnesium metal is placed in an aqueous solution of copper (II) nitrate, it replaces the copper. The products of the reaction are aqueous magnesium nitrate and solid copper metal.

$$Mg(s) + Cu(NO_3)_{2(aq)} \rightarrow Mg(NO_3)_{2(aq)} + Cu_{(s)}$$

This subcategory of single-replacement reactions is called a metal replacement reaction because it is a metal that is being replaced (copper).

Hydrogen replacement

Many metals react easily with acids, and when they do so, one of the products of the reaction is hydrogen gas. Zinc reacts with hydrochloric acid to produce aqueous zinc chloride and hydrogen (figure below).

$$Zn_{(s)} + 2HCl_{(aq)} \rightarrow ZnCl_{2(aq)} + H_{2(g)}$$

In a hydrogen replacement reaction, the hydrogen in the acid is replaced by an active metal. Some metals are so reactive that they are capable of replacing the hydrogen in water. The products of such a reaction are the metal hydroxide and hydrogen gas. All Group 1 metals undergo this type of reaction. Sodium reacts vigorously with water to produce aqueous sodium hydroxide and hydrogen:

$$2Na_{(s)} + 2H_2O_{(l)} \rightarrow 2NaOH_{(aq)} + H_{2(g)}$$

Halogen replacement

The element chlorine reacts with an aqueous solution of sodium bromide to produce aqueous sodium chloride and elemental bromine:

$$Cl_{2(g)} + 2NaBr_{(aq)} \rightarrow 2NaCl_{(aq)} + Br_{2(l)}$$

The reactivity of the halogen group (group 17) decreases from top to bottom within the group. Fluorine is the most reactive halogen, while iodine is the least. Since chlorine is above bromine, it is more reactive than bromine and can replace it in a halogen replacement reaction.

Double replacement reactions

A **double-replacement reaction** is a reaction in which the positive and negative ions of two ionic compounds exchange places to form two new compounds. The general form of a double-replacement (also called double-displacement) reaction is:

$$AB+CD \rightarrow AD+BC$$

In this reaction, A and C are positively charged cations, while B and D are negatively charged anions. Double-replacement reactions generally occur between substances in aqueous solution. For a reaction to occur, one of the products is usually a solid precipitate, a gas, or a molecular compound such as water.

Formation of a precipitate

A precipitate forms in a double-replacement reaction when the cations from one of the reactants combine with the anions from the other reactant to form an insoluble ionic compound. When aqueous solutions of potassium iodide and lead (II) nitrate are mixed, the following reaction occurs (Figure 3.3):

$$2KI_{(aq)}+Pb(NO_3)_{2(aq)} \rightarrow 2KNO_{3(aq)}+PbI_{2(s)}$$

Figure 3.3 Lead (II) iodide precipitates when potassium iodide is mixed with lead (II) nitrate.

Formation of a gas

Some double-replacement reactions produce a gaseous product that then bubbles out of the solution and escapes into the air. When solutions of sodium sulfide and hydrochloric acid are mixed, the products of the reaction are aqueous sodium chloride and hydrogen sulfide gas:

$$Na_2S_{(aq)}+2HCl_{(aq)} \rightarrow 2NaCl_{(aq)}+H_2S_{(g)}$$

Formation of a molecular compound

Another kind of double-replacement reaction is one that produces a molecular compound as one of its products. Many examples in this category are reactions that produce water. When aqueous hydrochloric acid is reacted with aqueous sodium hydroxide, the products are aqueous sodium chloride and water:

$$HCl_{(aq)}+NaOH_{(aq)} \rightarrow NaCl_{(aq)}+H_2O_{(l)}$$

Occasionally, a reaction will produce both a gas and a molecular compound. The reaction of a sodium carbonate solution with hydrochloric acid produces aqueous sodium chloride, carbon dioxide gas, and water:

$$Na_2CO_{3(aq)}+2HCl_{(aq)} \rightarrow 2NaCl_{(aq)}+CO_{2(g)}+H_2O_{(l)}$$

A base is a substance that will dissolve in water to yield hydroxide ions, OH^-. The most common bases are ionic compounds composed of alkali or alkaline earth metal cations (groups 1 and 2) combined with the hydroxide ion — for example, NaOH and $Ca(OH)_2$. When these compounds dissolve in water, hydroxide ions are released directly into the solution. For example, KOH and $Ba(OH)_2$ dissolve in water and dissociate completely to produce cations (K^+ and Ba^{2+}, respectively) and hydroxide ions, OH^-. These bases, along with other hydroxides that completely dissociate in water, are considered **strong bases**.

Consider, as an example, the dissolution of lye (sodium hydroxide) in water:

$$NaOH(s) \longrightarrow Na+(aq) + OH-(aq)$$

This equation confirms that sodium hydroxide is a base. When dissolved in water, NaOH dissociates to yield Na^+ and OH^- ions. This is also true for any other ionic compound containing hydroxide ions. Since the dissociation process is essentially complete when ionic compounds dissolve in water under typical conditions, NaOH and other ionic hydroxides are all classified as strong bases.

Unlike ionic hydroxides, some compounds produce hydroxide ions when dissolved by chemically reacting with water molecules. In all cases, these compounds react only partially and so are classified as **weak bases**. These types of compounds are also abundant in nature and important commodities in various technologies.

A neutralization reaction is a specific type of acid-base reaction in which the reactants are an acid and a base, the products are often salt and water, and neither reactant is the water itself:

$$\text{acid} + \text{base} \longrightarrow \text{salt} + \text{water}$$

To illustrate a neutralization reaction, consider what happens when a typical antacid, such as milk of magnesia (an aqueous solution of solid NaOH) reacts with excess chloric acid (HCl):

$$NaOH(s) + 2HCl(aq) \longrightarrow NaCl(aq) + 2H_2O(l).$$

Oxidation-Reduction reactions

An oxidation-reduction (redox) reaction is a type of chemical reaction that involves a transfer of electrons between two species. An oxidation-reduction reaction is any chemical reaction in which the oxidation number of a molecule, atom, or ion changes by gaining or losing an electron. Redox reactions are common and vital to some of the basic functions of life, including photosynthesis, respiration, combustion, and corrosion or rusting.

The oxidation state (OS) of an element corresponds to the number of electrons, e^-, that an atom loses, gains, or appears to use when joining with other atoms in compounds. In determining the oxidation state of an atom, there are seven guidelines to follow:

1. The oxidation state of an individual atom is 0.
2. The total oxidation state of all atoms in a *neutral species* is 0, and in an *ion* is equal to the ion charge.
3. Group 1 metals have an oxidation state of +1, and Group 2 an oxidation state of +2.
4. The oxidation state of fluorine is -1 in compounds.
5. Hydrogen generally has an oxidation state of +1 in compounds.
6. Oxygen generally has an oxidation state of -2 in compounds.
7. In binary metal compounds, Group 17 elements have an oxidation state of -1, Group 16 elements of -2, and Group 15 elements of -3.

1) for instance, determine the oxidation states of each element in the following reactions:

$$Fe(s)+O_2(g)\longrightarrow Fe_2O_3(g)$$

Fe and O_2 are free elements; therefore, they each have an oxidation state of 0 according to Rule 1. The product has a total oxidation state equal to 0, and following Rule 6, O has an oxidation state of -2, which means Fe has an oxidation state of +3.

2) Determine the oxidation states of the phosphorus atom bold element in each of the following species:

a. Na_3PO_3

b. $H_2PO_4^-$

Solutions

a. The oxidation numbers of Na and O are +1 and -2. Because sodium phosphite is a neutral species, the sum of the oxidation numbers must be zero. Letting *x* be the oxidation number of phosphorus, $0 = 3(+1) + x + 3(-2)$. x = oxidation number of P = +3.

b. Hydrogen and oxygen have oxidation numbers of +1 and -2. The ion has a charge of -1, so the sum of the oxidation numbers must be -1. Letting *y* be the oxidation number of phosphorus, $-1 = y + 2(+1) +4(-2)$, y = oxidation number of P = +5.

3) Determine which element is oxidized and which element is reduced in the following reactions (be sure to include the oxidation state of each):

$$Zn+2H^+ \longrightarrow Zn^{2+}+H_2$$

Solutions

Zn is oxidized (Oxidation number: 0 → +2); H^+ is reduced (Oxidation number: +1 → 0).

Redox reactions are comprised of two parts, a reduced half and an oxidized half, that always occur together. The reduced half gains electrons and the oxidation number decreases, while the oxidized half loses electrons and the oxidation number increases. Another species in the reduction half-reaction takes up those given off in the oxidation half-reaction.

The two species that exchange electrons in a redox reaction are given special names:

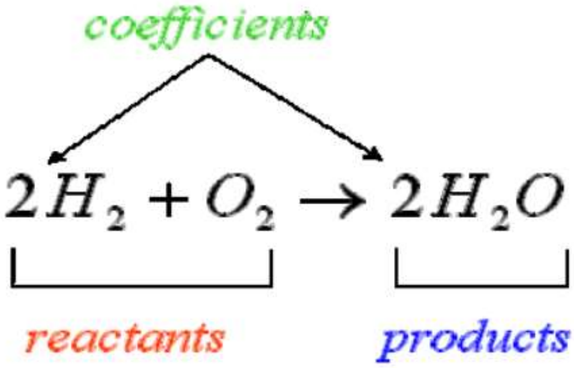
1. The ion or molecule that accepts electrons is called the **oxidizing agent -** by accepting electrons, it oxidizes other species.

2. The ion or molecule that donates electrons is called the **reducing agent -** by giving electrons, it reduces the other species.

3.3 Reaction Stoichiometry

Chemical formulas provide the identities of the reactants and products involved in the chemical change, allowing the classification of the reaction. Coefficients provide the relative numbers of these chemical species, allowing a quantitative assessment of the relationships between the amounts of substances consumed and produced by the reaction. These quantitative relationships are known as the reaction’s stoichiometry.

Chemical equations are symbolic representations of chemical reactions. The reacting materials (reactants) are given on the left, and the products are displayed on the right, usually separated by an arrow showing the direction of the reaction. The numerical coefficients next to each chemical entity denote the proportion of that chemical entity before and after the reaction. The law of conservation of mass dictates that the quantity of each element must remain unchanged in a chemical reaction. Therefore, in a balanced equation, each side of the chemical equation must have the same quantity of each element.



Stoichiometry is the field of chemistry that is concerned with the relative quantities of reactants and products in chemical reactions. For any balanced chemical reaction, whole numbers (coefficients) are used to show the quantities (generally in moles) of both the reactants and products. For example, when oxygen and hydrogen react to produce water, one mole of oxygen reacts with two moles of hydrogen to produce two moles of water.

Reaction stoichiometry describes the quantitative relationship among substances as they participate in various chemical reactions.

Molar Ratios or conversion factors identify the number of moles of each reactant needed to form a certain number of moles of each product.

Stoichiometric ratio: The ratio of the coefficients of the products and reactants in a balanced reaction. This ratio can be used to calculate the amount of products or reactants produced or used in a reaction.

The molar ratios identify how many moles of the product are formed from a certain amount of reactant, as well as the number of moles of a reactant needed to completely react with a certain amount of another reactant. For example, look at this equation:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

From this reaction equation, it is possible to deduce the following molar ratios:

- 1 mol CH_4: 1 mol CO_2
- 1 mol CH_4: 2 mol H_2O
- 1 mol CH_4: 2 mol O_2
- 2 mol O_2: 1 mol CO_2
- 2 mol O_2: 2 mol H_2O

In other words, 1 mol of methane will produce 1 mole of carbon dioxide (as long as the reaction goes to completion and there is plenty of oxygen present). These molar ratios can also be expressed as fractions. For example, 1 mol CH_4: 1 mol CO_2 can be expressed as *1 mol* CH_4 */ 1 mol* CO_2.

Mole-to-mole conversions can be facilitated by using conversion factors found in the balanced equation for the reaction of interest.

The law of conservation of mass dictates that the quantity of an element does not change for a reaction. Therefore, a chemical equation is balanced when all elements have equal values on both the left and right sides.

The balanced equation for the reaction of interest contains the stoichiometric ratios of the reactants and products; these ratios can be used as conversion factors for mole-to-mole conversions.

The next step is to inspect the coefficients of each element of the equation. The coefficients can be thought of as the number of moles used in the reaction.

For example, if 2.22 mol of O_2 reacts with excess hydrogen, how many moles of water are produced?

The chemical equation is $O_2+2H_2 \rightarrow 2H_2O$. Therefore, to calculate the number of moles of water produced:

$2.22 \text{ mol } O_2 \cdot 2 \text{ moles } H_2O / 1 \text{ mol } O_2 = 4.44 \text{ moles } H_2O$

Link to Learning

Have a look at this video to improve your practice (https://u.to/QZHOHw). This video shows how to determine the number of moles of reactants and products using the number of moles of one of the substances in the reaction.

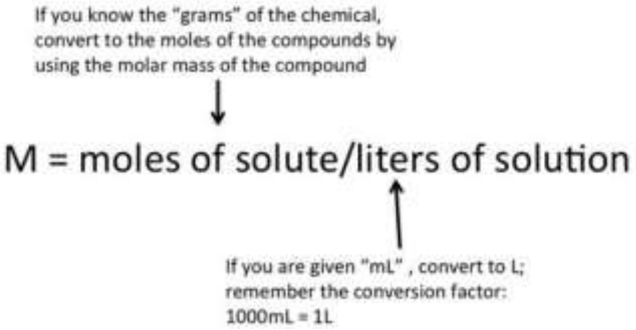
Mass-to-Mass Conversions

Mass-to-mass conversions cannot be done directly; instead, mole values must serve as intermediaries in these conversions. A chemical equation is a visual representation of a chemical reaction. A typical chemical equation follows the form

$$aA + bB \rightarrow cC + dD$$

where an arrow separates the reactants on the left and the products on the right. The coefficients before the reactants and products are their stoichiometric values.

For a mass-to-mass conversion, it is necessary to first convert one amount to moles, then use the conversion factor to find moles of the other substance, and then convert the molar value of interest back to mass.



Link to Learning

Have a look at this video to improve your practice (https://u.to/VZHOHw). This video shows how to determine the grams of the other substances in the chemical equation if the grams of one of the substances are known.

Mass-to-Mole conversions

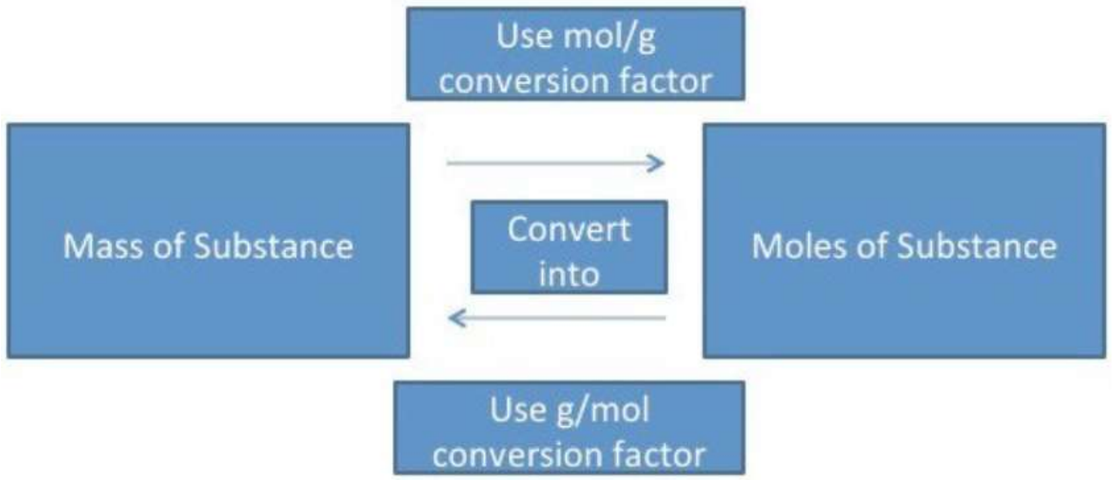
Mass-to-mole conversions can be facilitated by employing the molar mass as a conversion ratio.

Molar mass: The mass of a given substance (chemical element or chemical compound) divided by its amount (mol) of substance.

The compound‘s molar mass is necessary when converting from grams to moles. The molar mass value can be used as a conversion factor to facilitate mass-to-mole and mole-to-mass conversions.

- For a single element, the molar mass is equivalent to its atomic weight multiplied by the molar mass constant (1 g/mol).
- For a compound, the molar mass is the sum of the atomic weights of each element in the compound by the molar mass constant.

After the molar mass is determined, dimensional analysis can be used to convert from grams to moles.



If you have 24.5 g of NaCl, how many moles of NaCl do you have?

24.5 g NaCl ×1 mol NaCl / 58.5 g NaCl = 0.419 moles NaCl

Link to Learning

Have a look at this video to improve your practice (https://u.to/55LOHw). This video describes how to determine the number of moles of reactants and products if given the number of grams of one of the substances in the chemical equation.

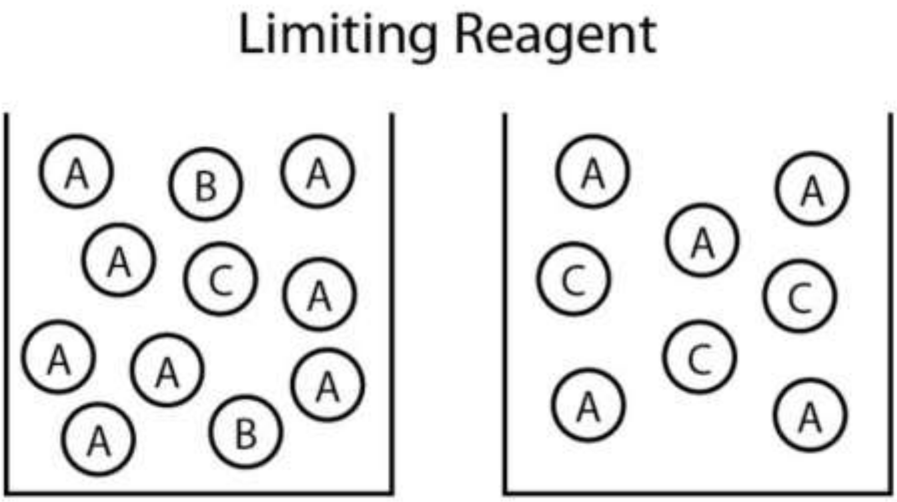
3.4 Reaction Yields

Limiting Reagents

Limiting reagent: The reactant in a chemical reaction that is consumed first prevents any further reaction from occurring.

In a chemical reaction, the limiting reagent, or limiting reactant, is the substance that has been completely consumed when the chemical reaction is complete. The amount of product produced by the reaction is limited by this reactant because the reaction cannot proceed further without it; often, other reagents are present more than the quantities required to react with the limiting reagent. From stoichiometry, the exact amount of reactant needed to react with another element can be calculated. However, if the reagents are not mixed or present in these correct stoichiometric proportions, the limiting reagent will be entirely consumed, and the reaction will not go to stoichiometric completion.

The limiting reagent in a reaction is the first to be completely used up and prevents any further reaction from occurring. In this reaction, reactant B is the limiting reagent because there is still some leftover A in the products. Therefore, A was in excess when B was all used up.



For example, What would be the limiting reagent if 80.0 grams of Na_2O_2 reacted with 30.0 grams of H_2O in the reaction?

$$2Na_2O_2+2H_2O \rightarrow 4NaOH+O_2$$

The comparison can be done with either product; for this example, NaOH will be the product compared. To determine how much NaOH is produced by each reagent, use the stoichiometric ratio given in the chemical equation as a conversion factor:

4 mol NaOH / 2 mol Na_2O_2 and 4 mol NaOH / 2 mol H_2O

Then convert the grams of each reactant into moles of NaOH to see how much NaOH each could produce if the other reactant were in excess.

80.0 g Na_2O_2×(1 mol Na_2O_2 / 77.98 g Na_2O_2) ×(4 mol NaOH/ 2 mol Na_2O_2) = 2.06 moles NaOH

30.0 g H_2O×(1 mol H_2O/18 g H_2O)×(4 mol NaOH / 2 mol H_2O) =3.33 moles NaOH

Na_2O_2 produces less NaOH than H_2O; therefore, Na_2O_2 is the limiting reagent.

Calculating Theoretical and Percent

The percent yield of a reaction measures the reaction's efficiency. It is the ratio between the actual yield and the theoretical yield (https://u.to/e_bSHw).

Actual yield: The amount of product obtained in a chemical reaction.

Percent yield: Refers to the efficiency of a chemical reaction; defined as:

(the actual yield / theoretical yield) ×100

Theoretical yield: The amount of product that could be produced in a given reaction, calculated according to the starting amount of the limiting reagent.

A reaction should theoretically produce as much of the product as the stoichiometric ratio of the product to the limiting reagent suggests. This number can be calculated and is called the theoretical yield. However, the amount of product produced by the reaction will usually be less than the theoretical yield and is referred to as the actual yield. This is because often reactions have "side reactions" that compete for reactants and produce undesired products. To evaluate the efficiency of the reaction, chemists compare the theoretical and actual yields by calculating the percent yield of a reaction:

To calculate percent yield using this equation, it is not necessary to use a particular unit of measurement (moles, mL, g, etc.), but the two values being compared must be consistent in units. The theoretical yield of a reaction is 100 percent, but this value becomes nearly impossible to achieve due to limitations.

To accurately calculate the yield, the equation needs to be balanced. Next, identify the limiting reagent. Then the theoretical yield of the product can be determined and, finally, compared to the actual yield. Then, the percent yield can be calculated.

For example, consider the preparation of nitrobenzene ($C_6H_5NO_2$), starting with 15.6g of benzene (C_6H_6) over nitric acid (HNO_3):

$$C_6H_6+HNO_3 \rightarrow C_6H_5NO_2+H_2O$$

15.6 g C_6H_6× (1 mol C_6H_6 / 78.1 g C_6H_6) × (1 mol $C_6H_5NO_2$ /1 mol C_6H_6) × (123.1 g $C_6H_5NO_2$ / 1 mol $C_6H_5NO_2$ = 24.6 g $C_6H_5NO_2$

In theory, therefore, if all C_6H_6 were converted to product and isolated, 24.6 grams of the product would be obtained (100 percent yield). If 18.0 grams were produced, the percent yield could be calculated:

$$\text{percent yield} = (18.0\ g / 24.6\ g) \times 100$$

$$\text{percent yield} = 73.2\%$$

CHAPTER 4

THERMOCHEMISTRY AND THERMODYNAMICS

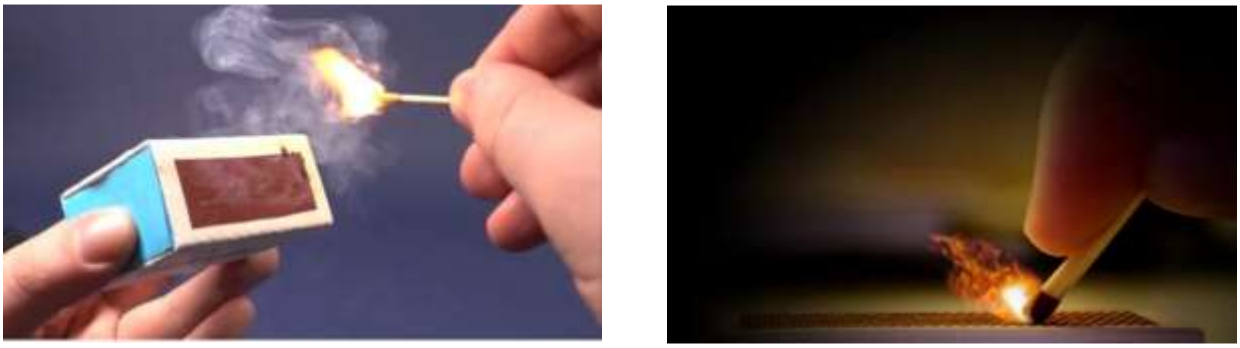


Figure 4.1 Sliding a match head along a rough surface initiates a combustion reaction that produces energy in the form of heat and light.

Chapter Outline

4.1 Energy Basics
4.2 Enthalpy
4.3 Entropy
4.4 Free Energy

4.1 Energy Basics

Chemical reactions, such as those that occur when you light a match, involve changes in energy as well as matter. The energy produced by the batteries in a cell phone, car, or flashlight results from chemical reactions.

An energy system converts primary energy resources like fossil fuels or wind into energy services. Energy services are what humans care about, like hot showers and cold beverages. There are energy losses each time we convert energy from one form to another. Energy systems are most efficient when we can closely match the resource with the service (e.g., using sunlight for illumination). The Earth is an open energy system that is always getting new energy from the sun.

Energy cannot be created or destroyed, but we can theoretically run out of certain forms of energy, like fossil fuels. Fossil fuels are a stock resource (we have a set amount on earth) that can meet the world’s energy needs many times over. However, we need to stop using fossil fuels due to their significant environmental and climate change impacts.

Transportation Basics: The future of sustainable transportation relies on domestic alternative fuels, more fuel-efficient engines, electric-drive vehicles, vehicle connectivity, and a grid powered by a variety of renewable and conventional energy sources.

Hydropower Basics: Hydropower — energy created from fresh, moving water—is the world's oldest form of renewable energy.

Solar Energy Basics: Solar energy is a powerful source of energy that can be used to heat, cool, and light homes and businesses (Figure 4.2).

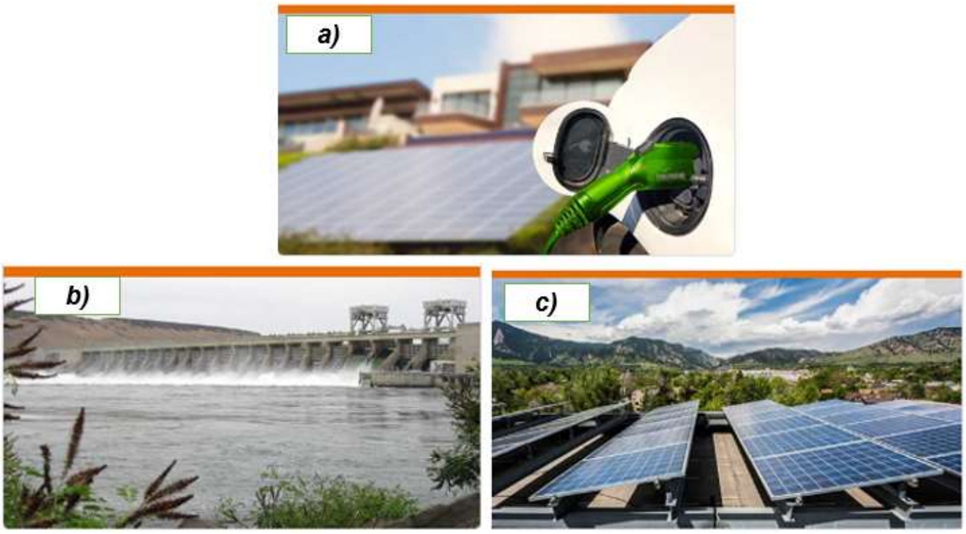


Figure 4.2 The types of energy in the different forms and their manifestation (*a*- transportations; *b)* Hydropower; *c*- solar energy).

Thermal Energy, Temperature, and Heat

Thermal energy is kinetic energy associated with the random motion of atoms and molecules. Temperature is a quantitative measure of "hot" or "cold." When the atoms and molecules in an object are moving or vibrating quickly, they have a higher average kinetic energy (KE), and we say that the object is "hot." When the atoms and molecules are moving slowly, they have lower KE, and we say that the object is "cold" (Figure 4.3). Assuming that no chemical reaction or phase change (such as melting or vaporizing) occurs, increasing the amount of thermal energy in a sample of matter will cause its temperature to increase. And, assuming that no chemical reaction or phase change (such as condensation or freezing) occurs, decreasing the amount of thermal energy in a sample of matter will cause its temperature to decrease.

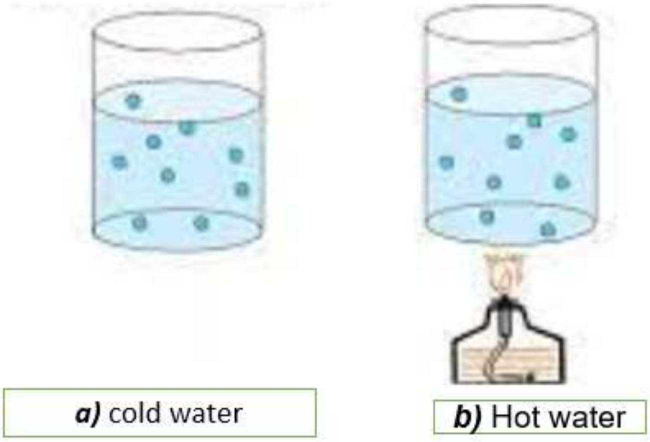


Figure 4.3 (*b*) The molecules in a sample of hot water move more rapidly than *a*) those in a sample of cold water.

We can calculate this thermal energy using the formula: $Q = mc\Delta T$.

Where m is the mass of the substance, c is the specific heat capacity, and ΔT is the temperature difference.

Link to Learning

Click on this interactive simulation (http://openstaxcollege.org/l/16PHETtempFX) to view the effects of temperature on molecular motion.

The definition of **heat** states that it is a flow of thermal energy from one object or substance to another. Heat can be transferred from the burner to the pot, which then transfers heat to the ingredients.

Convention, radiation, and conduction are the three ways of transferring heat energy. Being a form of energy, the SI unit of heat is joules. Also, when no heat energy is exchanged by substances in physical contact, it is called thermal equilibrium.

Compared to the above two terms, the temperature is very different. The hotness or coldness of an object is measured at a given time and is referred to as temperature. The definition of temperature states that it measures the average kinetic energy of the particles that make up a substance.

Temperature alone can't do anything; it’s an intrinsic property and just the temperature of an item at the moment.

Summary

- Thermal energy is the energy contained in a system.
- Heat is the flow of thermal energy.
- Temperature is the average kinetic energy of the molecule.

4.2 Enthalpy

Thermochemistry is a branch of chemical thermodynamics, the science that deals with the relationships between heat, work, and other forms of energy in the context of chemical and physical processes.

Substances act as reservoirs of energy, meaning that energy can be added to them or removed from them. Energy is stored in a substance when the kinetic energy of its atoms or molecules is raised. The greater kinetic energy may be in the form of increased translations (travel or straight-line motions), vibrations, or rotations of the atoms or molecules.

When thermal energy is lost, the intensities of these motions decrease, and the kinetic energy falls. The total of all possible kinds of energy present in a substance is called **internal energy (U),** sometimes symbolized as E.

As a system changes, its internal energy can change, and energy can be transferred from the system to the surroundings, or from the surroundings to the system. Energy is transferred into a system when it absorbs heat (Q) from the surroundings or when the surroundings do work (W) on the system. For example, energy is transferred into a room-temperature metal wire if it is immersed in hot water (the wire absorbs heat from the water) or if you rapidly bend the wire back and forth (the wire becomes warmer because of the work done on it). Both processes increase the internal energy of the wire, which is reflected in an increase in the wire’s temperature. Conversely, energy is transferred out of a system when heat is lost from the system, or when the system does work on the surroundings.

When a process occurs at constant pressure, the heat evolved (either released or absorbed) is equal to the change in enthalpy. Enthalpy (H) is the sum of the internal energy (U) and the product of pressure and volume (PΔV) given by the equation:

$$H = U + P\Delta V \qquad (1)$$

When a process occurs at constant pressure, the heat evolved (either released or absorbed) is equal to the change in enthalpy. **Enthalpy** is a state function that depends entirely on the state functions T, P, and U. Enthalpy is usually expressed as the change in enthalpy (ΔH) for a process between initial and final states:

$$\Delta H = \Delta U + \Delta PV \qquad (2)$$

If temperature and pressure remain constant through the process and the work is limited to pressure-volume work, then the enthalpy change is given by the equation:

$$\Delta H = \Delta U + P\Delta V \qquad (3)$$

Also at constant pressure, the heat flow (q) for the process is equal to the change in enthalpy, defined by the equation:

$$\Delta H = - Q \qquad (4)$$

By looking at whether q is exothermic or endothermic, we can determine a relationship between ΔH and Q. If the reaction absorbs heat, it is endothermic, meaning the reaction consumes heat from the surroundings so $Q < 0$ (negative). Therefore, at constant temperature and pressure, by the equation above, if Q is positive, then ΔH is positive. And the same goes for if the reaction releases heat, then it is exothermic, meaning the system gives off heat to its surroundings, so $Q > 0$ (positive). If Q is positive, then ΔH will be negative.

The first law of thermodynamics, $\Delta U = Q + W$, shows that the internal energy of a system changes through heat flow into or out of the system (positive Q is heat flow out; negative Q is heat flow in) or work done on or by the system.

we should use ΔH in the next cases:

1. A thermochemical equation is used to represent the changes in both matter and energy. In a thermochemical equation, the enthalpy change of a reaction is shown as a ΔH value following the equation for the reaction. This ΔH value indicates the amount of heat associated with the reaction involving the number of moles of reactants and products as shown in the chemical equation. For example, consider this equation:

$$H_2(g) + 1/2O_2(g) \longrightarrow H_2O \quad (l) \qquad \Delta H = -286 \text{ kJ/mole}$$

This equation indicates that when 1 mole of hydrogen gas and 1/2 mole of oxygen gas at some temperature and pressure change to 1 mole of liquid water at the same temperature and pressure, 286 kJ of heat are released to the surroundings. If the coefficients of the chemical equation are multiplied by some factor, the enthalpy change must be multiplied by that same factor (ΔH is an extensive property):

(two-fold increase in amounts)

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O \quad (l) \qquad \Delta H = 2 \times (-286 \text{ kJ}) = -572 \text{ kJ}$$

2. The enthalpy change of a reaction depends on the physical state of the reactants and products of the reaction (whether we have gases, liquids, solids, or aqueous solutions), so these must be shown. For example, when 1 mole of hydrogen gas and ½ mole of oxygen gas change to 1 mole of liquid water at the same temperature and pressure, 286 kJ of heat are released. If gaseous water forms, only 242 kJ of heat is released.

$$H_2(g) + 1/2O_2(g) \longrightarrow H_2O(g) \qquad \Delta H = -242 \text{ kJ}$$

3. A negative value of an enthalpy change, ΔH, indicates an exothermic reaction; a positive value of ΔH indicates an endothermic reaction. If the direction of a chemical equation is reversed, the arithmetic sign of its ΔH is changed (a process that is endothermic in one direction is exothermic in the opposite direction).

Enthalpy changes are typically tabulated for reactions in which both the reactants and products are under the same conditions. A standard state is a commonly accepted set of conditions used as a reference point for the determination of properties under other conditions. The IUPAC standard state refers to materials under a pressure of 1 bar and solutions at 1 M and does not specify a temperature. Many thermochemical tables list values with a standard state of 1 atm. Because the ΔH of a reaction changes very little with such small changes in pressure (1 bar = 0.987 atm), ΔH values (except for the most precisely measured values) are essentially the same under both sets of standard conditions. We will include a superscripted "o" in the enthalpy change symbol to designate a standard state.

Since the usual (but not technically standard) temperature is 298.15 K, we will use a subscripted "298" to designate this temperature. Thus, the symbol (ΔH^{o}_{298}) is used to indicate an enthalpy change for a process occurring under these conditions. (The symbol ΔH is used to indicate an enthalpy change for a reaction occurring under nonstandard conditions.)

Enthalpy of Combustion

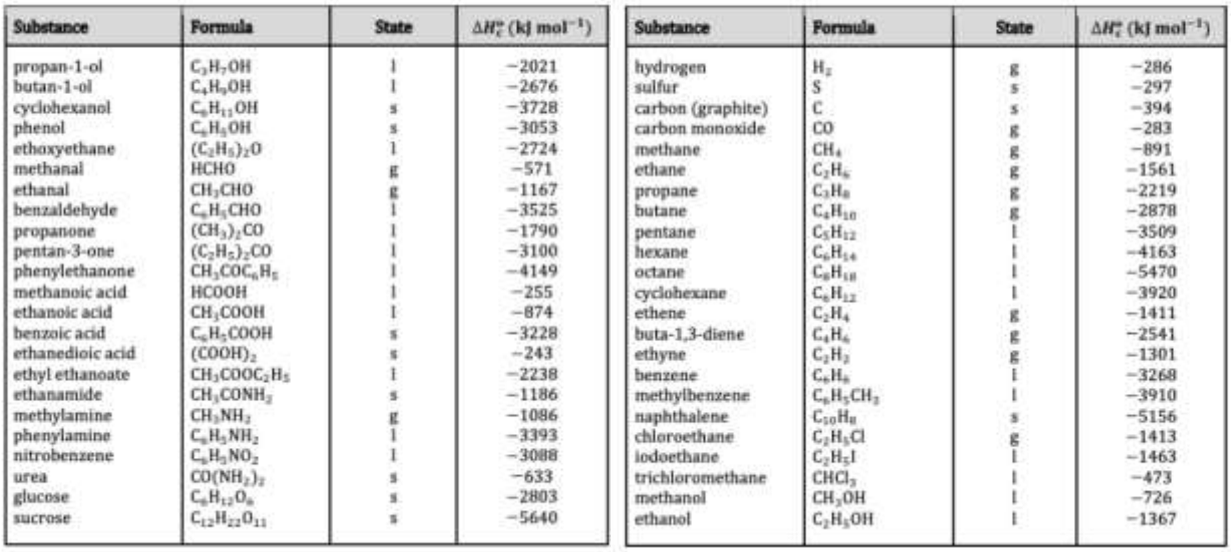
Standard enthalpy of combustion (ΔHC°) is the enthalpy change when 1 mole of a substance burns (combines vigorously with oxygen) under standard state conditions; it is sometimes called "heat of combustion." For example, the enthalpy of combustion of ethanol, −1366.8 kJ/mol, is the amount of heat produced when one mole of ethanol undergoes complete combustion at 25 °C and 1-atmosphere pressure, yielding products also at 25 °C and 1 atm.

$$C_2H_5OH_{(l)} + 3O_2(g) \longrightarrow 2CO_2 + 3H_2O \quad (l) \qquad \Delta H_{298}{}^{\circ} = -1366.8 \text{ kJ}$$

Enthalpies of combustion for many substances have been measured; a few of these are listed in Table 4.1.

Table 4.1

The values of the molar enthalpy of combustion (ΔH^{o}_{c}) in the following table refer to a temperature of 298 K and a pressure of $1.00 \cdot 10^5$ Pa.



Substance	**Formula**	**State**	ΔH_c° (kJ mol^{-1})
propan-1-ol	C_3H_7OH	l	−2021
butan-1-ol	C_4H_9OH	l	−2676
cyclohexanol	$C_6H_{11}OH$	s	−3728
phenol	C_6H_5OH	s	−3053
ethoxyethane	$(C_2H_5)_2O$	l	−2724
methanal	$HCHO$	g	−571
ethanal	CH_3CHO	g	−1167
benzaldehyde	C_6H_5CHO	l	−3525
propanone	$(CH_3)_2CO$	l	−1790
pentan-3-one	$(C_2H_5)_2CO$	l	−3100
phenylethanone	$CH_3COC_6H_5$	l	−4149
methanoic acid	$HCOOH$	l	−255
ethanoic acid	CH_3COOH	l	−874
benzoic acid	C_6H_5COOH	s	−3228
ethanedioic acid	$(COOH)_2$	s	−243
ethyl ethanoate	$CH_3COOC_2H_5$	l	−2238
ethanamide	CH_3CONH_2	s	−1186
methylamine	CH_3NH_2	g	−1086
phenylamine	$C_6H_5NH_2$	l	−3393
nitrobenzene	$C_6H_5NO_2$	l	−3088
urea	$CO(NH_2)_2$	s	−633
glucose	$C_6H_{12}O_6$	s	−2803
sucrose	$C_{12}H_{22}O_{11}$	s	−5640

Substance	**Formula**	**State**	ΔH_c° (kJ mol^{-1})
hydrogen	H_2	g	−286
sulfur	S	s	−297
carbon (graphite)	C	s	−394
carbon monoxide	CO	g	−283
methane	CH_4	g	−891
ethane	C_2H_6	g	−1561
propane	C_3H_8	g	−2219
butane	C_4H_{10}	g	−2878
pentane	C_5H_{12}	l	−3509
hexane	C_6H_{14}	l	−4163
octane	C_8H_{18}	l	−5470
cyclohexane	C_6H_{12}	l	−3920
ethene	C_2H_4	g	−1411
buta-1,3-diene	C_4H_6	g	−2541
ethyne	C_2H_2	g	−1301
benzene	C_6H_6	l	−3268
methylbenzene	$C_6H_5CH_3$	l	−3910
naphthalene	$C_{10}H_8$	s	−5156
chloroethane	C_2H_5Cl	g	−1413
iodoethane	C_2H_5I	l	−1463
trichloromethane	$CHCl_3$	l	−473
methanol	CH_3OH	l	−726
ethanol	C_2H_5OH	l	−1367

Many readily available substances with large enthalpies of combustion are used as fuels, including hydrogen, carbon (as coal or charcoal), and hydrocarbons (compounds containing only hydrogen and carbon), such as methane, propane, and the major components of gasoline.

Link to Learning

Click here (https://u.to/o-TcHw) to view the calculation of the combustion reactions, for example, the combustion of ethane.

Standard enthalpy of formation

A standard enthalpy of formation is the enthalpy change for a reaction in which exactly 1 mole of a pure substance is formed from free elements in their most stable states under standard state conditions. These values are especially useful for computing or predicting enthalpy changes for chemical reactions that are impractical or dangerous to carry out, or for processes for which it is difficult to make measurements. If we have values for the appropriate standard enthalpies of formation, we can determine the enthalpy change for any reaction, which we will practice in the next section on Hess's law. A standard enthalpy of formation is the enthalpy change for a reaction in which exactly 1 mole of a pure substance is formed from free elements in their most stable states under standard state conditions. These values are especially useful for computing or predicting enthalpy changes for chemical reactions that are impractical or dangerous to carry out, or for processes for which it is difficult to make measurements. If we have values for the appropriate standard enthalpies of formation, we can determine the enthalpy change for any reaction, which we will practice in the next section on Hess's law.

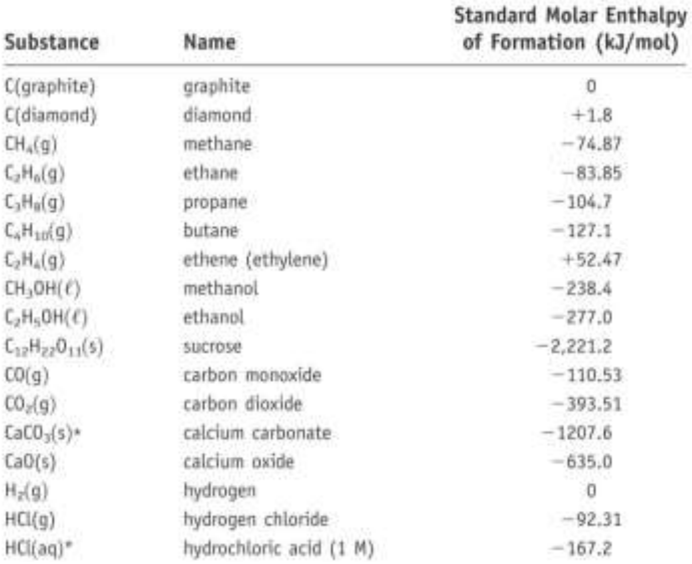
Enthalpy of formation is defined as the enthalpy change when 1 mole of a compound is produced from its elements under standard conditions.

- All elements in their standard states have a 0 standard enthalpy of formation.
- Enthalpies of formation are determined using Hess's law.
- Usually, but not always, exothermic.

Refer to Table 4.2 for relevant enthalpies of formation.

Table 4.2

Selected standard molar enthalpies of formation at 298 K.

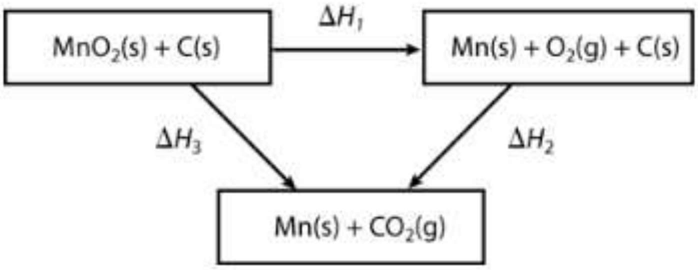


Substance	Name	Standard Molar Enthalpy of Formation (kJ/mol)
C(graphite)	graphite	0
C(diamond)	diamond	+1.8
CH_4(g)	methane	−74.87
C_2H_6(g)	ethane	−83.85
C_3H_8(g)	propane	−104.7
C_4H_{10}(g)	butane	−127.1
C_2H_4(g)	ethene (ethylene)	+52.47
$CH_3OH(\ell)$	methanol	−238.4
$C_2H_5OH(\ell)$	ethanol	−277.0
$C_{12}H_{22}O_{11}$(s)	sucrose	−2,221.2
CO(g)	carbon monoxide	−110.53
CO_2(g)	carbon dioxide	−393.51
$CaCO_3$(s)*	calcium carbonate	−1207.6
CaO(s)	calcium oxide	−635.0
H_2(g)	hydrogen	0
HCl(g)	hydrogen chloride	−92.31
HCl(aq)*	hydrochloric acid (1 M)	−167.2

Hess's Law

Which states: If a process can be written as the sum of several stepwise processes, the enthalpy change of the total process equals the sum of the enthalpy changes of the various steps. Hess's law is valid because enthalpy is a state function: Enthalpy changes depend only on where a chemical process starts and ends, but not on the path it takes from start to finish.

Hess's law states that the total enthalpy change for a reaction is independent of the route taken. It is a special case of the law of conservation of energy.



For example, we can consider of the reaction of carbon with oxygen to form carbon dioxide as occurring either directly or by a two-step process. The direct process is written:

$C(s) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H^o_{298} = -394$ kJ

In the two-step process, first carbon monoxide is formed:

$C(s) + 12O_2(g) \longrightarrow CO(g)$ $\Delta H^o_{298} = -111$ kJ

Then, carbon monoxide reacts further to form carbon dioxide:

$CO(g) + 1/2O_2(g) \longrightarrow CO(g)$ $\Delta H^o_{298} = -283$ kJ

The equation describing the overall reaction is the sum of these two chemical changes:

Step 1: $C(s) + 1/2O_2(g) \longrightarrow CO(g)$

Step 2: $CO(g) + 12O2(g) \longrightarrow CO_2(g)$

Sum: $C(s) + 1/2O_2(g) + CO(g) + 1/2O_2(g) \longrightarrow CO(g) + CO_2(g)$

Because the CO produced in Step 1 is consumed in Step 2, the net change is

$C(s) + O_2(g) \longrightarrow CO_2(g)$

According to Hess's law, the enthalpy change of the reaction will equal the sum of the enthalpy changes of the steps. We can apply the data from the experimental enthalpies of combustion in Table 4.2 to find the enthalpy change of the entire reaction from its two steps:

$C(s) + 1/2O_2(g) \longrightarrow CO(g)$ $\Delta H^o_{298} = -111$ kJ

$CO(g) + 1/2O_2(g) \longrightarrow CO_2(g)$ $\Delta H^o_{298} = -283$ kJ

$C(s) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H^o_{298} = -394$ kJ

Enthalpy of reaction

$\Delta H_{reaction}$ (using enthalpies of formation) $= \sum \Delta H_f$ (products) – $\sum \Delta H_f$ (reactants)

$\Delta H_{reaction}$ (using enthalpies of combustion) $= \sum \Delta H_f$ (reactants) – $\sum \Delta H_f$ (products)

The result is shown in Figure 4.4. We see that the ΔH of the overall reaction is the same whether it occurs in one step or two. This finding (overall ΔH for the reaction = sum of ΔH values for reaction "steps" in the overall reaction) is true in general for chemical and physical processes.

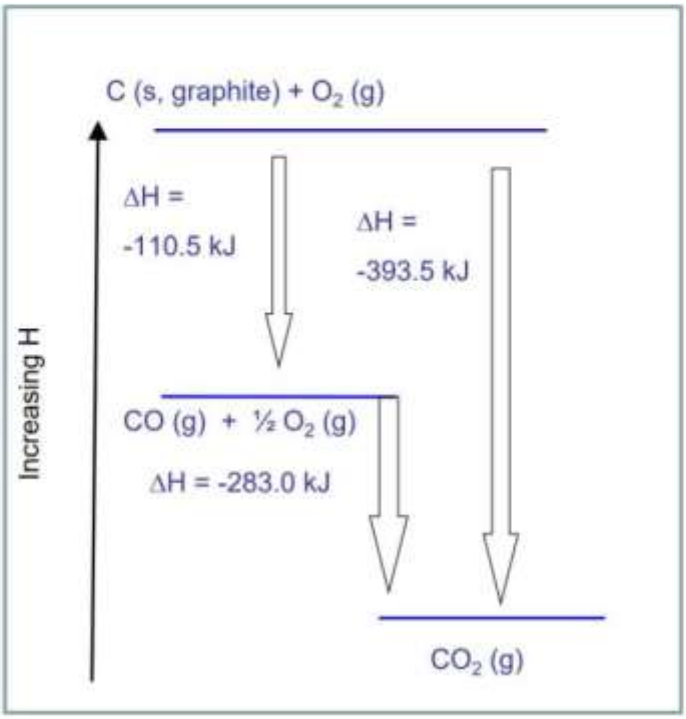
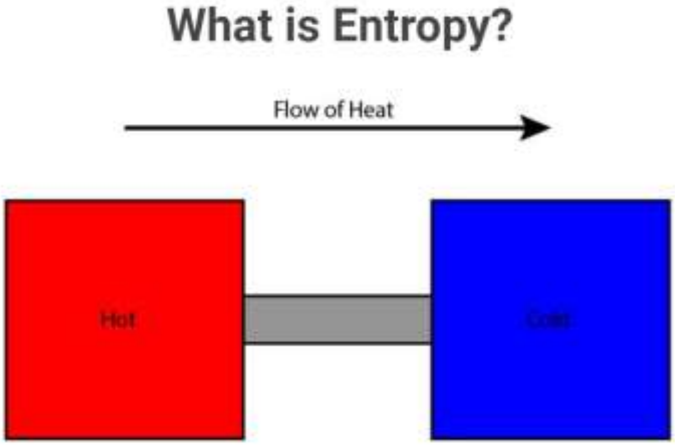


Figure 4.4 The formation of $CO_2(g)$ from its elements can be thought of as occurring in two steps, which sum to the overall reaction, as described by Hess's law. The horizontal blue lines represent enthalpies. For an exothermic process, the products are at lower enthalpy than are the reactants. The overall enthalpy change is the same if it is done in one step or two.

4.3 Entropy

Entropy is an important concept in physics and chemistry, plus it applies to other disciplines, including cosmology and economics. In physics, it is part of thermodynamics. In chemistry, it is a core concept in physical chemistry.



Entropy is the measure of the disorder of a system. It is an extensive property of a thermodynamic system, which means its value changes depending on the amount of matter that is present. In equations, entropy is usually denoted by the letter S and has units of joules per kelvin ($J \cdot K^{-1}$). A highly ordered system has low entropy.

Importantly, while the universe's entropy must increase without exception, that of the system may decrease spontaneously.

For instance, take a heat engine. In general, a heat engine works by taking heat energy and converting it to work. This conversion involves an entropic decrease in the system since the disordered energy of heat becomes ordered motion. Despite this, heat engines still function spontaneously in the real world. The reason is that some amount of heat from the engine is released into the universe (i.e., a cold sink). This heat, as a result of distribution into the universe, involves an increase in entropy that counteracts the decrease from the engine's work.

Example of entropy

A block of ice will increase in entropy as it melts. It's easy to visualize the increase in the disorder of the system. Ice consists of water molecules bonded to each other in a crystal lattice. As ice melts, molecules gain more energy, spread further apart, and lose structure to form a liquid. Similarly, the phase change from a liquid to a gas, as from water to steam, increases the energy of the system.

On the flip side, energy can decrease. This occurs as steam changes phase into water or as water changes to ice. The second law of thermodynamics is not violated because the matter is not in a closed system. While the entropy of the system being studied may decrease, that of the environment increases.

Entropy of an isothermal process

Calculus may be used to find the integral of dQ/T from the initial state to the final state, where Q is heat and T is the absolute (Kelvin) temperature of a system.

Another way to state this is that the change in entropy (ΔS) equals the change in heat (ΔQ) divided by the absolute temperature (T):

$$\Delta S = \Delta Q / T$$

Thermodynamic Definition

Rather than deal with microstates, most chemists measure entropic values using calorimetry instead. Thus, chemists can define entropy thermodynamically, using the flow of heat and the temperature of the system:

$$dS = \frac{dq_{rev}}{T}$$

dS = Small change in entropy (J/K); dq_{rev} = Small change in heat (J) ;
T = Temperature (K)

We can further simplify the above equation depending on whether temperature changes between the two states:

$$\Delta S = \frac{q_{rev}}{T} \qquad \Delta S = q_{rev}\left(\frac{1}{T_i} - \frac{1}{T_f}\right)$$

(Left: Entropy change if temperature remains constant. Right: Entropy changes if temperature changes.)

***Takeaways*:**

- Entropy is a measure of the randomness or disorder of a system.
- The value of entropy depends on the mass of a system. It is denoted by the letter S and has units of joules per kelvin.

- Entropy can have a positive or negative value. According to the second law of thermodynamics, the entropy of a system can only decrease if the entropy of another system increases.

4.4 Free Energy

Gibbs free energy is an important value in thermodynamics that allows you to predict aspects of a chemical reaction. In this tutorial, we will learn why the Gibbs free energy equation is important and how to solve problems in which it is involved. We will also define what a spontaneous reaction is.

So we've covered that negative enthalpic changes can happen, but only if heat, in the form of enthalpy, is released to raise universal S. To mathematically understand the relationship between spontaneity and these two variables, we must understand a third: Gibbs free energy (G). The following equation illustrates the relationship between entropy, enthalpy (H), Gibbs free energy, and temperature:

$$\Delta G = \Delta H - T\Delta S$$

ΔG = change in Gibbs free energy (kJ/mol); ΔH = change in enthalpy (kJ/mol);
ΔS = change in entropy (kJ/mol); T = temperature

For this equation to hold, we must make two assumptions:

- The temperature remains constant throughout the reaction.
- The pressure remains constant throughout the reaction.

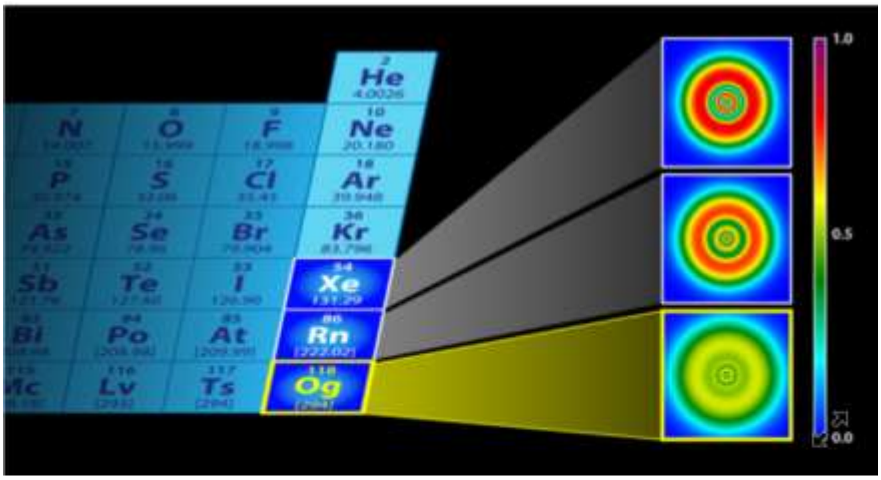
If a chemical reaction involves $\Delta G < 0$, the reaction is spontaneous. Thus, if $\Delta G > 0$, the reaction can only proceed spontaneously if $\Delta G = 0$, which involves heat given off by the reaction.

Link to Learning

Click here (**https://chemistrytalk.org/what-is-gibbs-free-energy/**) to view the explanation of Gibbs-free energy.

CHAPTER 5

ELECTRONIC STRUCTURE AND PERIODIC PROPERTIES OF ELEMENT



Chapter Outline

5.1 Electronic Structure of Atoms (electron configurations). Energy.
5.2 The filling of electrons into the orbitals.
5.3. Electron configuration.

5.1. Electronic Structure of Atoms (Electron Configurations). Energy.

The energy that is essential to take an electron present in that orbital to infinity or the release of energy when an electron from infinity is added to that orbital, is referred to as the energy of orbitals. This orbital energy is dependent upon the principle of the quantum number (n) as well as the azimuthal quantum number (l) which is that it depends on the shell and subshells. For all those orbitals that belong to the same subshell, it is the same, and those orbitals that have the same energy are stated as degenerate orbitals.

The order of the increase in energy along the various orbitals is stated as

$$1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f$$

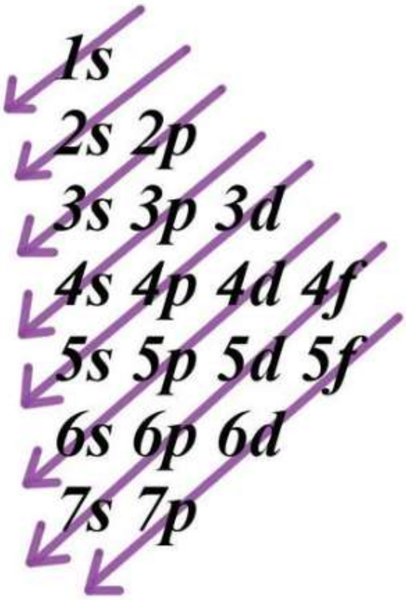
Factors Affecting the Orbital Energy

- The s orbital electron will be more tightly bound to the nucleus as compared to the p orbital electron, which is more tightly bound than a d orbital electron for a given value of the principal quantum number.
- As compared to p orbital electrons, s orbital electrons will have a more negative or smaller amount of energy. Here, the p orbital electrons will have less energy than the d orbital electrons.
- As the extent of shielding from the nucleus is different for the electrons in different orbitals, it leads to the splitting of energy levels that have the same principal quantum number. Therefore, the orbital energy would depend on the values of both the principal quantum number and azimuthal quantum number, symbolized as n and l, respectively. Hence, the lower the value of (n + 1) for an orbital, the lower its energy.
- With the increase in the atomic number (Zeff), the orbital energy decreases in the same subshell.

Electrons fill orbitals in a way to minimizes the energy of the atom. Therefore, the electrons in an atom fill the principal energy levels in order of increasing energy (the electrons are getting farther from the nucleus). The order of levels filled looks like this:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, and 7p

One way to remember this pattern, probably the easiest, is to refer to the periodic table and remember where each orbital block falls to logically deduce this pattern. Another way is to make a table like the one below and use vertical lines to determine which subshells correspond with each other.



The number of valence electrons of an element can be determined by the periodic table group (vertical column) in which the element is categorized. Except for groups 3–12 (the transition metals), the unit digit of the group number identifies how many valence electrons are associated with a neutral atom of an element listed under that particular column.

The principal quantum number

The principal quantum number (***n***) indicates the energy of the electron and the average distance of an electron from the nucleus: $n = 1, 2, 3, 4, \ldots$

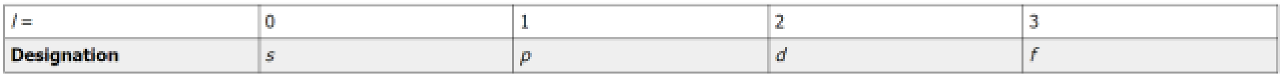
As n increases for a given atom, so does the average distance of an electron from the nucleus. A negatively charged electron that is, on average, closer to the positively charged nucleus is attracted to the nucleus more strongly than an electron that is farther out in space. This means that electrons with higher values of n are easier to remove from an atom.

The second quantum number is often called the azimuthal quantum number (***l***). The value of l describes the *shape* of the region of space occupied by the electron. The allowed values of l depend on the value of n and can range from 0 to $n - 1$:

$$l = 0, 1, 2, \ldots, n - 1$$

For example, if $n = 1$, l can be only 0; if $n = 2$, l can be 0 or 1; and so forth. The regions of space occupied by electrons in the same subshell usually have the same shape, but they are oriented differently in space.

Rather than specifying all the values of n and l every time we refer to a subshell or an orbital, chemists use an abbreviated system with lowercase letters to denote the value of l for a particular subshell or orbital:



l =	0	1	2	3
Designation	*s*	*p*	*d*	*f*

The third quantum number is the magnetic quantum number (**m_l**). The value of m_l describes the *orientation* of the region in space occupied by an electron concerning an applied magnetic field. The allowed values of m_l depend on the value of l: m_l can range from $-l$ to l in integral steps:

$$m_l = -l, -l + 1, \ldots, 0, \ldots, l - 1, l$$

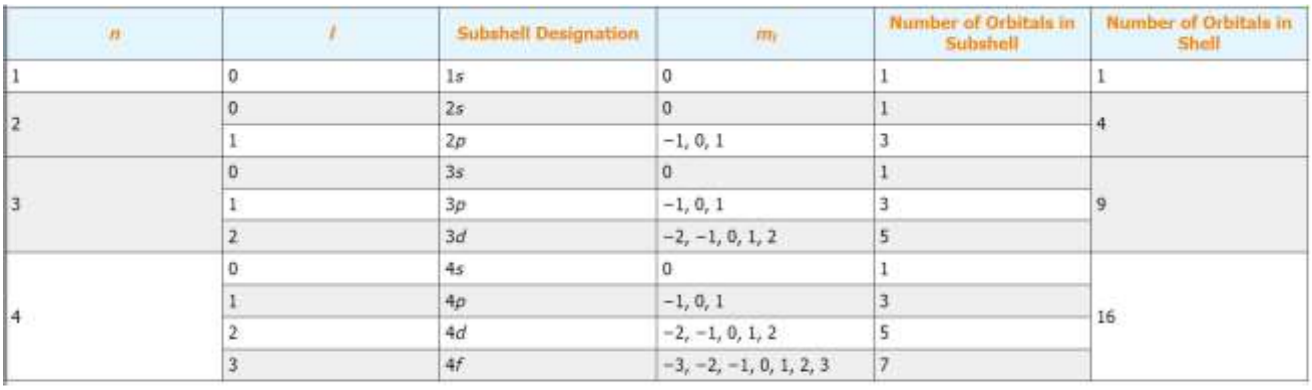
For example, if $l = 0$, m_l can be only 0; if $l = 1$, m_l can be −1, 0, or +1; and if $l = 2$, m_l can be −2, −1, 0, +1, or +2.

The principal quantum number is named first, followed by the letter *s*, *p*, *d*, or *f* as appropriate. These orbital designations are derived from corresponding spectroscopic characteristics of lines involving them: *s*harp, *principal*, *d*iffuse, and *f*undamental. A 1*s* orbital has $n = 1$ and $l = 0$; a 2*p* subshell has $n = 2$ and $l = 1$ (and has three 2*p* orbitals, corresponding to $m_l = -1$, 0, and +1); a 3*d* subshell has $n = 3$ and $l = 2$ (and has five 3*d* orbitals, corresponding to $m_l = -2$, −1, 0, +1, and +2); and so forth.

We can summarize the relationships between the quantum numbers and the number of subshells and orbitals as follows (Table 5.1):

Table 5.1

Allowed values of ***n***, ***l***, and ***m_l*** through ***n*** = 4.



n	l	Subshell Designation	m_l	Number of Orbitals in Subshell	Number of Orbitals in Shell
1	0	1*s*	0	1	1
2	0	2*s*	0	1	4
	1	2*p*	−1, 0, 1	3	
3	0	3*s*	0	1	9
	1	3*p*	−1, 0, 1	3	
	2	3*d*	−2, −1, 0, 1, 2	5	
4	0	4*s*	0	1	16
	1	4*p*	−1, 0, 1	3	
	2	4*d*	−2, −1, 0, 1, 2	5	
	3	4*f*	−3, −2, −1, 0, 1, 2, 3	7	

The fourth quantum number Spin quantum number (**m_s**): $m_s = +½$ or -½.

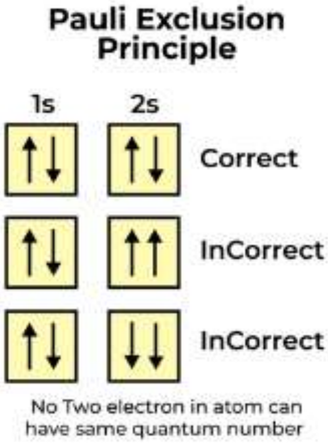
Specifies the orientation of the spin axis of an electron. An electron can spin in only one of two directions (sometimes called *up* and *down*).

Each wave function with an allowed combination of n, l, and m_l values describes an atomic orbital, a particular spatial distribution for an electron. For a given set of quantum numbers, each principal shell has a fixed number of subshells, and each subshell has a fixed number of orbitals.

5.2. The filling of electrons into the orbitals

The **Pauli exclusion principle** states that *no two electrons in the same atom can have identical values for all four of their quantum numbers*. What this means is that no more than two electrons can occupy the same orbital, and that two electrons in the same orbital must have opposite spins.

Because an electron spins, it creates a magnetic field, which can be oriented in one of two directions. For two electrons in the same orbital, the spins must be opposite to each other; the spins are said to be paired. These substances are not attracted to magnets and are said to be diamagnetic. Atoms with more electrons that spin in one direction than another contain unpaired electrons. These substances are weakly attracted to magnets and are said to be paramagnetic.

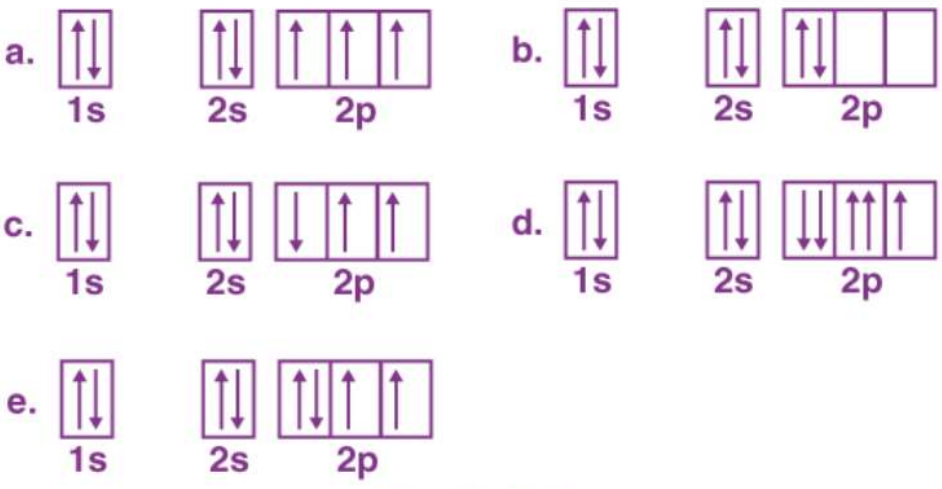


Hund's Rule: every orbital in a subshell is singly occupied with one electron before any one orbital is doubly occupied, and all electrons in singly occupied orbitals have the same spin.

According to Hund's rule:

- Before the double occupation of any orbital, every orbital in the sub-level is singly occupied.
- For the maximization of total spin, all electrons in a single occupancy orbital have the same spin.

An electron will not pair with another electron in a half-filled orbital, as it can fill all its orbitals with similar energy. Many unpaired electrons are present in atoms that are in the ground state. If two electrons come in contact, they would show the same behaviour as two magnets do. The electrons first try to get as far away from each other as possible before they have to pair up.



Hund's Rule

Klechkovsky rule.

Klechkovsky's rule (principle of least energy). In the basic state, each electron is arranged so that its energy is minimal. The smaller the sum (n + l), the smaller the energy of the orbital. At a given value (n + l), the smallest energy has an orbital with less than n.

How do orbitals fill up?

Energy levels, sub-levels, and orbitals are filled in the order of increasing energy (the principle of minimum energy). The sequence of sublevels in the first five levels is:

1s 2s 2s p3s 3p 4s 4p 5s 5d 5p

5.3. Electron configuration

Each period (horizontal row) of the periodic table corresponds to an energy shell. For example, atoms of carbon, C (row 2), have outer electrons in the 2nd energy shell; atoms of sodium, Na (row 3), have outer electrons in the 3rd energy shell, and so on. When writing electron configurations and determining which subshells to fill, be aware of what area and row the element is in. Then remember the following points:

- An element in the s area of row n has outer electrons in the n subshell.
- An element in the p area of row n has outer electrons in the np subshell.
- An element in the d area of row n has outer electrons in the (n − 1)d subshell.
- An element in the f area of row n has outer electrons in the (n-2)f subshell.

Let's put it all together and try writing the electron configuration for an atom of fluorine.

Step 1. Where do we start? At hydrogen, of course. It's in the *S* area of the row

1. Hydrogen (H) has an electron in its 1s subshell. Remember that although helium looks like it is in the p area, it is part of the 1s area. How Does This Work?

Consider an atom of phosphorus, P (row 3). It's in the p area, so its outer electrons are in the 3p subshell. What about an atom of nickel, Ni (row 4)? It's in the *D* area. That means its outer electrons go into the (4 − 1)d or 3d subshell.

Step 2. Now we have 2 electrons in the lone orbital of the 1s subshell. Since no orbital can hold 3 electrons, we need to go to a different (higher energy) subshell for the next addition.

Step 3. Follow the numbers to lithium (Li) and then beryllium (Be); they're in the s area of row 2 and fill the 2s subshell and keep going. Starting with boron (B) and continuing through fluorine (F), we are in the p area of row 2. Boron atoms have 1 electron in the 2p subshell, carbon atoms have 2, and so on, up to fluorine, which has 5 electrons in its 2p subshell.

Step 4. This makes the electron configuration of a fluorine atom $1s^2 2s^2 2p^5$. The superscripts indicate the number of electrons occupying a particular subshell. Adding these superscripts gives the total number of electrons in a species. Since fluorine has the atomic number 9, we expect fluorine atoms to have 9 electrons.

Finding the electron configuration of ions follows the same rules as those for atoms, but with one additional step. Suppose we need the electron configuration of the fluoride ion, F −. First, find the electron configuration for the atom. That would be $1s^2 2s^2 2p^5$. Now, how does F differ from the neutral F atom? It has 1 extra electron. So add 1 electron to the electron configuration. Thus, the electron configuration of F − is $1s^2 2s^2 2p^6$ (the same as that of a neon atom). If we were dealing with positive ions, we would find the atomic electron configuration and then remove one or more electrons.

What about the f subshell, which you might remember learning about in school? For the test, you don't have to know much about it. Just remember this: If an element has an atomic number greater than 57, some of its electrons are in the f subshell, which is another way of saying they're in f orbitals. So, element number 76, osmium (Os), has electrons in the f subshell, as do gold (Au), samarium (Sm), and terbium (Tb).

The Stable octet. Look at element 10, neon (Ne). Its electron configuration is $1s^2 2s^2 2p^6$. Neon's configuration has one 1 subshell and two 2 subshells. It has no 3 subshells or 4 subshells, so the two 2 subshells (indicating the 2nd subshell) constitute its outermost shell.

Take a look at neon's outermost shell: $1s^2 2s^2 2p^6$. Count the electrons in this shell: 2 + 6 = 8. The fact that neon has 8 electrons in its outermost shell means that it has a stable octet: 8 electrons.

Examine element number 18, argon (Ar), and look especially at its outermost shell, which is the 3rd shell: $1s^2 2s^2 2p^6 3s^2 3p^6$. Argon, too, has a stable octet. That is, it has 8 electrons in its outermost shell.

All of the elements with stable octets are called noble gases or inert gases. They're very stable. They don't like to react with anything or change themselves in any way. They're very happy the way they are. Why? Because atoms are happiest with 8 electrons in their outermost shell. Helium (He, atomic number 2) is also very stable. It, too, is an inert gas, although it has only 2 electrons in its outermost shell.

The electrons in an atom's outermost shell are called valence electrons. So, another way of saying "stable octet" is to say "8 valence electrons." All of the noble gases have 8 valence electrons. Beryllium, however, (Be, atomic number 4) —$1s^2 2s^2$— has 2 valence electrons. Oxygen —$1s^2 2s^2 2p^4$—has 6 valence electrons.

Remember:

- Valence electrons are the electrons in the outermost energy shell.
- Atoms with 8 valence electrons have a stable octet. They're very stable and are often referred to as the noble gases.

CHAPTER 6

CHEMICAL BONDING AND MOLECULAR GEOMETRY

Chapter Outline

Chemical bonding refers to the formation of a chemical bond between two or more atoms, molecules, or ions to give rise to a chemical compound. These chemical bonds are what keep the atoms together in the resulting compound.

6.1 Ionic Bonding

When an atom in a bond gives up 1 or more electrons to the atom it bonds with, an ionic bond is formed. Ionic bonds generally form between atoms that differ significantly in their electronegativity values. The atom that gives up the electron becomes a positively charged ion, and the one that accepts the electron becomes a negatively charged ion. The positively charged atom attracts the negatively charged atom, and this draws the two atoms together and results in the release of energy.

let's look at an example of an ionic bond. When sodium (Na) bonds with chlorine (Cl), the sodium atom gives up its outermost electron to become $Na^{+,}$ and the chlorine atom receives it to become Cl^{-}. The Na^{+} ion has 8 electrons in its outermost shell. (Its electron configuration looks like neon's.)

But what about chlorine? Having gained an electron, chlorine also ends up with 8 electrons in its outermost shell. Its electron configuration looks like argon's. The bond that results creates sodium chloride: NaCl. The attraction between a positive charge and a negative charge is called an electrostatic force; this force is very strong. The strength of an ionic bond gives ionic compounds their high melting points, hardness, and other physical properties.

When a metal and a nonmetal bond, the result is an ionic bond, in which the atoms are held together by an electrostatic attraction between a positive and a negative ion.

Let's take sulfur as an example. Sulfur has six valence electrons and can either gain two electrons to fill the third energy shell or lose six electrons to leave behind a full second energy shell. It is easier for a sulfur atom to gain two electrons than it is for it to lose six, so sulfur forms negative anions with a charge of negative two, represented by S^{2-}. Every other element in the same group as sulfur (like oxygen and selenium) will also form ions with a charge of negative two. The halogens are one group to the right. The easiest way for the halogens to achieve a full octet is by gaining one electron. So, a fluorine ion would have a charge of negative one, represented by F^{-}. Going in the other direction, the elements in the nitrogen group (such as phosphorus) typically form ions with a charge of negative three.

If we take an element like magnesium, we see that it has two valence electrons. It is going to be easier for a magnesium atom to lose those two electrons, leaving behind a full octet in the second shell, than it would be for that atom to gain the six electrons that would be necessary to fill the octet in the third shell. So, magnesium atoms form ions with a charge of positive 2, or Mg^{2+}. The same would be true for all other alkaline earth elements (such as Be or Ca). Alkaline metals (such as Li or Na) form ions with a charge of positive one, and the metals in the aluminum group form ions with a charge of positive 3.

To determine the formula of an ionic compound, the important rule to remember is that the total charge on any stable compound must be zero. When sodium forms an ion, it loses an electron to become Na^{+}. When sulfur forms an ion, it gains two electrons to become S^{2-}. To balance the charge, two sodium ions must be present to neutralize the charge on one sulfur ion, creating a compound with a formula of Na_2S. When an oxygen anion (O^{2-}) bonds with a magnesium cation (Mg^{2+}), the charges balance each other already, and only one of each ion is needed — thus the formula is MgO. When nitrogen ions (N^{3-}) bond with barium ions (Ba^{2+}), to zero out the total charge, two nitrogen ($-3 \times 2 = -6$) and three barium ($+2 \times 3 = +6$) ions are necessary, creating a compound with the formula Ba_3N_2. Notice the cation always comes first in the formula of an ionic compound.

The scheme example of ionic bonding (Figure 6.1)

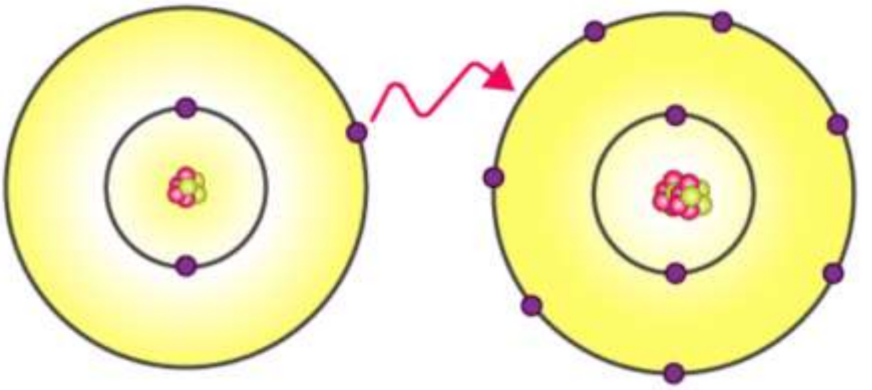


Fig. 6.1 Types of chemical bonds – ionic bonding.

6.2 Lewis diagrams

The easiest way to determine how the electrons are shared in a covalent molecule is to draw a Lewis diagram (also called an electron dot diagram) for the molecule. To draw a Lewis diagram, use the following steps:

1) Count the number of valence electrons in each atom and add them up.

2) Draw a skeletal structure of the molecule with the least electronegative atom in the center.

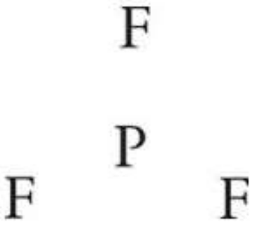
3) Create a single bond (shared electron pair) connecting the central atom to each terminal atom.

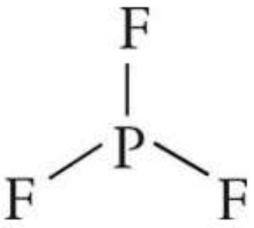
4) Add lone pairs around each terminal and central atom until each atom has eight total electrons (except hydrogen, which only needs two).

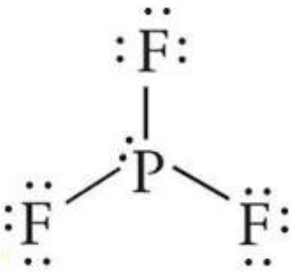
5) Count up the total number of electrons in the structure. If they equal the total number of valence electrons available (calculated in step 1), your structure is correct. If you have more assigned electrons than valence electrons, you need to shift some lone pairs over and create double or triple bonds.

Two examples: Draw the Lewis diagram for PF$_3$.

1) P + F(3)
5 + 7(3) = 26 valence e

2)


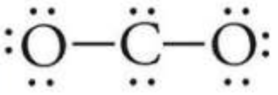
3)


4)


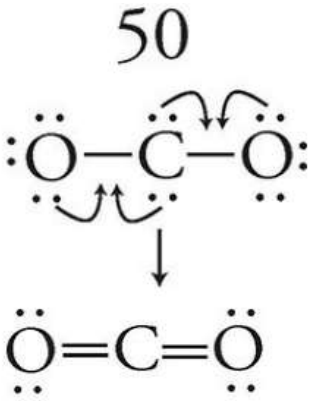
5) 26 assigned e$^-$ = 26 valence e$^-$ ✓

Draw the Lewis diagram for CO$_2$.

1) C + O(2) = 4 + 6(2) = 16 valence e$^-$
2) O C O
3) O—C—O

4)


5) 20 assigned $e^- \neq 16$ valence e



16 assigned $e^- = 16$ valence e^- ✓

6.3 Covalent Bonding

Covalent bonds can be either **polar or non-polar**. In polar covalent chemical bonding, electrons are shared unequally since the more electronegative atom pulls the electron pair closer to itself and away from the less electronegative atom. Water is an example of such a polar molecule. A difference in charge arises in different areas of the atom due to the uneven spacing of the electrons between the atoms. One end of the molecule tends to be partially positively charged, and the other end tends to be partially negatively charged.

The nonpolar covalent bond

When two nonmetals share electrons equally, they are said to be nonpolar covalent. Because this can only occur between atoms with identical electronegativity values, this means that the only truly nonpolar covalent bonds are those present in molecules made up of one type of atom. For example, both oxygen atoms in O_2 have the same "pull" on electrons, which means the electrons in the shared bond between them are shared equally, with neither atom gaining a negative charge. Look how two oxygen atoms bond to form a molecule of O_2. The dots signify oxygen's 6 valence electrons.

Each atom donates a pair of electrons, and the shared pairs are attracted to the nuclei of both atoms. In a sense, each atom has 8 valence electrons instead of 6. Each atom is happy. The sharing keeps the atoms together because each atom now has a stable octet. The next example in Figure 6.2:

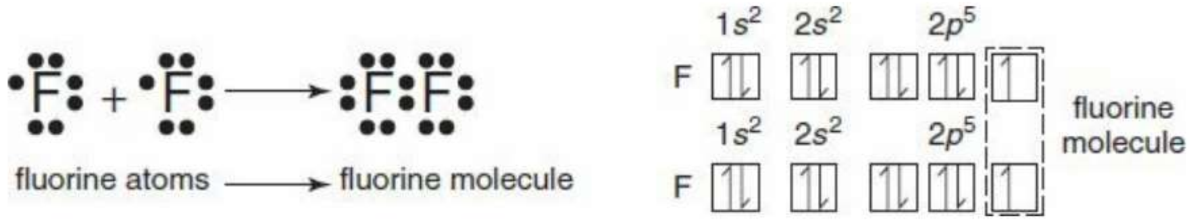


Fig. 6.2 Diagram of the formation of a covalent non-polar bond of Fluor.

The Polar covalent bond

The two oxygen atoms that we just looked at form a bond and share their electrons equally. But sometimes in a covalent bond, one atom tends to hog the electrons. It still shares them with the other atom, but it tends to keep the electrons for more than its fair share of the time. This hogging of the electrons is a result of one atom having a greater electronegativity value than the other. (Remember that electronegativity increases as we move from left to right across a period and decreases as we move from top to bottom in a column.)

A polar covalent bond is caused by a difference in electronegativity between atoms.

Let's see a water molecule. It's made of 2 hydrogen atoms and 1 oxygen atom. Each hydrogen atom has 1 valence electron, which it shares with oxygen. The oxygen atom donates 2 electrons to be shared with the hydrogen atoms. Each hydrogen atom acquires an electron and has a configuration like helium's (which is very stable), and the oxygen atom acquires 2 electrons and has an electron configuration like neon's (an octet). So a water molecule can be represented as follows:

But oxygen's electronegativity is greater than hydrogen's. Oxygen "hogs" the electrons it shares with hydrogen, and the shared electrons spend more time around the oxygen than they do around the hydrogen. Each hydrogen atom has a partial positive charge, while the oxygen atom has a partial negative charge. When, in a covalent bond, certain atoms have a partial positive charge and others have a partial negative charge, we say that the covalent bond is polar.

Notice that the electron pair in the bond is shown closer to the more electronegative atom. When these nonsymmetrical polar bonds are placed around a central atom, the overall molecule is polar. In the examples above, chlorine (in HCl) and oxygen (in H_2O) are considered the central atoms. Both the bonds and the molecules could be described as polar. Polar molecules are also referred to as dipoles because the whole molecule itself has two distinct ends from a charge perspective. Because of this unequal sharing, the molecules shown are said to be polar molecules or dipoles. However, polar covalent bonds exist in some nonpolar molecules. Examples are CO_2, CH_4, and CCl_4 in Figure 6.3.

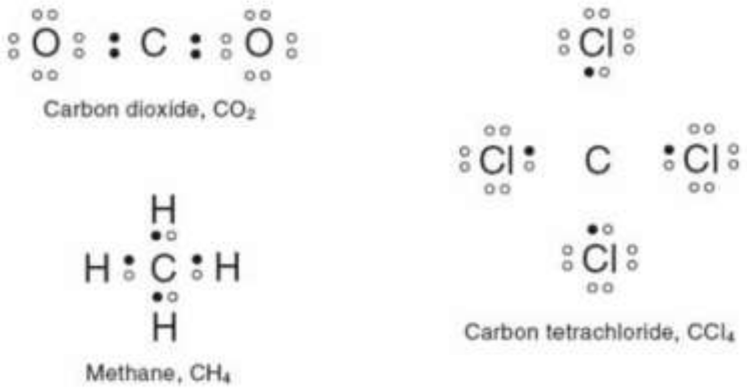
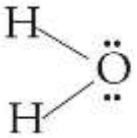


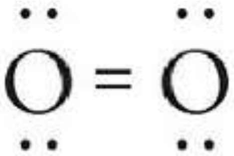
Fig. 6.3 Polar covalent bonds in nonpolar molecules.

6.4 Single, double, and triple bonds

Covalent bonds in which one pair of electrons is shared between two atoms; these types of bonds are also called **single bonds.** In the structural formula of a compound, a single bond is represented by a single line. For example, water has two single bonds.

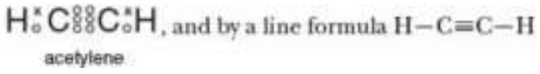


However, more than one pair of electrons can be shared between atoms in a covalent bond. If two pairs of electrons are shared, the bond is called a **double bond.** If three pairs of electrons are shared, it is a **triple bond.** In general, as more pairs of electrons are shared between atoms, the bond gets stronger and the distance between bonded nuclei gets shorter. The oxygen molecule we looked at earlier contains a double bond. It is represented by a double line, as follows:



As you might expect, a triple bond such as the one that's present in hydrogen cyanide (HCN) is represented by a triple line. Take a look:

$$H - C \equiv N;$$



, and by a line formula H−C≡C−H

acetylene

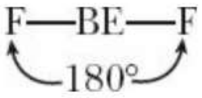
6.5. Hybridization

The chemical formula reveals little information about a molecule's geometry. It is only after doing many tests designed to reveal the shapes of the various molecules that chemists developed two different yet equally successful theories to explain certain aspects of their findings. One theory accounts structurally for molecular bond angles. The other is used to describe changes in the orbitals that contain the valence electrons of a molecule's atoms. The structural theory that deals with the bond angles is called the **VSEPR theory**, whereas the one that describes changes in the orbitals that contain the valence electrons is called the **hybridization theory**. (VSEPR represents Valence shell electron pair repulsion.

The molecular configurations derived by VSEPR can also be arrived at through the concept of **hybridization**. Briefly stated, this means that chemists envision that two or more pure atomic orbitals (usually *s*, *p*, and *d*) can be mixed to form two or more new hybrid atomic orbitals that are identical and conform to the known shapes of molecules. Hybridization can be illustrated as follows:

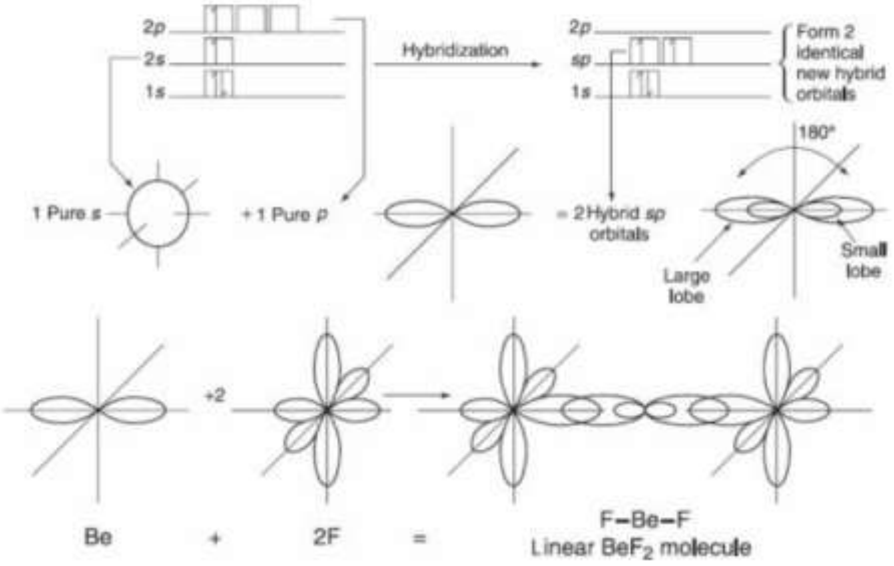
1. *sp* Hybrid orbitals

Spectroscopic measurements of beryllium fluoride, BeF_2, reveal a bond angle of 180° and equal bond lengths:



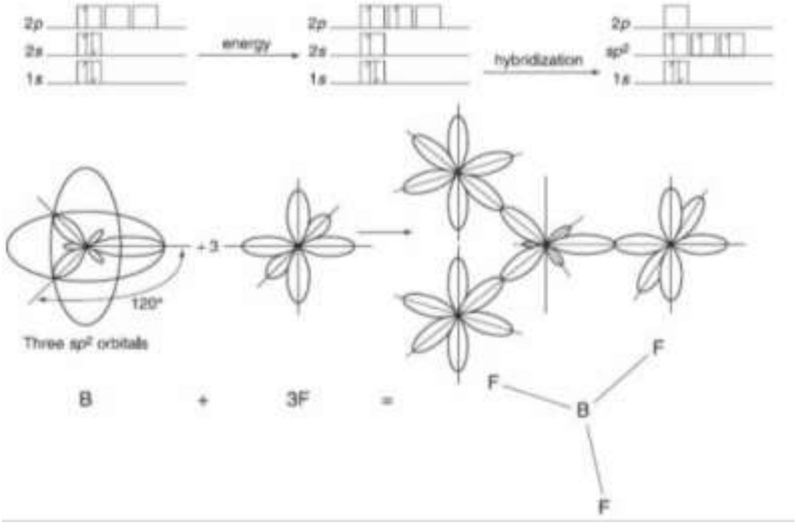
The ground state of beryllium is:

To accommodate the experimental data, we theorize that a 2*s* electron is excited to a 2*p* orbital; then the two orbitals hybridize to yield two identical orbitals called *sp* orbitals. Each contains one electron but is capable of holding two electrons.



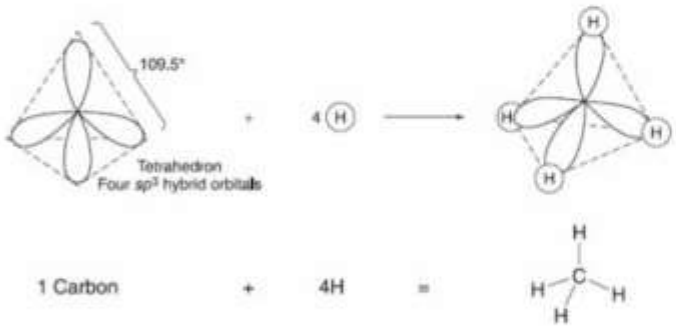
2. *sp* ^{2} Hybrid orbitals

Boron trifluoride, BF_3, has bond angles of 120° of equal strength. To accommodate these data, the boron atom hybridizes from its ground state of $1s^22s^22p^1$ to:



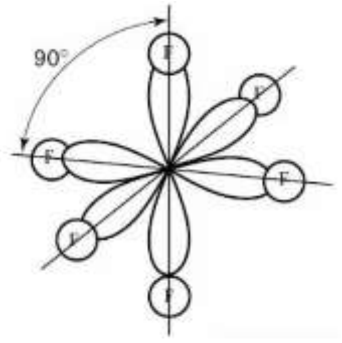
3. *sp*^{3} Hybrid orbitals

Methane, CH_4, can be used to illustrate this hybridization. Carbon has a ground state of $1s^22s^22p^2$. One 2*s* electron is excited to a 2*p* orbital, and the four involved orbitals then form four new identical *sp*^{3} orbitals:



4. *sp^3d^2* Hybrid orbitals

These orbitals are formed from the hybridization of an *s* and a *p* electron promoted to a *d* orbital, s and transformed into six equal *sp^3d^2* orbitals. The spatial form is shown below. Sulfur hexafluoride, SF_6, illustrates this hybridization:



6.6. Sigma and Pi bonds

In chemistry, sigma (σ) and pi (π) bonds are types of covalent bonds that describe the overlap of atomic orbitals and the resulting electron density distribution in a molecule. Understanding these bonds is crucial for predicting the behavior and properties of molecules.

Sigma (σ) Bonds:

Formation:

Sigma bonds are formed by the atomic orbitals' end-to-end (axial) overlap.
This overlap can occur between:
Two s orbitals (e.g., in H_2).
An s orbital and a p orbital (e.g., in HCl).
Two p orbitals (e.g., in F_2).
Hybrid orbitals (e.g., sp^3 orbitals in alkanes).

Characteristics:

Sigma bonds are the first bonds formed between two atoms.
They have cylindrical symmetry around the bond axis.
They allow for free rotation of the bonded atoms around the bond axis.
Sigma bonds are generally stronger than pi bonds due to greater overlap of orbitals.

Pi (π) Bonds:

Formation:

Pi bonds are formed by the side-by-side (lateral) overlap of p orbitals.

This overlap occurs above and below the bond axis.

Pi bonds typically happen in addition to a sigma bond in double and triple bonds.

Characteristics:

Pi bonds are found in molecules with double or triple bonds.

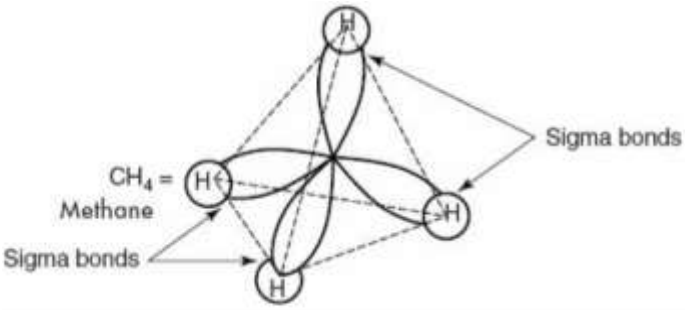
A double bond has one sigma bond and one pi bond (e.g., in ethene, C_2H_4).

A triple bond has one sigma bond and two pi bonds (e.g., in ethyne, C_2H_2).

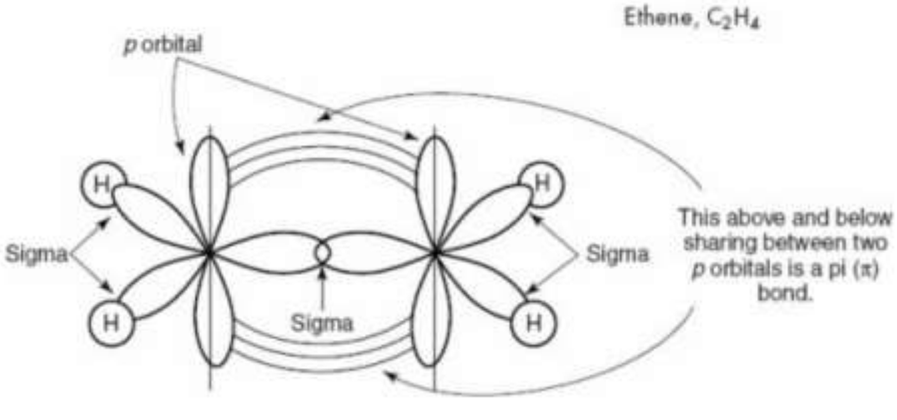
Pi bonds restrict the rotation around the bond axis due to their electron cloud positioning.

They are generally weaker than sigma bonds because the overlap is less efficient.

The sp^3 orbitals are bonded to hydrogen atoms in the methane molecule. These are **sigma bonds:**



When two *p* orbitals share electrons in a covalent bond, the result is a **pi bond**. Here is an example:

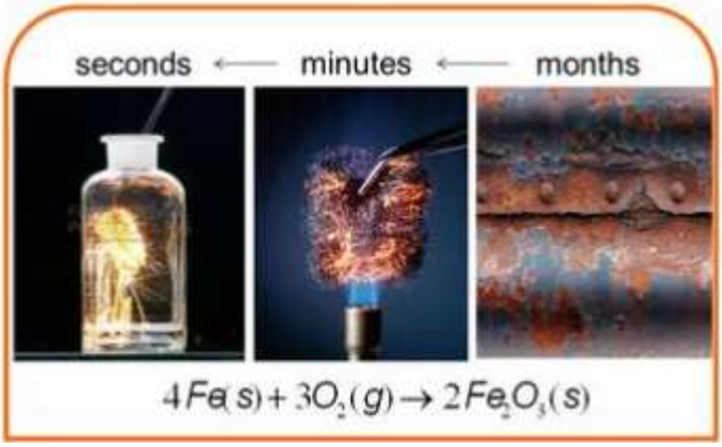


Summary:

- **Sigma (σ) Bonds**: Formed by axial overlap of orbitals, present in all single bonds, allow rotation, and are generally stronger.
- **Pi (π) Bonds**: Formed by the lateral overlap of p orbitals, present in double and triple bonds, restrict rotation, and are generally weaker.

CHAPTER 7

KINETICS



Chapter Outline

Chemical reaction rates refer to the speed at which reactants are converted into products in a chemical reaction. Understanding these rates is crucial in fields such as chemistry, biochemistry, engineering, and environmental science, as it helps in controlling reactions in industrial processes, understanding biological pathways, and addressing environmental issues.

7.1 Chemical Reaction Rates

Reaction rate, in chemistry, is the speed at which a chemical reaction proceeds. It is often expressed in terms of either the concentration (amount per unit volume) of a product formed in a unit of time or the concentration of a reactant consumed in a unit of time. Alternatively, it may be defined in terms of the amounts of the reactants consumed or products formed in a unit of time.

During the reaction shown below, reactants A and B are consumed while the concentration of product AB increases. The reaction rate can be determined by measuring how fast the concentration of A or B decreases, or by how fast the concentration of AB increases (Figure 7.1).

$$A+B \longrightarrow AB$$

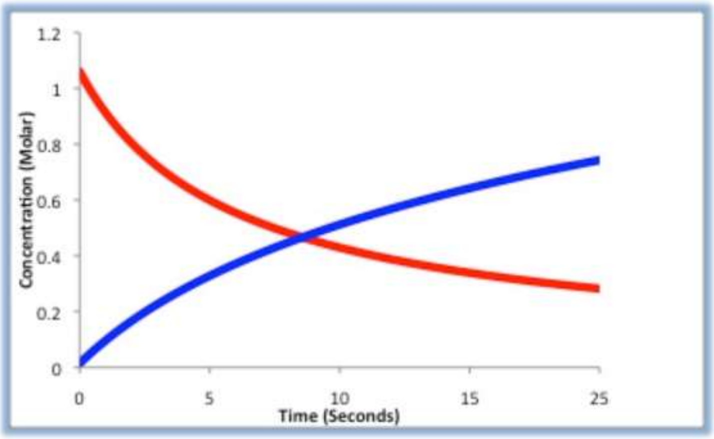


Figure 7.1: The above picture shows a hypothetical reaction profile in which the reactants (red) decrease in concentration as the products increase in concentration (blue).

$$\text{rate} = \frac{\Delta\text{concentration}}{\Delta\text{time}}$$

For a reaction of the form $A + B \rightarrow C$, the rate can be expressed in terms of the change in concentration of any of its components

$$\text{rate} = -\frac{\Delta[A]}{\Delta t}$$

$$\text{rate} = -\frac{\Delta[B]}{\Delta t}$$

$$\text{rate} = \frac{\Delta[C]}{\Delta t}$$

in which $\Delta[A]$ is the difference between the concentration of A over the time interval $t_2 – t_1$:

$$\Delta[A] = [A]_2 - [A]_1$$

Notice the minus signs in the first two examples above. The concentration of a reactant always decreases with time, so Δ[A] and Δ[B] are both negative. Since negative rates do not make much sense, rates expressed in terms of a reactant concentration are **always** preceded by a minus sign to make the rate come out positive.

Consider now a reaction in which the coefficients are different:

$$A + 3B \rightarrow 2D$$

It is clear that [B] decreases three times as rapidly as $[A]$, so to avoid ambiguity when expressing the rate in terms of different components, it is customary to divide each change in concentration by the appropriate coefficient:

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{\Delta[B]}{3\Delta t} = \frac{\Delta[D]}{2\Delta t}$$

7.2 Factors Affecting Reaction Rates

For a reaction to occur, the particles that are reacting must collide with each other. Only some of the collisions that take place cause a chemical change to happen. These are called 'successful' collisions. The greater the number of 'successful' collisions, the faster the rate of a reaction. This is called the 'collision theory'.

1. **Concentration of Reactants**: if the concentration of reactants is increased, more reactant particles move together. There will be more collisions and so the reaction rate is increased. The higher the concentration of reactants, the faster the rate of a reaction will be.

2. **Temperature**: if the temperature is increased, the particles have more energy and so move quickly. Increasing the temperature increases the rate of reaction because the particles collide more often and with more energy. The higher the temperature, the faster the rate of a reaction will be (Figure 7.2).

Sodium and chlorine react vigorously when heated, giving an orange flame and producing white sodium chloride.

$$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$$

Look at the graph of the reaction between hydrochloric acid and calcium carbonate. Notice how an increase in temperature leads to an increase in the speed of release of carbon dioxide, but not the total volume of carbon dioxide released.

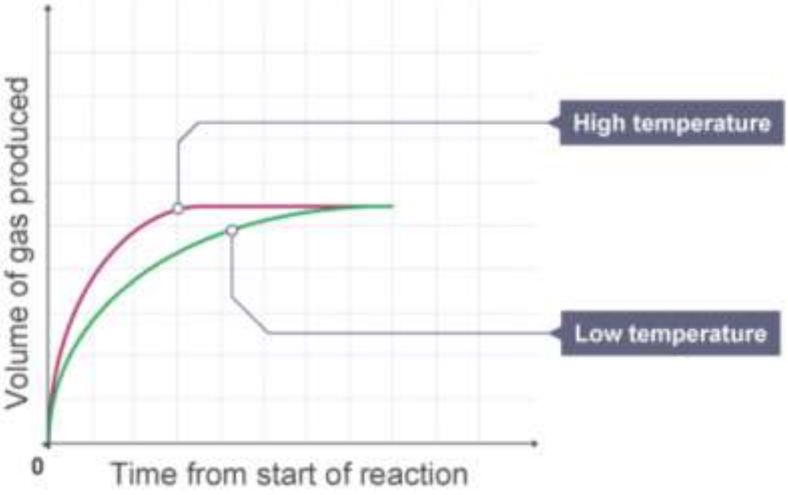


Figure 7.2 Dependence of the reaction time on the formation gas.

Surface Area: By decreasing the particle size of a reactant, we are increasing its surface area. The greater the surface area, the higher the chance of collisions, thus the faster the rate of reaction. The smaller the particle size, the faster the reaction.

3. **Catalysts**: Catalysts are substances that increase the reaction rate without being consumed in the process. They provide an alternative reaction pathway with a lower activation energy.

4. **Pressure**: For reactions involving gases, increasing the pressure effectively increases the concentration of gas molecules, leading to more frequent collisions and a higher reaction rate.

5. **Nature of Reactants**: Different substances react at different rates. For example, ionic compounds in aqueous solutions generally react faster than covalent compounds because ions can move freely and collide more easily.

7.3 Rate Laws

Rate laws are mathematical expressions that describe the relationship between a chemical reaction's rate and its reactants' concentration. They are fundamental in understanding and predicting how fast a reaction proceeds under given conditions.

Basic Form of Rate Laws:

For a general reaction: aA + bB → cC + dD

the rate law can be written as rate =k $[A]^a$ $[B]^{b,}$ where:

The rate is the reaction rate.

- K is the rate constant.
- [A] and [B] are the molar reactants A and B.
- a and b are the reaction orders concerning reactants A and B, respectively.

Rate Constant (k):

The rate constant k is a proportionality constant specific to a particular reaction at a given temperature. It can be calculated once the rate law is known.

Reaction Order

The sum of the concentration term exponents in a rate law equation is known as the **reaction order**. We can also refer to the relationship for each reactant in terms of its exponent as an order.

For the following reaction between nitrogen dioxide and carbon monoxide:

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

The rate law is experimentally determined to be: rate = $k[NO_2]^2$

Therefore, we would say that the overall reaction order for this reaction is second-order (the sum of all exponents in the rate law is 2), but zero-order for [CO] and second-order for $[NO_2]$. The reaction order is most often a whole number such as 0, 1, or 2; however, there are instances where the reaction order may be a fraction or even a negative value.

Key Takeaways

1) The rate law is a mathematical relationship obtained by comparing reaction rates with reactant concentrations.
2) The reaction order is the sum of the concentration term exponents in a rate law equation.
3) A reaction's rate law may be determined by the initial rates method.

7.4 Reaction Mechanisms

In kinetics, a reaction mechanism provides a detailed pathway for how reactants transform into products, including all the intermediate steps and species formed along the way. Understanding the mechanism helps explain observed reaction rates and predict the behavior of reactions under different conditions.

Key Concepts in Reaction Mechanisms:

1. **Elementary Steps**:
   - These are the individual reactions that occur as part of the overall reaction mechanism.
   - Each step involves a small number of molecules (typically one or two, rarely three).
   - The rate law for each elementary step can be written directly from its molecularity:
     - **Unimolecular** (one reactant molecule): A→ Products, Rate = k[A]
     - **Bimolecular** (two reactant molecules): A+B→ Products, Rate = k[A][B]

2. **Reaction Intermediates**:

- Species that are formed in one step of the mechanism and consumed in a subsequent step.
- They do not appear in the overall balanced equation for the reaction.

3. **Rate-Determining Step (RDS)**:

- The slowest step in the reaction mechanism.
- It controls the overall reaction rate and determines the rate law for the overall reaction.
- The rate law of the RDS often matches the experimentally determined rate law for the overall reaction.

Example:

Consider the reaction: $2NO_2 + F_2 \rightarrow 2NO_2F$

Suppose the proposed mechanism is:

1. $NO_2 + F_2 \rightarrow NO_2F + F$ (slow)
2. $NO_2 + F \rightarrow NO_2F$ (fast)

Identifying the Rate-Determining Step:

- Step 1 is the slow step (RDS), which determines the overall rate.
- The rate law for this step is: Rate = $k_1[NO_2][F_2]$

Mechanisms with intermediates:

Consider the reaction: $2H_2+2NO \rightarrow N_2+2H_2O$

A proposed mechanism might be:

1. $2NO \rightarrow N_2O_2$ (fast equilibrium)
2. $N_2O_2+H_2 \rightarrow N_2O+H_2O$ (slow, RDS)
3. $N_2O+H_2 \rightarrow N_2+H_2O$ (fast)

Here:

- N_2O_2 and N_2O are intermediates.
- The slow step (Step 2) determines the overall rate law: Rate = $k[NO]^2[H_2]$

Catalysts in Reaction Mechanisms:

Catalysts provide an alternative reaction pathway with a lower activation energy. They appear in the mechanism but are not consumed by the reaction. They are involved in the formation of intermediates that lead to the final products.

Summary:

- **Elementary Steps**: Simple reactions make up the overall mechanism.
- **Molecularity**: Number of reactant molecules in an elementary step.
- **Intermediates**: Species formed and consumed within the mechanism.
- **Rate-Determining Step**: The slowest step that controls the reaction rate.
- **Rate Laws**: Derived from the rate-determining step.
- **Steady-State Approximation**: Assumes constant intermediate concentration for simplification.
- **Catalysts**: Provide alternative pathways with lower activation energy.

7.5 Catalysis

Catalysis is a process by which the rate of a chemical reaction is increased by the presence of a substance called a catalyst. Catalysts are not consumed in the reaction and can be used repeatedly. They work by providing an alternative reaction pathway with a lower activation energy.

Types of Catalysis:

1. **Homogeneous Catalysis**:

- The catalyst is in the same phase as the reactants (e.g., all are in the liquid phase).
- Example: The acid-catalyzed esterification reaction, where sulfuric acid (H_2SO_4) acts as a homogeneous catalyst.

$$R\text{-}COOH + R'\text{-}OH \rightarrow R\text{-}COOR' + H_2O \text{ (by means } H+)$$

Here, the acid (H^+) is the catalyst that protonates the carboxylic acid, making it more electrophilic and easier to react with the alcohol.

2. **Heterogeneous Catalysis**:

- The catalyst is in a different phase from the reactants (e.g., a solid catalyst with gaseous reactants).
- Example: The hydrogenation of ethene using a platinum catalyst.

$$C_2H_4 + H_2 \rightarrow C_2H_6 \text{ (Pt- catalyst)}$$

The ethane and hydrogen adsorb onto the platinum surface, where they react to form ethane.

Mechanism of Catalysis:

1. **Lowering Activation Energy**:

- Catalysts provide an alternative pathway for the reaction with lower activation energy compared to the uncatalyzed pathway.

2. **Formation of Intermediates**:

- In some cases, the catalyst forms an intermediate with the reactants, which then reacts to form the final products while regenerating the catalyst.
- Example: In the catalytic hydrogenation of alkenes, the metal catalyst forms an intermediate complex with hydrogen and the alkene.

Characteristics of Catalysts:

Selectivity: catalysts can selectively accelerate specific reactions over others; **regeneration**: catalysts are regenerated at the end of the reaction cycle and can be reused; **activity**: the ability of a catalyst to increase the rate of a reaction; **stability**: the ability of a catalyst to maintain its activity over time without being deactivated.

Summary:

Catalysis is a fundamental concept in chemistry that enhances reaction rates without the catalyst being consumed. Understanding the types and mechanisms of catalysis is crucial for applications in industrial processes, environmental protection, and biological systems.

Link to Learning

Click here (http://surl.li/tyyicn) to view the initial rates method.

CHAPTER 8

FUNDAMENTAL EQUILIBRIUM CONCEPTS

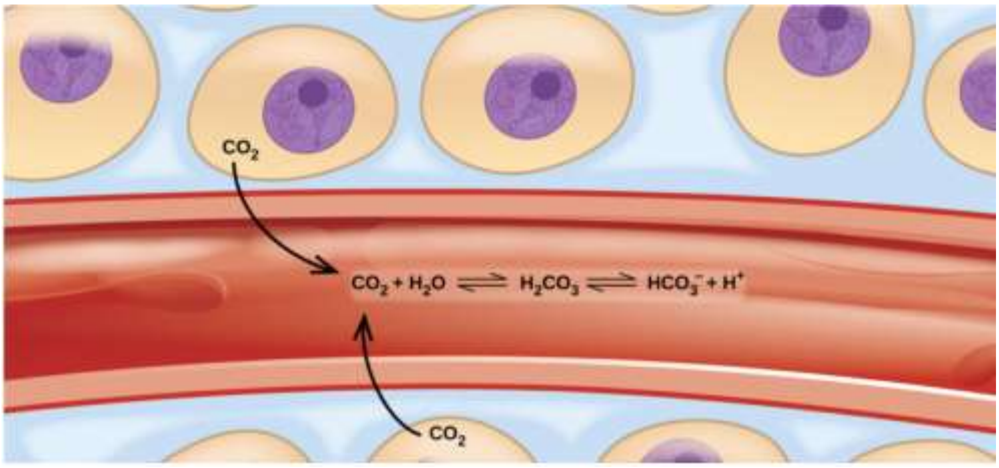


Figure 8.1 Movement of carbon dioxide through tissues and blood cells involves several equilibrium reactions.

Chapter Outline

8.1 Chemical Equilibria
8.2 Equilibrium Constants
8.3 Shifting Equilibria: Le Châtelier's Principle

8.1 Chemical Equilibria

Chemical equilibrium is a state in which the forward reaction rate equals the backward reaction rate. In other words, there is no net change in concentrations of reactants and products. This kind of equilibrium is also called dynamic equilibrium. Understanding chemical equilibria is fundamental in predicting the behavior of chemical reactions in closed systems.

In a chemical reaction, chemical equilibrium is the state in which both the reactants and products are present in concentrations that have no further tendency to change with time so that there is no observable change in the properties of the system.

What are the 3 conditions of chemical equilibrium?

The forward and reverse rates of reactions must be equal. The number of reactants and products need not be equal. However, after equilibrium is achieved, the amounts of reactants and products will always be constant.

A few real-life examples of chemical reactions that attain equilibrium are mentioned below:

Lime CaO production from limestone $CaCO_3$:

$$CaCO_3 \leftrightarrow CaO + CO_2$$

Hydrogen and iodine gases react to form hydrogen iodide according to the following reaction:

$$H_2(g)+I_2(g) \rightleftharpoons 2HI(g)$$

Forward reaction: $H_2(g)+I_2(g) \rightarrow 2HI(g)$

Reverse reaction: $2HI(g) \rightarrow H_2(g)+I_2(g)$

Initially, only the forward reaction occurs because no HI is present. As soon as some HIHI has formed, it begins to decompose back into H_2 and I_2. Gradually, the rate of the forward reaction decreases while the rate of the reverse reaction increases. Eventually, the rate of combination of H_2 and I_2 to produce HI becomes equal to the rate of decomposition of HI into H_2 and I_2. When the rates of the forward and reverse reactions have become equal, the reaction has achieved a state of balance. **Chemical equilibrium** is the state of a system in which the rate of the forward reaction is equal to the rate of the reverse reaction (Figure 8.2).

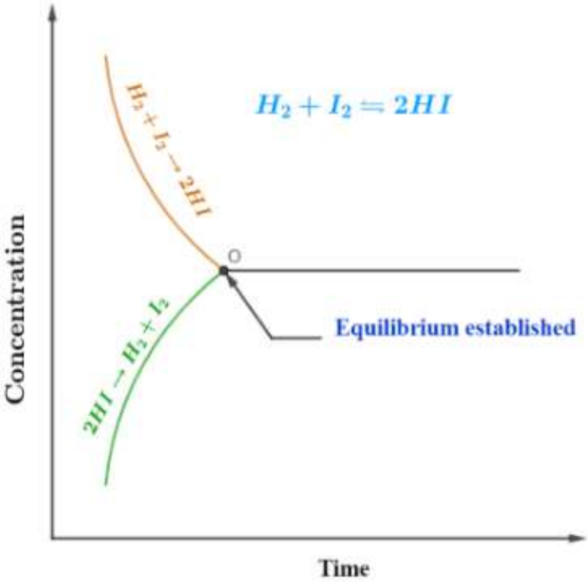


Figure 8.2 Equilibrium in reaction $H_2(g)+I_2(g) \rightarrow 2HI(g)$.

Conditions for Equilibrium and Types of Equilibrium

It may be tempting to think that once equilibrium has been reached, the reaction stops. Chemical equilibrium is a dynamic process. The forward and reverse reactions continue to occur even after equilibrium has been reached. However, because the rates of the reactions are the same, there is no change in the relative concentrations of reactants and products for a reaction that is at equilibrium. The conditions and properties of a system at equilibrium are summarized below.

1. The system must be closed, meaning no substances can enter or leave the system.
2. Equilibrium is a dynamic process. Even though we don't necessarily see the reactions, both forward and reverse are taking place.
3. The rates of the forward and reverse reactions must be equal.
4. The amount of reactants and products does not have to be equal. However, after equilibrium is attained, the amounts of reactants and products will be constant.

8.2 Equilibrium Constants

Consider the hypothetical reversible reaction in which reactants A and B react to form products C and D. This equilibrium can be shown below, where the lowercase letters represent the coefficients of each substance.

$$aA + bB \rightleftharpoons cC + dD$$

As we have established, the rates of the forward and reverse reactions are the same at equilibrium, and so the concentrations of all of the substances are constant. Since that is the case, it stands to reason that a ratio of the concentration for any given reaction at equilibrium maintains a constant value. The **equilibrium constant** (K_{eq}, K_c) is the ratio of the mathematical product of the products of a reaction to the mathematical product of the concentrations of the reactants of the reaction. Each concentration is raised to the power of its coefficient in the balanced chemical equation. For the general reaction above, the equilibrium constant expression is written as follows:

$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

- K_c is used for concentrations in mol/L, and K_p is used for partial pressures in atm for gaseous reactions.
- The value of K provides insight into the position of equilibrium (whether products or reactants are favored).

The concentrations of each substance, indicated by the square brackets around the formula, are measured in molarity units (mol/L).

The value of the equilibrium constant for any reaction is only determined by experiment. As detailed in the above section, the position of equilibrium for a given reaction does not depend on the starting concentrations, and so the value of the equilibrium constant is truly constant. It does, however, depend on the temperature of the reaction. This is because equilibrium is defined as a condition resulting from the rates of forward and reverse reactions being equal. If the temperature changes, the corresponding change in those reaction rates will alter the equilibrium constant. For any reaction in which a K_{eq} is given, the temperature should be specified.

When Keq is greater than 1, the numerator is larger than the denominator so the products are favored, meaning the concentration of its products is greater than that of the reactants.

If K_{eq} is less than 1, then the reactants are favored because the denominator (reactants) is larger than the numerator (products).

When K_{eq} is equal to 1, then the concentration of reactants and products are approximately equal.

Reaction Quotient

The reaction quotient, Q, is used when questioning if we are at equilibrium. The calculation for Q is the same as for K , but we can only use K when we know we are at equilibrium. Comparing Q and K allows the direction of the reaction to be predicted.

- $Q = K$ equilibrium;
- $Q < K$ reaction proceeds to the right to form more products and decrease the amount of reactants so the value of Q will increase;
- $Q > K$ reaction proceeds to the left to form more reactants and decrease the amount of products, so the value of Q will decrease.

We need to look at two different types of equilibria (homogeneous and heterogeneous) separately because the equilibrium constants are defined differently.

A homogeneous equilibrium has everything present in the same phase. The usual examples include reactions where everything is a gas, or everything is present in the same solution.

A heterogeneous equilibrium has things present in more than one phase. The usual examples include reactions involving solids and gases, or solids and liquids.

Kc in homogeneous equilibria

This is the more straightforward case. It applies where everything in the equilibrium mixture is present as a gas, or everything is present in the same solution.

A good example of a gaseous homogeneous equilibrium is the conversion of sulfur dioxide to sulfur trioxide at the heart of the contact process:

$$SO_2+ O_2 \leftrightarrow SO_3$$

Write the Kc expression for this reaction according to the expression of the equilibrium constant:

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

Kc in heterogeneous equilibria

Typical examples of a heterogeneous equilibrium include:

The equilibrium is established if steam is in contact with red-hot carbon. Here we have gases in contact with a solid.

$$H_2O(g) + C(s) \leftrightarrow H_2(g) + CO(g)$$

Write the Kc expression for this reaction according to the expression of the equilibrium constant:

$$K = \frac{[CO][H_2]}{[H_2O]}$$

8.3 Shifting Equilibria: Le Châtelier’s Principle

Le Chatelier's principle implies that a pressure increase shifts an equilibrium to the side of the reaction with the fewer number of moles of gas, while a pressure decrease shifts an equilibrium to the side of the reaction with the greater number of moles of gas.

How does Le Châtelier's principle predict how the system will shift to restore equilibrium?

To re-establish equilibrium, the system will either shift toward the products (if $Q \leq K$) or the reactants (if $Q \geq K$) until Q returns to the same value as K. This process is described by Le Chatelier's principle.

A chemical system at equilibrium can be temporarily shifted out of equilibrium by adding or removing one or more of the reactants or products. The concentrations of both reactants and products then undergo additional changes to return the system to equilibrium (Figure 8.3).

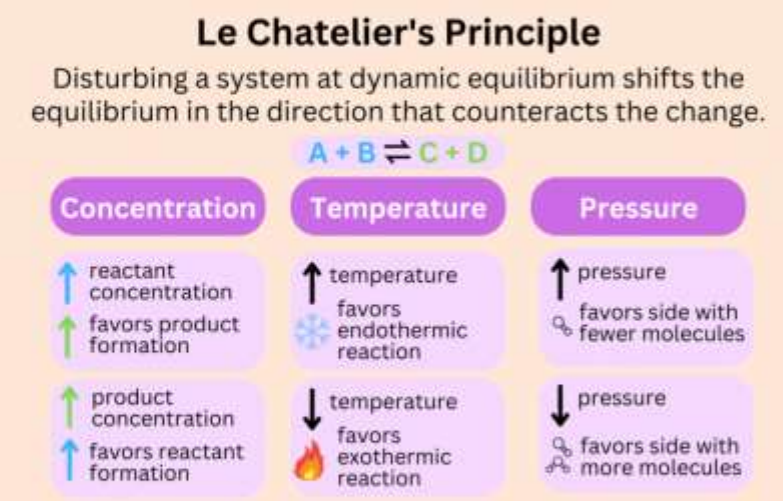


Figure 8.3. The scheme explanation of Chatelier's principle

If a system at equilibrium is disturbed by changing the concentration, temperature, or pressure, the system will shift to counteract the disturbance and re-establish equilibrium.

Concentration: Adding or removing reactants/products shifts the equilibrium to consume the added substance or produce more of the removed substance.

Temperature:

- For exothermic reactions (ΔH<0), increasing temperature shifts the equilibrium to the left.
- For endothermic reactions (ΔH>), increasing temperature shifts the equilibrium to the right.

Pressure: For gaseous reactions, increasing pressure by decreasing volume shifts the equilibrium towards the side with fewer gas molecules.

Le Chatelier's principle does not apply to catalysts. Adding a catalyst does not shift the equilibrium of a chemical reaction because it increases the rates of the forward and reverse reactions equally.

Link to Learning

Click here: http://surl.li/rrygpr to view the *Equilibrium calculations*
http://surl.li/cjcwbr to view the *Chemical equilibrium: introduction and definitions*

CHAPTER 9

ACID-BASE EQUILIBRIA

Chapter Outline

9.1 Brønsted-Lowry Acids and Bases
9.2 pH and pOH
9.3 Hydrolysis of Salt Solutions
9.4 Buffers

9.1 Brønsted-Lowry Acids and Bases

In 1923, chemists Johannes Nicolaus Brønsted and Thomas Martin Lowry independently developed definitions of acids and bases based on the compounds' abilities to either donate or accept protons (H^+ ions). In this theory, acids are defined as proton donors, whereas bases are defined as proton acceptors. Amphoteric is a compound that acts as both a Brønsted-Lowry acid and base.

The Brønsted-Lowry theory of acid and bases took the Arrhenius definition one step further, as a substance no longer needed to be composed of hydrogen (H^+) or hydroxide (OH^-) ions to be classified as an acid or base. For example, consider the following chemical equation:

$$HCl_{(aq)} + NH_{3(aq)} \rightarrow NH_4{}^+{}_{(aq)} + Cl^-{}_{(aq)}$$

Here, hydrochloric acid (HCl) "donates" a proton (H^+) to ammonia (NH_3), which "accepts" it, forming a positively charged ammonium ion (NH_4^+) and a negatively charged chloride ion (Cl^-). Therefore, HCl is a Brønsted-Lowry acid (donates a proton) while ammonia is a Brønsted-Lowry base (accepts a proton). Also, Cl^- is called the **conjugate base** of the acid HCl, and NH_4^+ is called the **conjugate acid** of the base NH_3.

- A Brønsted-Lowry acid is a proton (hydrogen ion) donor.
- A Brønsted-Lowry base is a proton (hydrogen ion) acceptor.

In this theory, an **acid is a substance that can release a proton** (like in the Arrhenius theory), and a **base is a substance that can accept a proton**. A basic salt, such as Na^+F^-, generates OH^- ions in water by taking protons from the water itself (to make HF):

$$F^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HF_{(aq)} + OH^-$$

When a Brønsted acid dissociates, it increases the concentration of hydrogen ions in the solution, $[H^+]$; conversely, Brønsted bases dissociate by taking a proton from the solvent (water) to generate $[OH^-]$.

Acid dissociation

$$HA_{(aq)} \rightleftharpoons A^-(aq) + H^+_{(aq)} \qquad (3)$$

Acid Ionization Constant:

$$K_a = \frac{[A^-][H^+]}{[HA]}$$

Base dissociation:

$$B_{(aq)} + H_2O_{(l)} \rightleftharpoons HB^+_{(aq)} + OH^-_{(aq)} \qquad (5)$$

Base Ionization Constant

$$K_b = \frac{[HB^+][OH^-]}{[B]}$$

Determining a substance as a Brønsted-Lowery acid or base can only be done by observing the reaction. In the case of the HOH, it is a base in the first case and an acid in the second case (Figure 9.1).

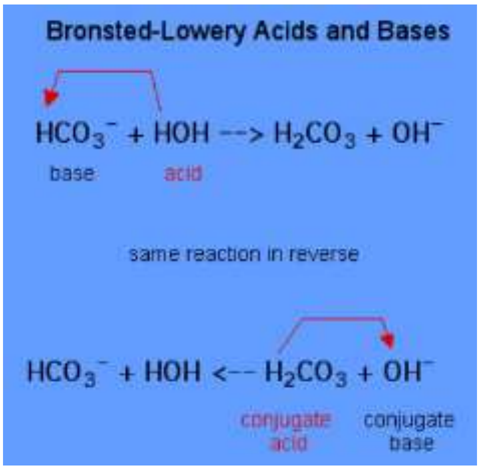


Fig. 9.1 The examples of the acids and the bases according to the Brønsted-Lowry theory.

Count the hydrogens on each substance before and after the reaction to determine whether a substance is an acid or a base. If the number of hydrogens has decreased, that substance is the acid (donates hydrogen ions). If the number of hydrogens has increased, that substance is the base (accepts hydrogen ions). These definitions are normally applied to the reactants on the left. If the reaction is viewed in reverse, a new acid and base can be identified. The substances on the right side of the equation are called the conjugate acid and the conjugate base, compared to those on the left. Also, note that the original acid turns into the conjugate base after the reaction is over.

For a reaction to be in equilibrium, a transfer of electrons needs to occur. The acid will give an electron away, and the base will receive the electron. Acids and Bases that work together in this fashion are called *conjugate pairs* made up of *conjugate acids* and *conjugate bases*.

$$HA + Z \rightleftharpoons A^{-} + HZ^{+}$$

A stands for an Acidic compound, and Z stands for a Basic compound

- A Donates H to form HZ^{+}
- Z Accepts H from A which forms HZ^{+}
- A^{-} becomes the conjugate base of HA and in the reverse reaction it accepts a H from HZ to recreate HA to remain in equilibrium
- HZ^{+} becomes a conjugate acid of Z and in the reverse reaction it donates a H to A^{-} recreating Z to remain in equilibrium

9.2 pH and pOH

What is pH? pH or potential of hydrogen ion, is a scale used to determine the hydrogen ion (H^{+}) concentration in a solution. It is a quantitative measure of the acidity or alkalinity of a solution. It equals the negative log of hydrogen ion (H^{+}) concentration.

$$pH = -\log [H^{+}]$$

What is pOH? pOH, or the potential of hydroxide ion, is a scale used to determine the hydroxide ion (OH^{-}) concentration in a solution. It is a quantitative measure of the acidity or alkalinity of a solution. It equals the negative log of hydroxide ion (OH^{-}) concentration.

$$pH = -\log [OH^{-}]$$

pH, or the potential of hydrogen ion, is a scale used to determine the hydrogen ion (H^{+}) concentration in a solution. It is a quantitative measure of the acidity or alkalinity of a solution. It equals the negative log of hydrogen ion (H^{+}) concentration.

$$pH = -\log [H^{+}]$$

At pH 7 solution is found to be neutral. In contrast, if the pH value is less than 7, the solution will be acidic, and if the pH value is more than 7, the solution will be basic.

In contrast, pOH or the potential of hydroxide ion is a scale used to determine the hydroxide ion (OH^{-}) concentration in a solution. It is a quantitative measure of the acidity or alkalinity of a solution. It equals the negative log of hydrogen ion (OH^{-}) concentration.

$$pOH = -\log [OH^{-}]$$

At pOH 7 solution is found to be neutral. In contrast, if the pOH value is less than 7, the solution will be basic, and if the pOH value is more than 7, the solution will be acidic.

Both pH and pOH are related to each other. pH is inversely proportional to pOH, i.e., pH increases with decreasing pOH.

Consider a reaction,

$$H_2O \leftrightarrows H^{+} + OH^{-}$$

For the above reaction dissociation constant, $K_{w,}$ would be,

$K_w = [H^{+}][OH^{-}]$

Here, K_w refers to the dissociation constant, and $[H^{+}]$ and $[OH^{-}]$ refer to hydrogen and hydroxide ion concentrations.

We are taking the negative logarithm of both sides.

$-\log K_w = -\log [H^{+}] [OH^{-}]$

$-\log K_w = -(\log [H^{+}] + [OH^{-}])$

$-\log K_w = -\log [H^{+}] - \log [OH^{-}] \qquad (1)$

We know that,

$K_w = 1*10^{-14}$ at 298 K

$-\log [H^+] = pH$

$-\log [OH^-] = pOH$

Putting value in equation 1

$-\log 1*10^{-14} = pH + pOH$

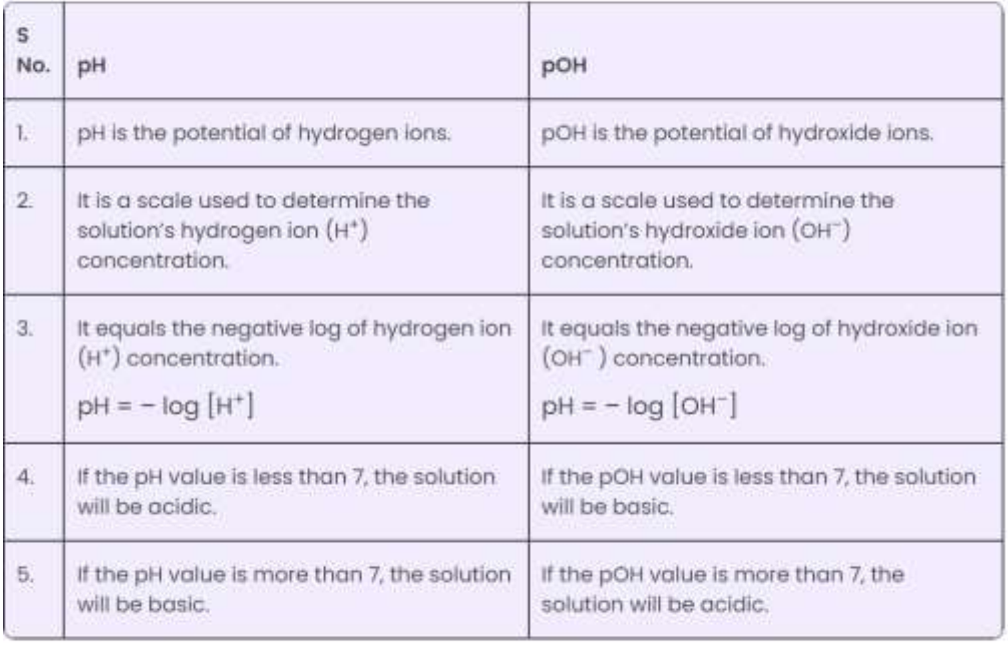
$14 = pH + pOH$

$pOH = 14 – pH$

$pH = 14 – pOH$

Hence if the pH is known, we can quickly determine the pOH value.

Difference between pOH and pH



S No.	pH	pOH
1.	pH is the potential of hydrogen ions.	pOH is the potential of hydroxide ions.
2.	It is a scale used to determine the solution's hydrogen ion (H^+) concentration.	It is a scale used to determine the solution's hydroxide ion (OH^-) concentration.
3.	It equals the negative log of hydrogen ion (H^+) concentration. $pH = -\log [H^+]$	It equals the negative log of hydroxide ion (OH^-) concentration. $pH = -\log [OH^-]$
4.	If the pH value is less than 7, the solution will be acidic.	If the pOH value is less than 7, the solution will be basic.
5.	If the pH value is more than 7, the solution will be basic.	If the pOH value is more than 7, the solution will be acidic.

9.3 Hydrolysis of Salt Solutions

Baking seems easy with all the pre-mixed items available. ("just add water and stir"). However, there is a good amount of chemistry involved in baking with ingredients that are measured out. One important ingredient is baking powder. The fluffiness in the final product of a non-yeast recipe is usually due to the carbon dioxide formed by baking powder. One popular brand uses a mix of sodium bicarbonate and sodium aluminum sulfate to produce CO_2. The reaction is:

$$3NaHCO_3 + NaAl(SO_4)_2 \rightarrow Al(OH)_3 + 2Na_2SO_4 + 3CO_2$$

If all goes well, the biscuits rise, the pancakes are fluffy, and everybody is happy.

A salt is an ionic compound that is formed when an acid and a base neutralize each other. While it may seem that salt solutions are always neutral, they can frequently be either acidic or basic.

Consider the salt formed when the weak acid hydrofluoric acid is neutralized by the strong base sodium hydroxide. The molecular and net ionic equations are shown below.

$$HF_{(aq)} + NaOH_{(aq)} \rightarrow NaF_{(aq)} + H_2O_{(l)}$$

Since sodium fluoride is soluble, the sodium ion is a spectator ion in the neutralization reaction. The fluoride ion is capable of reacting, to a small extent, with water, accepting a proton.

$$F^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HF_{(aq)} + OH^-_{(aq)}$$

The fluoride ion acts as a weak Brønsted-Lowry base. The hydroxide ion that is produced as a result of the above reaction makes the solution slightly basic. **Salt hydrolysis** is a reaction in which one of the ions from a salt reacts with water, forming either an acidic or basic solution.

Salts That Form Basic Solutions

When solid sodium fluoride is dissolved in water, it completely dissociates into sodium ions and fluoride ions. The sodium ions do not have any capability of hydrolysis, but the fluoride ions hydrolyze to produce a small amount of hydrofluoric acid and hydroxide ions.

$$F^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HF_{(aq)} + OH^-_{(aq)}$$

The equilibrium constant for this reaction is K_b of the conjugate base Ac^- of the acid HAc:

$$K_b = \frac{[HAc][OH^-]}{[Ac^-]}$$

$$K_b = \frac{[HAc][OH^-]}{[Ac^-]}\frac{[H^+]}{[H^+]}$$

$$K_b = \frac{[HAc]}{[Ac^-][H^+]}[OH^-][H^+] = \frac{K_w}{K_a}$$

Salts that are derived from the neutralization of a weak acid (HF) by a strong base (NaOH) will always produce basic salt solutions.

Salts That Form Acidic Solutions

Ammonium chloride (NH_4Cl) is a salt that is formed when the strong acid HCl is neutralized by the weak base NH_3. Ammonium chloride is soluble in water. The chloride ion produced is incapable of hydrolysis because it is the conjugate base of the strong acid HCl. In other words, the Cl^- ion cannot accept a proton from water to form HCl and OH^-, as the fluoride ion did in the previous section. However, the ammonium ion is capable of reacting slightly with water, donating a proton and so acting as an acid.

$$NH_4^+(aq) + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + NH_{3(aq)}$$

The acidity constant can be derived from K_w and K_b.

$$K_a = \frac{[H_3O^+][NH_3]}{[NH_4^+]}\frac{[OH^-]}{[OH^-]} = \frac{K_w}{K_b} = \frac{1.00 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.7 \times 10^{-10}$$

Salts of Weak Acids and Weak Bases

A salt formed between a weak acid and a weak base can be neutral, acidic, or basic depending on the relative strengths of the acid and base.

- If K_a(cation) > K_b(anion) the solution of the salt is acidic.
- If K_a(cation) = K_b(anion) the solution of the salt is neutral.
- If K_a(cation) < K_b(anion) the solution of the salt is basic.

Arrange the three salts according to their acidity. NH_4CH_3COO (ammonium acetate), NH_4CN (ammonium cyanide), and $NH_4HC_2O_4$ (ammonium oxalate).

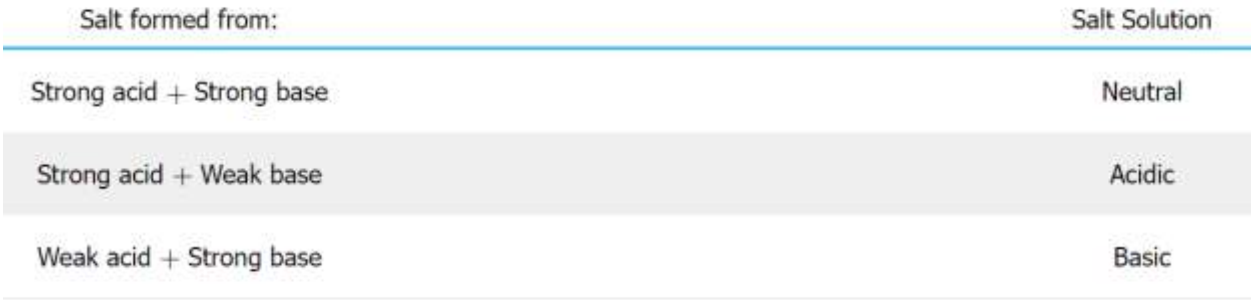
Ka(acetic acid)=1.85E-5,
Ka(hydrogen cyanide)=6.2E-10,
Ka(oxalic acid)=5.6E-2,
Kb(NH_3)=1.8E-5.

Solution
ammonium oxalate -- acidic, Ka (o) > Kb (NH_3)
ammonium acetate -- neutral, Ka = Kb
ammonium cyanide -- basic, Ka (c) < Kb (NH_3)

Salts That Form Neutral Solutions

A salt that is derived from the reaction of a strong acid with a strong base forms a solution that has a pH of 7. An example is sodium chloride, formed from the neutralization of HCl by NaOH. A solution of NaCl in water has no acidic or basic properties since neither ion is capable of hydrolysis. Other salts that form neutral solutions include potassium nitrate (KNO_3) and lithium bromide (LiBr). The table below summarizes how to determine the acidity or basicity of a salt solution.

Now, we can jump to the conclusions:



Salt formed from:	Salt Solution
Strong acid + Strong base	Neutral
Strong acid + Weak base	Acidic
Weak acid + Strong base	Basic

Summary

- Salt hydrolysis is a reaction in which one of the ions from a salt reacts with water, forming either an acidic or basic solution.
- Salts that are derived from the neutralization of a weak acid by a strong base will always produce basic salt solutions.
- Salts that are derived from the neutralization of a strong acid by a weak base will always produce acidic salt solutions.
- A salt that is derived from the reaction of a strong acid with a strong base forms a solution that has a pH of 7.

9.4 Buffers

Buffers are solutions that resist changes in pH when small amounts of acid or base are added. They are crucial in maintaining a stable pH in biological systems, industrial processes, and chemical reactions.

A buffer is a special solution that stops massive changes in pH levels. Every buffer that is made has a certain buffer capacity and buffer range. The buffer capacity is the amount of acid or base that can be added before the pH begins to change significantly. It can also be defined as the quantity of strong acid or base that must be added to change the pH of one liter of solution by one pH unit.

Components of a buffer: A buffer solution typically consists of:

1. A weak acid and its conjugate base**, or**
2. A weak base and its conjugate acid**.**

How buffers work

To illustrate the function of a buffer solution, consider a mixture of roughly equal amounts of acetic acid and sodium acetate. The presence of a weak conjugate acid-base pair in the solution imparts the ability to neutralize modest amounts of added strong acid or base. For example, adding a strong base to this solution will neutralize hydronium ions and shift the acetic acid ionization equilibrium to the right, partially restoring the decreased H_3O^+ concentration:

Example: acetic acid (CH_3COOH) and sodium acetate (CH_3COONa) buffer

- Acid Component**:** acetic acid (CH_3COOH)
- Conjugate base component: acetate ion (CH_3COO^-)

When an acid (H^+) is added: $CH_3COO^- + H^+ \rightarrow CH_3COOH$

When a base (OH^-) is added: $CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$

Figure 9.2 provides a graphical illustration of the changes to the buffer solution when strong acid and base are added. The buffering action of the solution is essentially a result of the added strong acid and base being converted to the weak acid and base that make up the buffer's conjugate pair. The weaker acid and base undergo only slight ionization, as compared to the complete ionization of the strong acid and base. The solution pH, therefore, changes much less drastically than it would in an unbuffered solution.

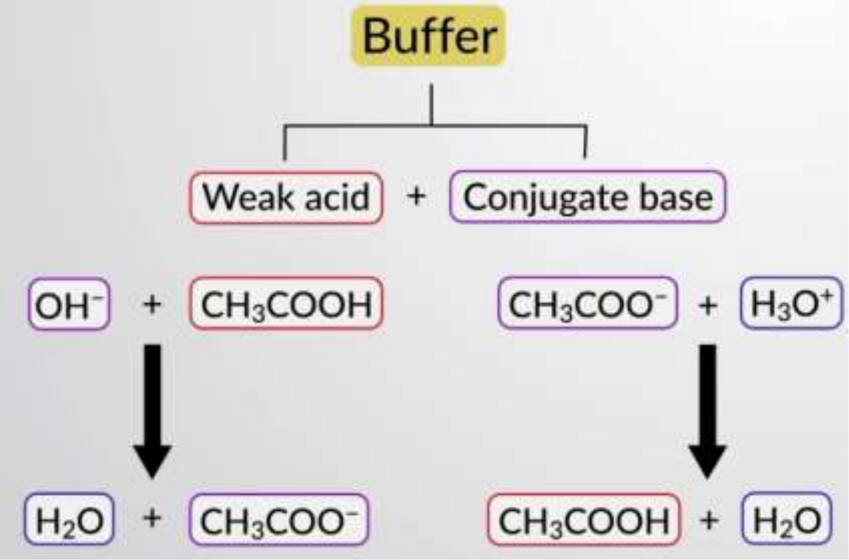


Figure 9.2 Buffering action in a mixture of acetic acid and acetate salt.

Buffer Capacity

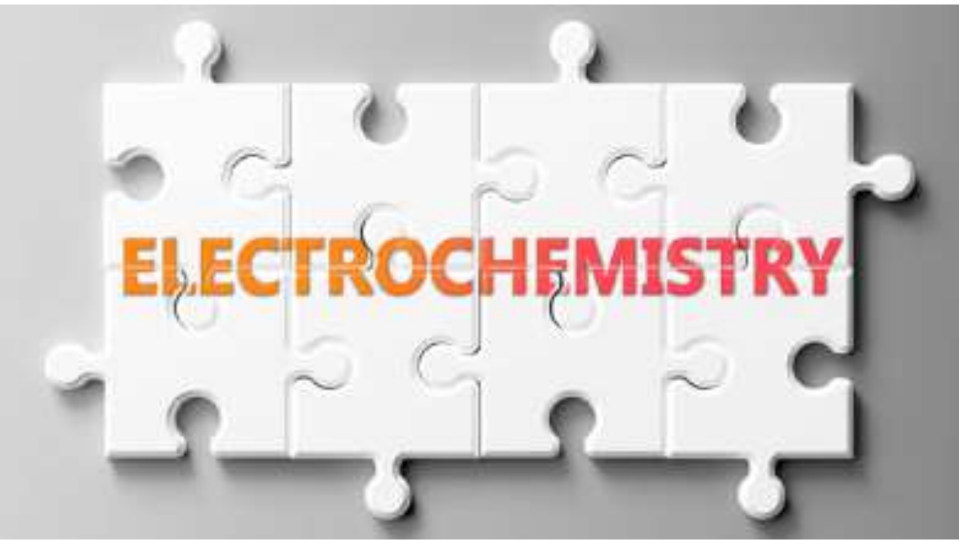
Buffer capacity refers to the amount of acid or base a buffer can neutralize before a significant change in pH occurs. It depends on the concentrations of the weak acid and its conjugate base. The greater the concentrations, the higher the buffer capacity.

Link to Learning

Click here: http://surl.li/nbnaxx to view pH, pOH, H_3O^+, OH^-, K_w, K_a, K_b, pK_a, and pK_b basic calculations - acids and bases chemistry problems; http://surl.li/bzajhb to view acid base strength - which is stronger?

CHAPTER 10

ELECTROCHEMISTRY



Chapter Outline
10.1 Balancing oxidation-reduction reactions
10.2 Galvanic cells
10.3 Standard reduction potentials
10.4 The Nernst equation
10.5 Electrolysis

Electrochemistry is a branch of chemistry that studies the relationship between electricity and chemical reactions. It encompasses various processes where electrons are transferred between species, often involving redox (reduction-oxidation) reactions. Key concepts in electrochemistry include electrode potentials, galvanic cells, electrolytic cells, and the Nernst equation.

10.1 Balancing oxidation-reduction reactions

Oxidation-reduction reactions, or redox reactions, are reactions in which one reactant is oxidized and one is reduced simultaneously.

Identifying Redox Reactions

The first step in balancing any redox reaction is determining whether or not it is even an oxidation-reduction reaction. This requires that one and typically more species change oxidation states during the reaction. To maintain charge neutrality in the sample, the redox reaction will entail both reduction and oxidation components. These are often separated into two independent hypothetical **half-reactions** to aid in understanding the reaction. This requires identifying which element is oxidized and which element is reduced. For example, consider this reaction:

$$Cu(s) + 2Ag^{+}(aq) \rightarrow Cu^{2+}(aq)+2Ag(s)$$

The first step in determining whether the reaction is redox is to split the equation into two hypothetical *half-reactions*. Let's start with the half-reaction involving the copper atoms:

$$Cu(s) \rightarrow Cu^{2+}(aq)$$

The oxidation state of copper on the left side is 0 because it is an element on its own. The oxidation state of copper on the right-hand side of the equation is +2. The copper in this half-reaction is oxidized as the oxidation state increases from 0 in Cu to +2 in Cu^{2+}. Now consider the silver atoms

$$2Ag^+(aq) \rightarrow 2Ag(s)$$

In this half-reaction, the oxidation state of silver on the left side is a +1. The oxidation state of silver on the right is 0 because it is a pure element. Because the oxidation state of silver decreases from +1 to 0, this is the reduction half-reaction.

Consequently, this reaction is a redox reaction as both reduction and oxidation half-reactions occur. Once confirmed, it is often necessary to balance the reaction (the reaction in equation 1 is balanced already, though), which can be accomplished in two ways because the reaction could take place in neutral, acidic, or basic conditions.

Balancing Redox Reactions

Balancing redox reactions is slightly more complex than balancing standard reactions, but still follows a relatively simple set of rules. One major difference is the necessity to know the half-reactions of the involved reactants; a half-reaction table is very useful for this. Half-reactions are often useful in that two half-reactions can be added to get a total net equation. Although the half-reactions must be known to complete a redox reaction, it is often possible to figure them out without having to use a half-reaction table. This is demonstrated in the acidic and basic solution examples. Besides the general rules for neutral conditions, additional rules must be applied for aqueous reactions in acidic or basic conditions.

One method used to balance redox reactions is called the **half-equation method**. In this method, the equation is separated into two half-equations: one for oxidation and one for reduction.

Half-Equation Method to Balance Redox Reactions in Acidic Aqueous Solutions

Each reaction is balanced by adjusting coefficients and adding H_2O, H^+, and e^- in this order:

1. Balance elements in the equation other than O and H.
2. Balance the oxygen atoms by adding the appropriate number of water (H_2O) molecules to the opposite side of the equation.
3. Balance the hydrogen atoms (including those added in step 2 to balance the oxygen atom) by adding H^+ ions to the opposite side of the equation.
4. Add up the charges on each side. Make them equal by adding enough electrons (e) to the more positive side. (Rule of thumb: e and H^+ are almost always on the same side.)
5. Electron on each side must be made equal; if they are not equal, they must be multiplied by appropriate integers (the lowest common multiple) to be made the same.
6. The half-equations are added together, canceling out the electrons to form one balanced equation. Common terms should also be canceled out.

The equation can now be checked to make sure that it is balanced.

Acidic conditions usually imply a solution with an excess of H^+ concentration, hence making the solution acidic. The balancing starts by separating the reaction into half-reactions. However, instead of immediately balancing the electrons, balance all the elements in the half-reactions that are not hydrogen and oxygen. Then, add H_2O molecules to balance any oxygen atoms. Next, balance the hydrogen atoms by adding protons (H^+). Now, balance the charge by adding electrons and scale the electrons (multiply by the lowest common multiple) so that they will cancel out when added together. Finally, add the two half-reactions and cancel out common terms.

Balance the following redox reaction in acidic conditions.

$$\mathrm{Cr_2O_7^{2-}(aq) + HNO_2(aq) \rightarrow Cr^{3+}(aq) + NO_3^-(aq)}$$

Solution

Step 1: Separate the half-reactions. The table provided does not have acidic or basic half-reactions, so just write out what is known.

$$\mathrm{Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq)}$$

$$\mathrm{HNO_2(aq) \rightarrow NO_3^-(aq)}$$

Step 2: Balance elements other than O and H. In this example, only chromium needs to be balanced. This gives:

$$\mathrm{Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq)}$$

and

$$\mathrm{HNO_2(aq) \rightarrow NO_3^-(aq)}$$

Step 3: Add H_2O to balance oxygen. The chromium reaction needs to be balanced by adding $7H_2O$ molecules. The other reaction also needs to be balanced by adding one water molecule. This yields:

$$\mathrm{Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O\ (l)}$$

and

$$\mathrm{HNO_2(aq) + H_2O(l) \rightarrow NO_3^-(aq)}$$

Step 4: Balance hydrogen by adding protons (H^+). 14 protons need to be added to the left side of the chromium reaction to balance the 14 (2 per water molecule * 7 water molecules) hydrogens. 3 protons need to be added to the right side of the other reaction.

$$\mathrm{14H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)}$$

and

$$\mathrm{HNO_2(aq) + H_2O(l) \rightarrow 3H^+(aq) + NO_3^-(aq)}$$

Step 5: Balance the charge of each equation with electrons. The chromium reaction has (14+) + (2-) = 12+ on the left side and (2 * 3+) = 6+ on the right side. To balance, add 6 electrons (each with a charge of -1) to the left side:

$$\mathrm{6e^- + 14H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)}$$

For the other reaction, there is no charge on the left, and a (3+) + (-1) = 2+ charge on the right. So add 2 electrons to the right side:

$$\mathrm{HNO_2(aq) + H_2O(l) \rightarrow 3H^+(aq) + NO_3^-(aq) + 2e^-}$$

Step 6: Scale the reactions so that the electrons are equal. The chromium reaction has 6e- and the other reaction has 2e-, so it should be multiplied by 3. This gives:

$$\mathrm{6e^- + 14H{+}(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)\cdot}$$

and

$$\mathrm{3\times[HNO_2(aq) + H_2O(l) \rightarrow 3H^+(aq) + NO_3^-(aq) + 2e^-]}$$

$$\mathrm{3HNO_2(aq) + 3H_2O(l) \rightarrow 9H^+(aq) + 3NO_3^-(aq) + 6e^-}$$

Step 7: Add the reactions and cancel out common terms.

$$\mathrm{3HNO_2(aq) + 3H_2O(l) \rightarrow 9H^+(aq) + 3NO_3^-(aq) + 6e^-}$$

$$\mathrm{6e^- + 14H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)}$$

Summarize (the blue color means these elements are downsized):

$$\mathrm{3HNO_{2(aq)} + 3H_2O_{(l)} + 6\mathit{e}^- + 14H^+_{(aq)} + Cr_2O_7^{2-}{}_{(aq)} \rightarrow 9H^+_{(aq)} + 3NO_3^-{}_{(aq)} + 6\mathit{e}^- + 2Cr^{3+}_{(aq)} + 7^4H_2O_{(l)}}$$

The electrons cancel out as well as 3 water molecules and 9 protons. This leaves the balanced net reaction of:

$$\mathrm{3HNO_2(aq) + 5H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 3NO^{3-}(aq) + 2Cr^{3+}(aq) + 4H_2O(l)}$$

Half-Equation Method to Balance Redox Reactions in Basic Aqueous Solutions

If the reaction is being balanced in a basic solution, the above steps are modified with the addition of one step between №3 and №4:

Add the appropriate number of OH^- to neutralize all H^+ and convert it into water molecules.

The equation can now be checked to make sure that it is balanced.

Bases dissolve into OH^- ions in solution; hence, balancing redox reactions in basic conditions requires OH^-. Follow the same steps as for acidic conditions. The only difference is adding hydroxide ions to each side of the net reaction to balance any H^+. OH^- and H^+ ions on the same side of a reaction should be added together to form water. Again, any common terms can be canceled out.

Balance the following redox reaction in basic conditions.

$$Ag(s) + Zn^{2+}(aq) \rightarrow Ag_2O(aq) + Zn(s)$$

Solution

Go through all the same steps as if it was in acidic conditions.

Step 1: Separate the half-reactions.

$$Ag(s) \rightarrow Ag_2O(aq)$$
$$Zn^{2+}(aq) \rightarrow Zn(s)$$

Step 2: Balance elements other than O and H.

$$2Ag(s) \rightarrow Ag_2O(aq)$$
$$Zn^{2+}(aq) \rightarrow Zn(s)$$

Step 3: Add H_2O to balance oxygen.

$$H_2O(l) + 2Ag(s) \rightarrow Ag_2O(aq)$$
$$Zn^{2+}(aq) \rightarrow Zn(s)$$

Step 4: Balance hydrogen with protons.

$$H_2O(l) + 2Ag(s) \rightarrow Ag_2O(aq) + 2H^+(aq)$$
$$Zn^{2+}(aq) \rightarrow Zn(s)$$

Step 5: Balance the charge with e^-.

$$H_2O(l) + 2Ag(s) \rightarrow Ag_2O(aq) + 2H^+(aq) + 2e^-$$
$$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$$

Step 6: Scale the reactions so that they have an equal number of electrons. In this case, it is already done.

Step 7: Add the reactions and cancel the electrons.

$$H_2O(l) + 2Ag(s) + Zn^{2+}(aq) \rightarrow Zn(s) + Ag_2O(aq) + 2H^+(aq)\cdot$$

Step 8: Add OH^- to balance H^+. There are 2 net protons in this equation, so add 2 OH^- ions to each side.

$$H_2O(l) + 2Ag(s) + Zn^{2+}(aq) + 2OH^-(aq) \rightarrow Zn(s) + Ag_2O(aq) + 2H^+(aq) + 2OH^-(aq)$$

Step 9: Combine OH^- ions and H^+ ions that are present on the same side to form water.

$$H_2O(l) + 2Ag(s) + Zn^{2+}(aq) + 2OH^-(aq) \longrightarrow Zn(s) + Ag_2O(aq) + 2H_2O(l)$$

Step 10: Cancel common terms.

$$2Ag(s) + Zn^{2+}(aq) + 2OH^-(aq) \rightarrow Zn(s) + Ag_2O(aq) + H_2O(l)$$

Neutral conditions

The first step to balance any redox reaction is to separate the reaction into half-reactions. The substance being reduced will have electrons as reactants, and the oxidized substance will have electrons as products. (Usually, all reactions are written as reduction reactions in half-reaction tables. To switch to oxidation, the whole equation is reversed, and the voltage is multiplied by 1.)

Sometimes it is necessary to determine which half-reaction will be oxidized and which will be reduced. In this case, whichever half-reaction has a higher reduction potential will be reduced and the other will oxidize.

Example 1: Balancing in a neutral solution

Balance the following reaction

$$Cu^{+}(aq) + Fe(s) \rightarrow Fe^{3+}(aq) + Cu(s)$$

Solution

Step 1: Separate the half-reactions. By searching for the reduction potential, one can find two separate reactions:

$$Cu^{+}(aq) + e^{-} \rightarrow Cu(s) \text{ and } Fe^{3+}(aq) + 3e^{-} \rightarrow Fe(s)$$

The copper reaction has a higher potential and thus is being reduced. Iron is being oxidized so the half-reaction should be flipped. This yields:

$$Cu^{+}(aq) + e^{-} \rightarrow Cu(s)$$

$$\text{and } Fe(s) \rightarrow Fe^{3+}(aq) + 3e^{-}$$

Step 2: Balance the electrons in the equations. In this case, the electrons are simply balanced by multiplying the entire $Cu^{+}(aq) + e^{-} \rightarrow Cu(s)$ half-reaction by 3 and leaving the other half-reaction as it is. This gives:

$$3Cu^{+}(aq) + 3e^{-} \rightarrow 3Cu(s) \text{ and } Fe(s) \rightarrow Fe^{3+}(aq) + 3e^{-}$$

Step 3: Adding the equations gives:

$$3Cu^{+}(aq) + 3e^{-} + Fe(s) \rightarrow 3Cu(s) + Fe^{3+}(aq) + 3e^{-}$$

The electrons cancel out and the balanced equation is left.

$$3Cu^{+}(aq) + Fe(s) \rightarrow 3Cu(s) + Fe^{3+}(aq)$$

10.2 Galvanic Cells

Galvanic cells, also known as voltaic cells, are devices that convert chemical energy into electrical energy through spontaneous redox reactions. These cells are fundamental in understanding the principles of electrochemistry and are the basis for batteries and many other electrochemical devices.

Components of a Galvanic Cell

1. *Electrodes:*

Anode: the electrode where oxidation occurs. It is the source of electrons and is considered the negative electrode in a galvanic cell.

Cathode: the electrode where reduction occurs. It is where the electrons flow to and is considered the positive electrode in a galvanic cell.

2. *Electrolyte:*

A solution that contains ions and allows for the transfer of ions to balance the charges as the reaction proceeds.

3. *Salt Bridge:*

A device, often a tube filled with a gel containing an inert electrolyte, maintains electrical neutrality by allowing the transfer of ions between the two half-cells.

4. *External Circuit:*

The pathway through which electrons flow from the anode to the cathode. It typically includes a wire and a load (such as a light bulb or a resistor).

Oxidation and reduction reactions cannot be carried out separately. They have to appear together in a chemical reaction. Thus oxidation and reduction reactions are often called **redox reactions**. In terms of redox reactions, a reducing agent and an oxidizing agent form a **redox couple** as they undergo the reaction:

Oxidant +ne^{-} → Reductant

Reducant → Oxidant + ne^{-}

An **oxidant** is an oxidizing reagent, and a **reductant** is a reducing agent. The *reductant* | *oxidant* or *oxidant* | *reductant*

Two members of the couple are the same element or compound but of different oxidation states.

Copper-Zinc Voltaic Cells (Figure 10.1).

As an introduction to electrochemistry, let us take a look at a simple voltaic cell or a galvanic cell.

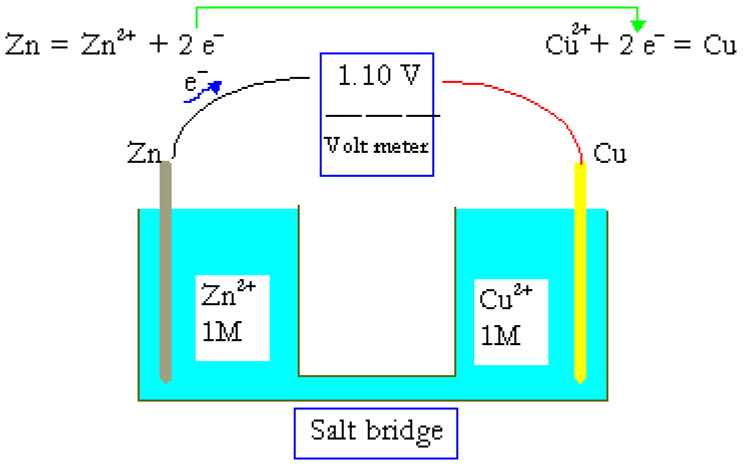


Figure 10.1 Copper-Zinc voltaic cells.

When a stick of zinc (Zn) is inserted in a salt solution, there is a tendency for Zn to lose electrons according to the reaction,

$$Zn \rightarrow Zn^{2+} + 2e^{-}$$

The arrangement of a Zn electrode in a solution containing Zn^{2+} ions is a **half cell**, which is usually represented by the notation:

$$Zn|Zn^{2+},$$

Zinc metal and Zn^{2+} ion form a **redox couple**, Zn^{2+} being the oxidant, and Zn the reductant. The same notation was used to designate a redox couple earlier.

Similarly, when a stick of copper (Cu) is inserted in a copper salt solution, there is also a tendency for Cu to lose electrons according to the reaction,

$$Cu \rightarrow Cu^{2+} + 2e^{-}$$

This is another half-cell or redox couple: Cu|Cu^{2+}.

However, the tendency for Zn to lose electrons is stronger than that for copper. When the two cells are connected by a **salt bridge** and an **electric conductor,** as shown, to form a closed circuit for electrons and ions to flow, copper ions (Cu^{2+}) gain electrons to become copper metal. The reaction and the redox couple are represented below,

$$Cu^{2+} + 2e^{-} \rightarrow Cu, \quad Cu^{2+}|Cu$$

This arrangement is called a **galvanic cell** or battery as shown here. In a text form, this battery is represented by,

$$Zn|Zn^{2+}||Cu^{2+}|Cu,$$

in which the two vertical lines (||) represent a salt bridge, and a single vertical line (|) represents the boundary between the two phases (metal and solution). Electrons flow through the electric conductors connecting the electrodes, and ions flow through the salt bridge. When

$$[Zn^{2+}]=[Cu^{2+}]=1.0\ M,$$

The voltage between the two terminals has been measured to be 1.100 V for this battery.

A battery is a package of one or more galvanic cells used for the production and storage of electric energy. The simplest battery consists of two half-cells, a reduction half-cell, and an oxidation half-cell.

Oxidation and reduction reactions - a review

The overall reaction of the galvanic cell is:

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$$

10.3 Standard reduction potentials

Standard reduction potentials are fundamental electrochemical properties that describe the tendency of a chemical species to gain electrons and be reduced. They are measured in volts (V) relative to the standard hydrogen electrode (SHE), which is assigned a potential of 0.00 V. These potentials are crucial for understanding and predicting the direction of redox reactions.

List the key concepts:

1. **Standard Conditions**:
   Temperature: 298 K (25°C)
   Pressure: 1 atm
   Concentration: 1 M for all solutions
2. **Standard Hydrogen Electrode (SHE)**:
   The SHE is used as the reference electrode with a defined potential of 0.00 V.
   Half-reaction: $2H^+(aq) + 2e^- \rightarrow H_2(g)$
3. **Reduction Potentials**:
   Listed as half-reactions with their corresponding potentials.
   Positive potential: indicates a greater tendency to gain electrons (be reduced).
   Negative potential: indicates a lesser tendency to gain electrons.

Example half-reactions and potential:

1. **Fluorine**: $F_2(g) + 2e^- \rightarrow 2F^-(aq)$ $E^\circ = +2.87\ V$
2. **Copper**: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $E^\circ = +0.34\ V$

Using Reduction Potentials

1. **Determining Spontaneity**: The more positive the reduction potential, the more likely the species will be reduced. To determine if a redox reaction is spontaneous, compare the reduction potentials of the two half-reactions. The species with the higher (more positive) reduction potential will be reduced, and the species with the lower (more negative) potential will be oxidized.

2. **Calculating Cell Potential**: For a galvanic cell, the standard cell potential (E^0_{cell}) is calculated by subtracting the anode potential (oxidation) from the cathode potential (reduction). $E^0_{cell} = E^0_{cathode} - E^0_{anode}$

3. **Example Calculation**: for a cell composed of copper and zinc:

Reduction half-reaction (cathode): $Cu^{2+}+2e^{-} \rightarrow Cu$; $E^{\circ} = +0.34$ V,

Oxidation half-reaction (anode): $Zn \rightarrow Zn^{2+}+2e^{-}$; $E^{\circ} = +0.76$ V (note: we take the absolute value for oxidation potential)

Cell potential: $E^{0}_{cell} = 0.34\ V-(-0.76\ V) = 1.10\ V$; $E^{0}_{cell} = 0.34V-(-0.76V)=1.10V$

Understanding standard reduction potentials allows you to predict the behavior of electrochemical cells, understand battery operation, and analyze redox reactions in various chemical processes.

10.4 The Nernst equation

The Nernst equation is a fundamental equation in electrochemistry that relates the reduction potential of a cell to the standard electrode potential, temperature, and activities (or concentrations) of the chemical species involved. It allows you to determine the cell potential under non-standard conditions.

The *Nernst equation* is derived from the Gibbs free energy **under standard conditions**.

$$E_o = E_o(\text{reduction}) - E_o(\text{oxidation}) \qquad (1)$$

ΔG is also related to E under general conditions (standard or not) via

$$\Delta G = -nFE \qquad (2)$$

with

- n is the number of electrons transferred in the reaction (from a balanced reaction),
- F is the Faraday constant (96,500 Kl/mol), and
- E is a potential difference.

Under standard conditions, equation (2) is then

$$\Delta G_o = -nFE_o \qquad (3)$$

Hence, when E^{o} is positive, the reaction is spontaneous, and when E^{o} is negative, the reaction is non-spontaneous. From thermodynamics, the Gibbs energy change under non-standard conditions can be related to the Gibbs energy change under standard conditions via

$$\Delta G = \Delta G_o + RT \ln Q$$

Substituting $\Delta G = -nFE$ into equation 4, we have:

$$-\quad nFE = -nFE_o + RT \ln Q \qquad (5)$$

Divide both sides of the equation above by −nF, we have the equation (6):

$$E = E^{o} - \frac{RT}{nF}\ln Q$$

Equation (6) can be rewritten in the form of log10 (7)

$$E = E^{o} - \frac{2.303RT}{nF}\log_{10} Q$$

At standard temperature T = 298 K, the 2.303/ RTF term equals 0.0592V, and equation (7) can be rewritten (8):

$$E = E^{o} - \frac{0.0592\,V}{n}\log_{10} Q$$

The equation above indicates that the electrical potential of a cell depends upon the reaction quotient Q of the reaction. As the redox reaction proceeds, reactants are consumed, and thus the concentration of reactants decreases. Conversely, the product concentration increases due to the increase in product formation. As this happens, cell potential gradually decreases until the reaction is at equilibrium, at which point $\Delta G = 0$. At equilibrium, the reaction quotient $Q = K_{eq}$. Also, at equilibrium, $\Delta G = 0$ and $\Delta G = -nFE$, so $E = 0$.

Therefore, substituting $Q = K_{eq}$ and $E = 0$ into the Nernst equation, we have (9):

$$0 = E^o - \frac{RT}{nF}\ln K_{eq}$$

At room temperature, equation (9) simplifies into (notice natural log was converted to log base 10):

$$0 = E^o - \frac{0.0592\,V}{n}\log_{10} K_{eq}$$

This can be rearranged into:

$$\log K_{eq} = \frac{nE^o}{0.0592\,V}$$

The Equation above indicates that the equilibrium constant K_{eq}, is proportional to the standard potential of the reaction. Specifically, when:

- $K>1$, $E_o>0$, reaction favors product formation.
- $K<1$, $E_o<0$, reaction favors reactants formation

10.5 Electrolysis

Electrolysis is a chemical process that uses electricity to cause a non-spontaneous reaction. It is commonly used to decompose chemical compounds, especially water and various salts, by directing an electric current through them. The free-moving ions in electrolytes are attracted to the oppositely charged *electrodes*, which connect to the direct current (DC) supply.

Here are some key points about electrolysis:

1. **Basic Principle**:

1. Electrolysis occurs in an electrolytic cell.
2. It involves an electrolyte (a substance that produces an electrically conductive solution when dissolved), an anode (positive electrode), and a cathode (negative electrode).
3. When an electric current is passed through the electrolyte, ions in the solution migrate toward the electrodes, where redox reactions occur.

2. **Electrodes**:

1. The anode attracts negatively charged ions (anions), where oxidation reactions occur.
2. The cathode attracts positively charged ions (cations), where reduction reactions occur (Figure 10.2).

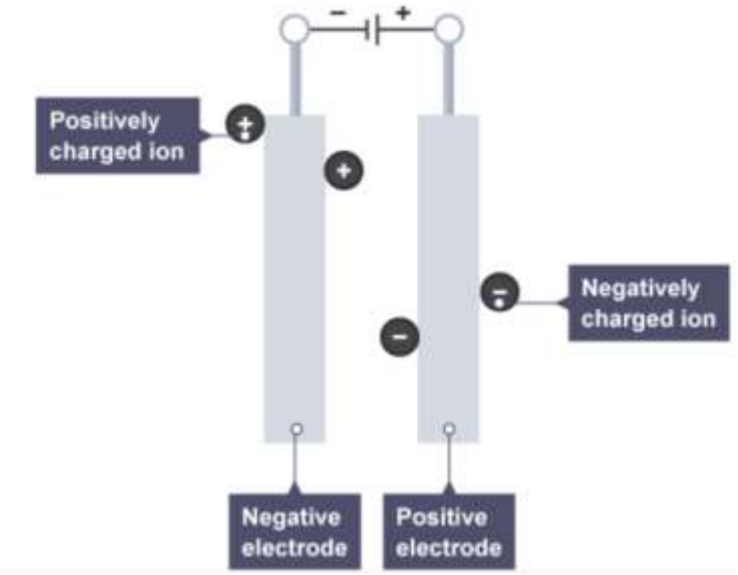


Figure 10.2: Ions move towards their oppositely charged electrode.

3. Important Factors:

1. Voltage: The minimum voltage needed to drive the electrolysis must be greater than the cell potential of the redox reactions.
2. Electrolyte concentration: affects the efficiency and rate of the reactions.
3. Temperature: Higher temperatures can increase reaction rates.

Electrolysis is a vital process in various industrial applications, particularly in the fields of chemistry, manufacturing, and energy production.

Electrolysis of molten salts.

Electrolytes are *ionic compounds* that are: in the *molten* state (heated so they become liquids), or *dissolved* in water.

Under these conditions, the *ions* in electrolytes are free to move within the liquid or solution.

Electrolysis is a process in which electrical energy, from a direct current supply, breaks down electrolytes. The free-moving ions in electrolytes are attracted to the oppositely charged *electrodes*, which connect to a direct current supply.

For example, predict the products of the electrolysis of molten calcium chloride.

Positively charged calcium ions move to the negative electrode. Here, they gain electrons to form calcium atoms, so calcium is formed at the negative electrode.

Negatively charged chloride ions move to the positive electrode. Here, they lose electrons to form chlorine atoms. The atoms join up in pairs to form Cl_2 molecules, so chlorine gas is formed at the positive electrode.

Key fact

During the electrolysis of molten salts, a metal forms at the cathode and a non-metal forms at the anode.

Electrolysis of solutions. Electrolysis of acidified water.

Water is a poor conductor of electricity, but it does contain some hydrogen ions, H^+, and hydroxide ions, OH^-. These ions are formed when a small proportion of water molecules *naturally* dissociate. If water is acidified with a little dilute sulfuric acid:

- H^+ ions are attracted to the *cathode*, gain *electrons*, and form hydrogen gas
- OH^- ions are attracted to the *anode*, lose electrons, and form oxygen gas

The overall balanced equation *for the process is:*

$2H_2O (l) \rightarrow 2H_2(g) + O_2(g)$

The volume of hydrogen given off is twice the volume of oxygen given off.

Electrolysis of dissolved ionic compounds

An electrolyte formed by dissolving an *ionic compound* contains:

- hydrogen ions from the water, and positive ions from the compound
- hydroxide ions from the water, and negative ions from the compound

The ions compete at each electrode to gain or lose electrons.

At the cathode

Whether hydrogen or metal is produced at the cathode depends on the position of the metal in the metal reactivity series:

- the metal is produced at the cathode if it is less reactive than hydrogen
- hydrogen is produced at the cathode if the metal is more reactive than hydrogen (Figure 10.3).

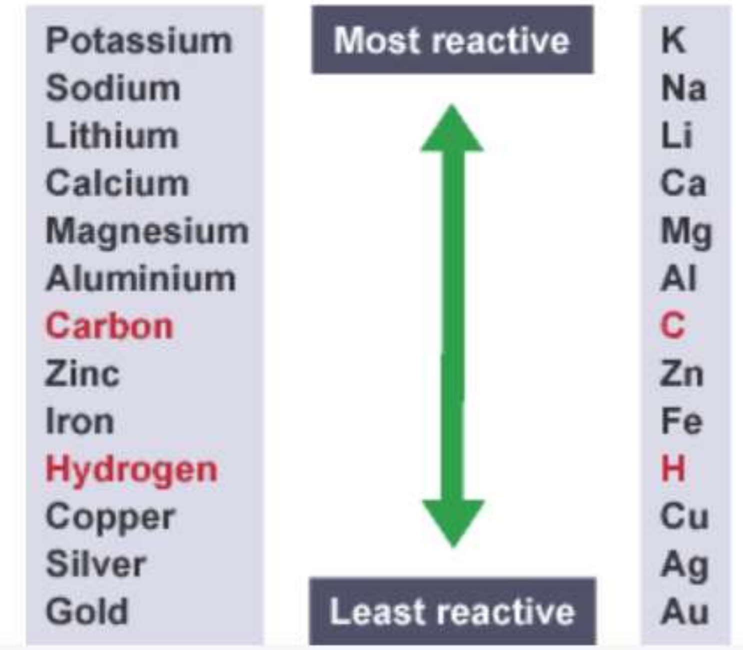


Figure 10.3 The reactivity series of metals - carbon and hydrogen are non-metals, shown for comparison.

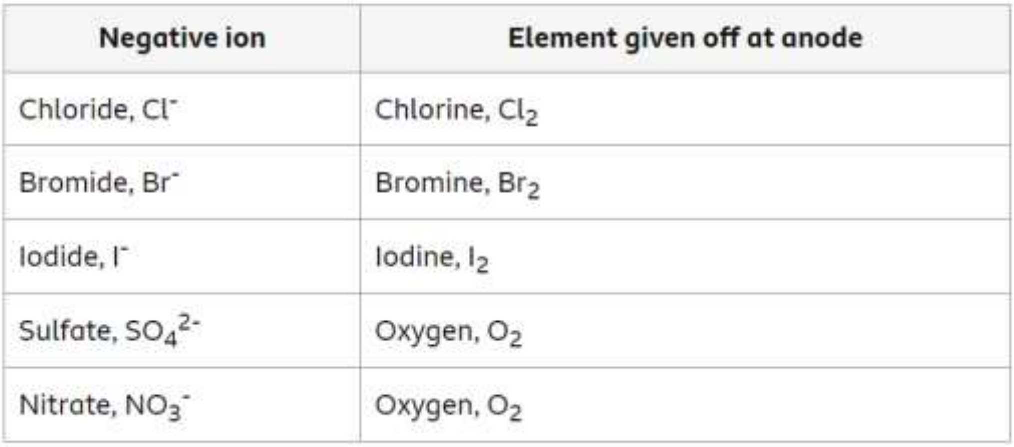
At the anode

Oxygen is produced (from hydroxide ions) unless halide ions (chloride, bromide, or iodide ions) are present. In that case, the negatively charged halide ions lose electrons and form the corresponding halogen (chlorine, bromine, or iodine).

The table summarises the product formed at the anode during the electrolysis of different electrolytes in solution (Table 10.1).

Table 10.1

An example of some ions oxidizing at the anode.



Negative ion	Element given off at anode
Chloride, Cl^-	Chlorine, Cl_2
Bromide, Br^-	Bromine, Br_2
Iodide, I^-	Iodine, I_2
Sulfate, SO_4^{2-}	Oxygen, O_2
Nitrate, NO_3^-	Oxygen, O_2

Identifying the products

Any gases produced can be collected in the test tubes. They need to be stopped and tested later. Gas tests include:

1. The hydrogen-lighted splint goes out with a squeaky pop
2. Oxygen - a glowing splint relights
3. chlorine - damp blue litmus paper turns red and is then bleached white

The electrodes need to be examined carefully each time to see if metal has been deposited on them.

Hazards, risks, and precautions.

It is vital to identify hazards, the possible harm they can cause, and suitable precautions. The table below shows how to do this. It does not include all possible hazards (Table 10.2).

Table 10.2

The examples of hazardous substances and processes of electrolysis.

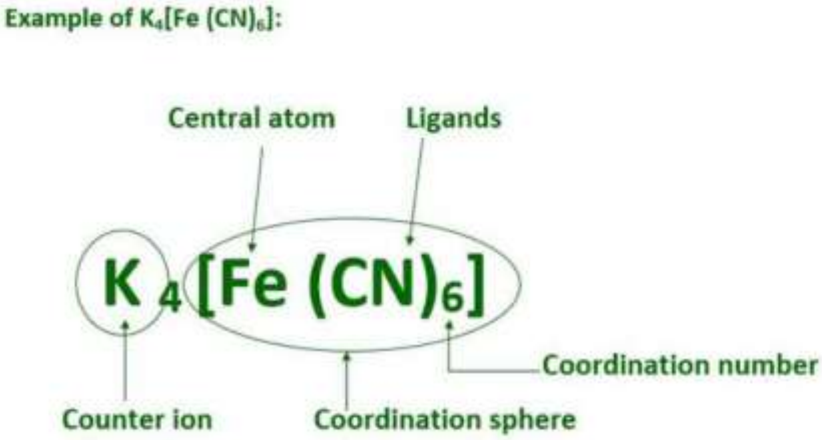
Hazard	Harm	Precaution
Copper sulfate solution	Causes skin irritation	Wear gloves
Copper sulfate solution	Causes serious eye irritation	Wear eye protection
dc electricity supply	Electric shock	Make sure electrodes do not touch; make sure that electricity supply is switched off before handling apparatus

Link to Learning

Click here: http://surl.li/mjygoj to view the Half reaction method, balancing redox reactions in basic & acidic solutions.

CHAPTER 11

COORDINATION COMPLEX



Chapter Outline

11.1 The general imagination about the complex nature
11.2 Types of ligands
11.3 Isomerism in coordination compounds
11.4 Dissociation of complex compounds

Coordination chemistry emerged from the work of Alfred Werner, a Swiss chemist who examined different compounds composed of cobalt (III) chloride and ammonia. Upon the addition of hydrochloric acid, Werner observed that ammonia could not be completely removed. He then proposed that the ammonia must be bound more tightly to the central cobalt ion. However, when aqueous silver nitrate was added, one of the products formed was solid silver chloride. The amount of silver chloride formed was related to the number of ammonia molecules bound to the cobalt (III) chloride. For example, when silver nitrate was added to $CoCl_3\cdot 6NH_3$, all three chlorides were converted to silver chloride. However, when silver nitrate was added to $CoCl_3\cdot 5NH_3$, only 2 of the 3 chlorides formed silver chloride. When $CoCl_3\cdot 4NH_3$ was treated with silver nitrate, one of the three chlorides precipitated as silver chloride.

The resulting observations suggested the formation of **complex coordination compounds**. In the **inner coordination sphere**, which is also referred to in some texts as the **first sphere**, ligands are directly bound to the central metal. In the **outer coordination sphere**, sometimes referred to as the **second sphere**, other ions are attached to the complex ion. Werner was awarded the Nobel Prize in 1913 for his coordination theory. The following table is a summary of Werner's observations:

Initial compound	Resulting compounds upon adding $AgNO_3$
$CoCl_3 \cdot 6NH_3$	$[Co(NH_3)_6]^{3+}(Cl^-)_3$
$CoCl_3 \cdot 5NH_3$	$[Co(NH_3)_5Cl]^{2+}(Cl^-)_2$
$CoCl_3 \cdot 4NH_3$	$[Co(NH_3)_4Cl_2]^{+}(Cl^-)$
$CoCl_3 \cdot 3NH_3$	$[Co(NH_3)_3Cl_3]$

As the table above shows, the three chloride ions countered the complex ion $[Co(NH_3)_6]^{3+}$. The multi-level binding of coordination complexes plays an important role in determining the dissociation of these complexes in aqueous solution. For example, $[Co(NH_3)_5Cl]Cl_2$ dissociates into three ions while $[Co(NH_3)_4Cl_2]Cl$ dissociates into two ions. Werner measured the electrical conductivity and thus the dissociation properties of the complex compounds by applying a current through the aqueous solutions of the resulting complex compounds. The results confirmed his hypothesis of the formation of complex compounds. It is important to note that the above compounds have a coordination number of 6, a common coordination number for many inorganic complexes. Coordination numbers for complex compounds typically range from 1 to 16.

11.1 The general imagination about the complex nature

A ***coordination complex*** is the product of a Lewis acid-base reaction in which neutral molecules or anions (called ***ligands***) bond to a central metal atom (or ion) by ***coordinate covalent bonds***.

Basic definitions and concepts:

- **Complex compounds** consist of a central metal atom coordinated with ligands.
- **Ligands** are molecules or ions that bind to the central metal atom through a donor-acceptor bond.
- **Coordination number** refers to the number of ligands bound to the central metal atom.
- **The coordination sphere** is the region around the central metal atom where the ligands are located.
- **A complex ion** is a charged complex composed of a central metal atom and ligands.
- Metal atoms/ions are Lewis acids - they can accept pairs of electrons from Lewis bases.
- Within a ligand, the atom directly bonded to the metal atom/ion is called the ***donor atom***.

Types of coordination complexes

- **Cationic complexes:** In this coordination, the sphere is a cation. For example, $[Co(NH_3)_6]Cl_3$.
- **Anionic complexes:** In this coordination, the sphere is an anion. For example, $K_4[FeCl_6]$
- **Neutral Complexes:** In this coordination, the sphere is neither a cation nor an anion. For example, $[Ni(CO)_4]$.
- **Homoleptic complex:** The complex consists of a similar type of ligand. For example, $K_4[Fe(CN)_6]$.
- **Heteroleptic complexes:** These consist of different types of ligands. For example, $[Co(NH_3)_5Cl]SO_4$.
- **Mononuclear complexes:** The sphere has a single transition metal ion in this coordination. For example, $K_4[Fe(CN)_6]$.

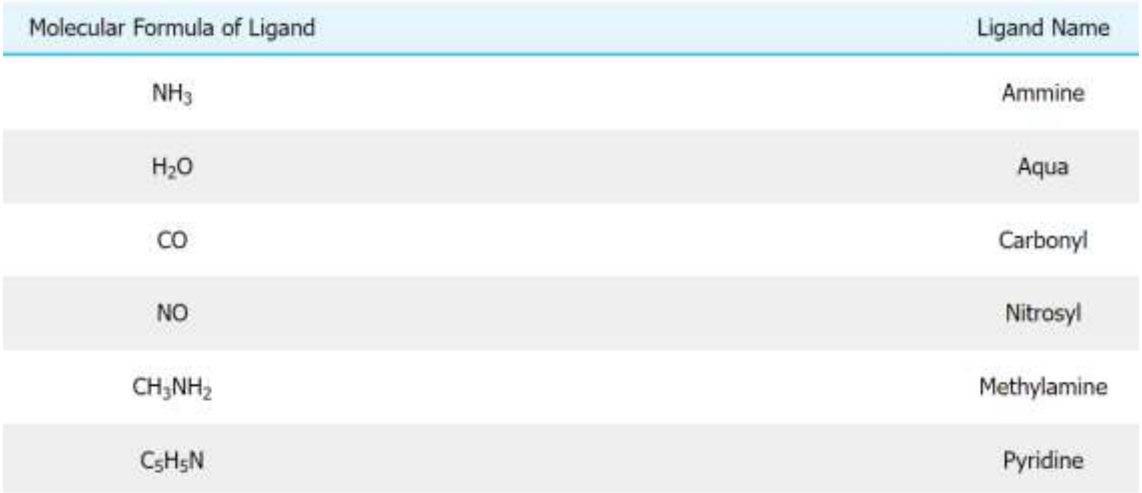
- **Polynuclear complexes:** More than one transition metal ion is present.

IUPAC nomenclature of coordination compounds

Rules for naming coordination compounds

The standard rules that must be followed in the nomenclature of coordination compounds are explained below.

1. The ligands are always written before the central metal ion in the name of complex coordination complexes.
2. When the coordination center is bound to more than one ligand, the names of the ligands are written in alphabetical order, which is not affected by the numerical prefixes that must be applied to the ligands.
3. When there are many monodentate ligands present in the coordination compound, the prefixes that give insight into the number of ligands are of the type: di-, tri-, tetra-, and so on.
4. When there are many polydentate ligands attached to the central metal ion, the prefixes are of the form bis-, tris-, and so on.
5. The names of the anions present in a coordination compound must end with the letter ‘o’, which generally replaces the letter ‘e’. Therefore, the sulfate anion must be written as ‘sulfato’, and the chloride anion must be written as ‘chloro’ (Table 11.1). Anions ending with "-ite" and "-ate" are replaced with endings "-ito" and "-ato" respectively (e.g., Nitrite → Nitrito, Nitrate → Nitrato).
6. The following neutral ligands are assigned specific names in coordination compounds: NH_3 (ammine), H_2O (aqua or aquo), CO (carbonyl), and NO (nitrosyl):



Molecular Formula of Ligand	Ligand Name
NH_3	Ammine
H_2O	Aqua
CO	Carbonyl
NO	Nitrosyl
CH_3NH_2	Methylamine
C_5H_5N	Pyridine

7. After the ligands are named, the name of the central metal atom is written. If the complex has an anionic charge associated with it, the suffix ‘-ate’ is applied.
8. When writing the name of the central metallic atom in an anionic complex, priority is given to the Latin name of the metal if it exists (except mercury).
9. The oxidation state of the central metal atom/ion must be specified with the help of Roman numerals that are enclosed in a set of parentheses.
10. If the coordination compound is accompanied by a counter ion, the cationic entity must be written before the anionic entity.

Table 11.1

Anionic monodentate ligands.

Molecular Formula	Ligand Name	Molecular Formula	Ligand Name
F^-	Fluoro	OH^-	Hydroxo
Cl^-	Chloro	SO_4^{2-}	Sulfato
Br^-	Bromo	$S_2O_3^{2-}$	Thiosulfato
I^-	Iodo	NO_2^-	Nitrito-N-; Nitro
O^{2-}	Oxo	ONO^-	Nitrito-O-; Nitrito
CN^-	Cyano	SCN^-	Thiocyanato-S-; Thiocyanato
NC^-	Isocyano	NCS^-	Thiocyanato-N-; Isothiocyanato

The cations are often called first, followed by the **anions**. The name of the metal atom is then written in Roman numerals, followed by its oxidation state**.** Finally, the anion is given a name.

Examples of naming coordination compounds

Some examples of the nomenclature of coordination compounds can be found below.

- $K_4[Fe(CN)_6]$: Potassium hexacyanide ferrate (II)
- $[Ni(CN)_4]^{-2}$: Tetra cyano nickelate (II) ion.
- $[Zn(OH)_4]^{-2}$: Tetrahydroxide zincate (II) ion.
- $[Ni(CO)_4]$: Tetra carbonyl Nickel (o).
- $[Cu(NH_3)_4]SO_4$ Tetra ammine copper (II) sulphate

Properties of complex compounds:

- **Color:** Many complex compounds exhibit distinctive colors due to the presence of d-orbitals in the central metal atom.
- **Magnetic properties:** The magnetic properties of complex compounds depend on the number of unpaired electrons in the d-orbitals of the central metal atom.
- **Stability:** The stability of complex compounds is influenced by factors such as the nature of the metal ion, the type of ligands, and the reaction conditions.
- **Reactivity:** Complex compounds often exhibit unique reactivity due to the presence of the central metal atom and the ligands.

11.2. Types of ligands

Based on the nature of the bond between the ligand and the central atom, ligands are classified as follows:

- Anionic ligands: CN^-, Br^-, Cl^-
- Cationic ligands: NO^+
- Neutral ligands: CO, H_2O, NH_3

Ligands can be further classified as:

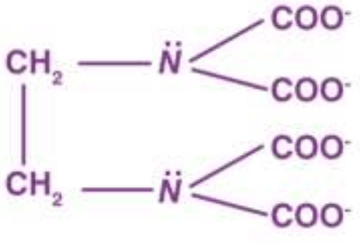
Unidentate ligands

The ligands that only have one atom that can bind to the coordination center are called unidentate ligands. Ammonia (NH3) is a great example of an unidentate ligand. Some common unidentate are Cl^-, H_2O, etc.

Bidentate Ligands

Ligands that can bind to the central atom via two separate donor atoms, such as ethane-1,2-diamine, are referred to as bidentate ligands.

Oxalate ion is a bidentate, as it can bond through two atoms to the central atom in a coordination compound, and ethane-1, 2-diamine:

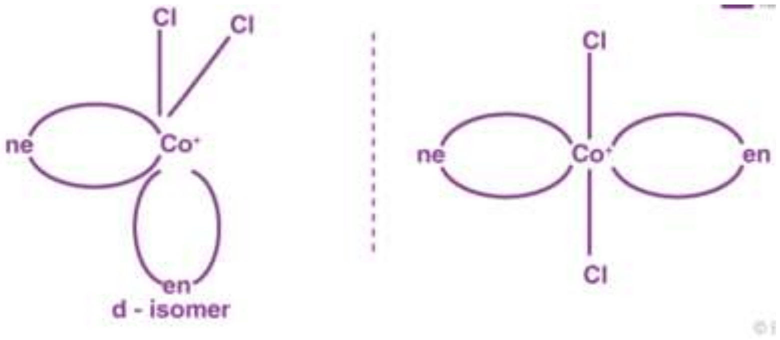


- **Monodentate** ligands bind to the central metal atom with only one atom. Examples include water (H_2O), ammonia (NH_3), and chloride ions (Cl^-).
- **Bidentate** ligands bind to the central metal atom with two atoms. Examples include ethylenediamine (en) and oxalate ion ($C_2O_4^{2-}$).
- **Polydentate** ligands bind to the central metal atom with three or more atoms. Examples include ethylenediaminetetraacetic acid (EDTA).

11.3 Isomerism in coordination compounds

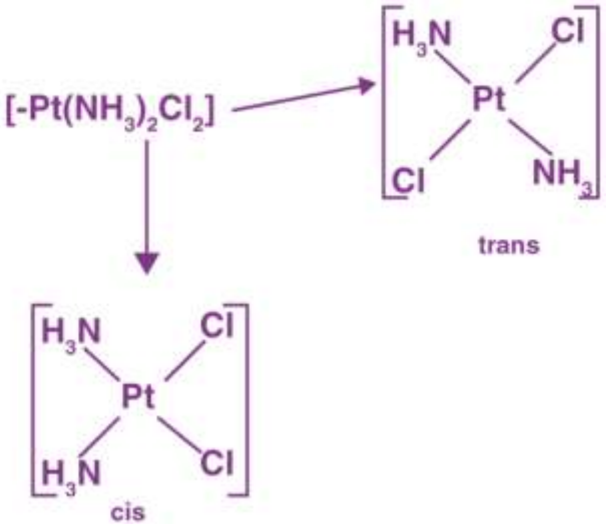
Two or more compounds that have the same chemical formula but a different arrangement of atoms are known as isomers. Due to this difference in the arrangement of atoms, coordination compounds predominantly exhibit two types of isomerism, namely, **stereoisomerism and structural isomerism**.

Example of Optical Isomerism:

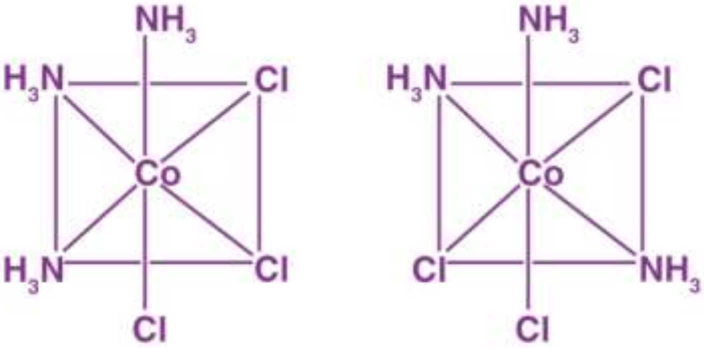


Geometrical Isomerism

Geometrical isomerism is observed in heteroleptic complexes (complexes with more than one type of ligand) due to different possible geometric arrangements of the ligands. This behavior is mainly observed in coordination compounds having coordination numbers equal to 4 and 6. Geometrical isomerism of complexes with coordination number 4:



For example, $[Co(NH_3)_4Cl_2]^+$



Coordination isomerism

In coordination isomerism, the interchange of ligands between cationic and anionic entities of different metal ions present in coordination compounds takes place.

For example, $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$.

Ionisation Isomerism

Ionisation isomerism arises when the counter ion in a complex salt which is a potential ligand, replaces the ligand.

For example, $[Co(NH_3)_5(SO_4)]Br$ and $[Co(NH_3)_5Br]SO_4$.

Solvate isomerism

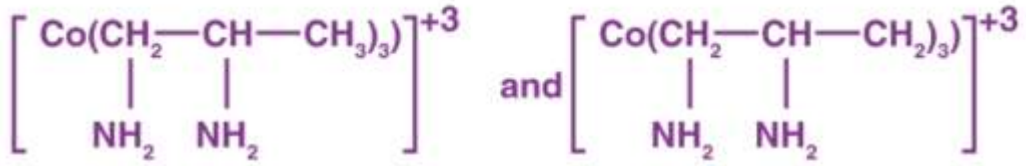
Solvate isomers are a special case of ionization in which compounds differ depending on the number of solvent molecules directly bonded to the metal ion.

For example,

- $[Co(H_2O)_6]Cl_3$
- $[Co(H_2O)_5Cl]Cl_2 \cdot H_2O$
- $[Co(H_2O)_4Cl_2]Cl \cdot 2H_2O$
- $[Co(H_2O)_3Cl_3] \cdot 3H_2O$

Ligand isomerism

In this type, ligands show isomerism. For example,



A characteristic feature of this class of reactions is the sensitivity of the rate of substitution of a given ligand to the nature of the ligand in the *transposition*. The *trans* ligand activates a ligand for replacement as follows, in decreasing order:

$$CO, CN^-, C_2H_4 > PR_3, H^- > NO_2^-, I^-, SCN^- > Br^-, Cl^- > NH_3, H_2O.$$

Complex compounds are fascinating and diverse molecules that play a vital role in various scientific fields. Their unique properties and applications make them essential in modern chemistry, biology, medicine, and beyond.

11.4 Dissociation of complex compounds

Dissociation refers to the process where a complex compound breaks down into simpler ions or molecules when dissolved in a solvent, usually water. This can occur in two ways:

- **Stepwise Dissociation:** The complex loses ligands one at a time in a series of steps.
- **Complete Dissociation:** The complex dissociates entirely in one step.

Example 1: Dissociation of $[Cu(NH_3)_4]^{2+}$ Stepwise dissociation can be described by the following equilibrium steps:

1. $Cu(NH_3)_4]^{2+} \rightleftharpoons [Cu(NH_3)_3]^{2+} + NH_3$
2. $[Cu(NH_3)_3]^{2+} \rightleftharpoons [Cu(NH_3)_2]^{2+} + NH_3$
3. $[Cu(NH_3)_2]^{2+} \rightleftharpoons [Cu(NH_3)]^{2+} + NH_3$
4. $[Cu(NH_3)]^{2+} \rightleftharpoons Cu^{2+} + NH_3$

$$K_d = [Cu^{2+}]^* [NH_3] / [[Cu(NH_3)]^{2+}]$$

Factors Affecting Dissociation**:** several factors influence the dissociation of complex compounds:

- *pH of the solution*: Certain complexes are more stable at specific pH levels.
- *Concentration of the complex*: Higher concentrations can shift the equilibrium, affecting dissociation.
- *Nature of the solvent*: Solvents with different polarities can stabilize or destabilize complexes.
- *Temperature*: Higher temperatures generally increase the dissociation rate.

The instability constant (K_d) is a quantitative measure of the tendency of a complex compound to dissociate into its components in a solution. Essentially, it is the equilibrium constant for the dissociation reaction of a complex ion into its central metal ion and ligands.

Relationship with stability constant: an inverse relationship exists between the instability constant (K_d) and the stability constant (K_f). The stability constant measures the formation tendency of a complex, whereas the instability constant measures its dissociation tendency.

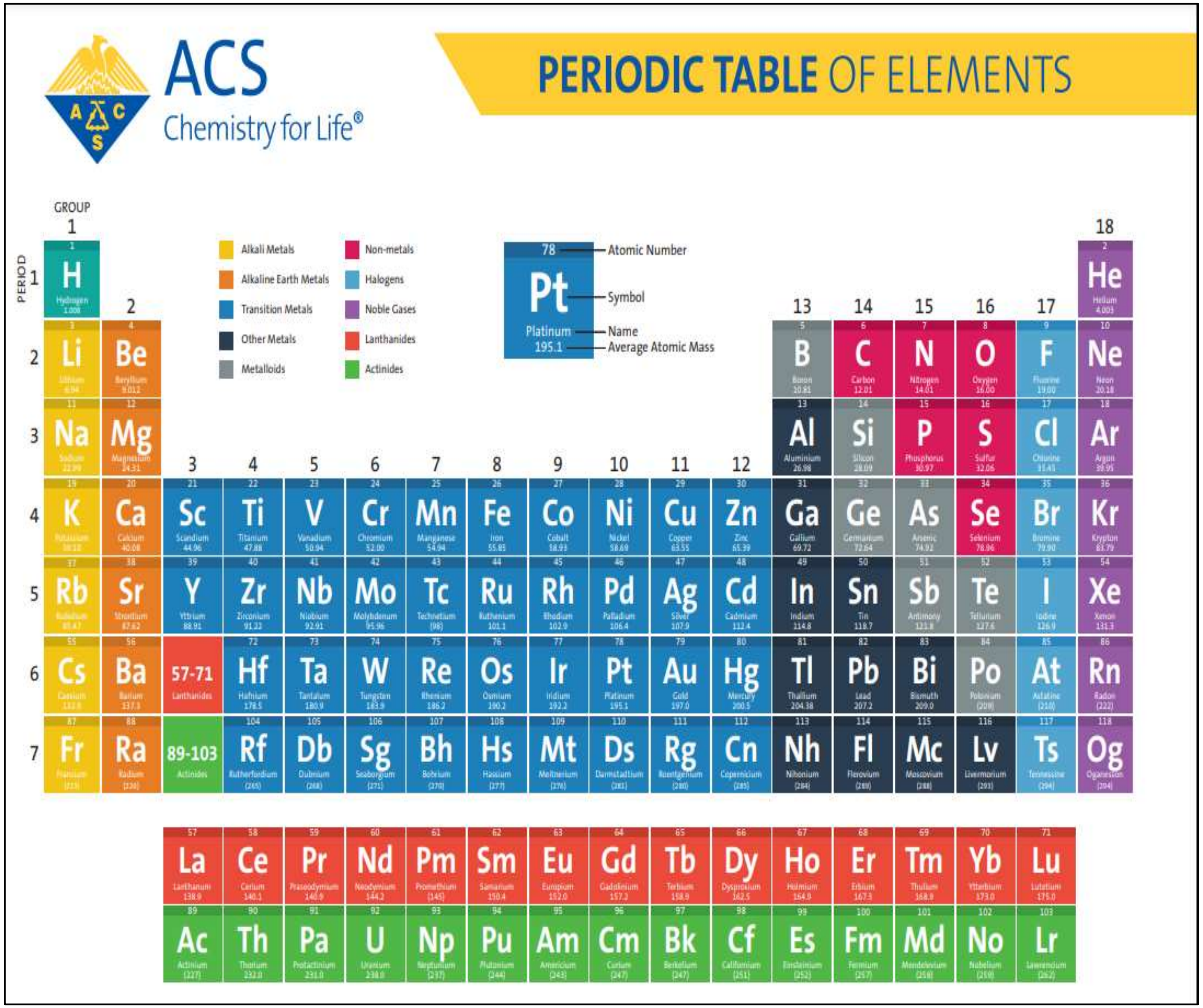
A high K_f value signifies a stable complex, while a lower K_f indicates a dissociation tendency.

Conclusion: The dissociation of complex compounds is a fundamental aspect of coordination chemistry. By understanding the factors and principles governing this process, chemists can predict the behavior of complex compounds in various environments and design new compounds with desired properties.

Link to Learning

Click here: http://surl.li/rvtstj to view the Crystal field theory.
http://surl.li/zjenpz to view the Colour of complex ions.

A



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PERIODIC TABLE OF ELEMENTS

- 🟨 Alkali Metals
- 🟧 Alkaline Earth Metals
- 🟦 Transition Metals
- ⬛ Other Metals
- ⬜ Metalloids
- 🟥 Non-metals
- 🟦 Halogens
- 🟪 Noble Gases
- 🟥 Lanthanides
- 🟩 Actinides

78 — Atomic Number
Pt — Symbol
Platinum — Name
195.1 — Average Atomic Mass

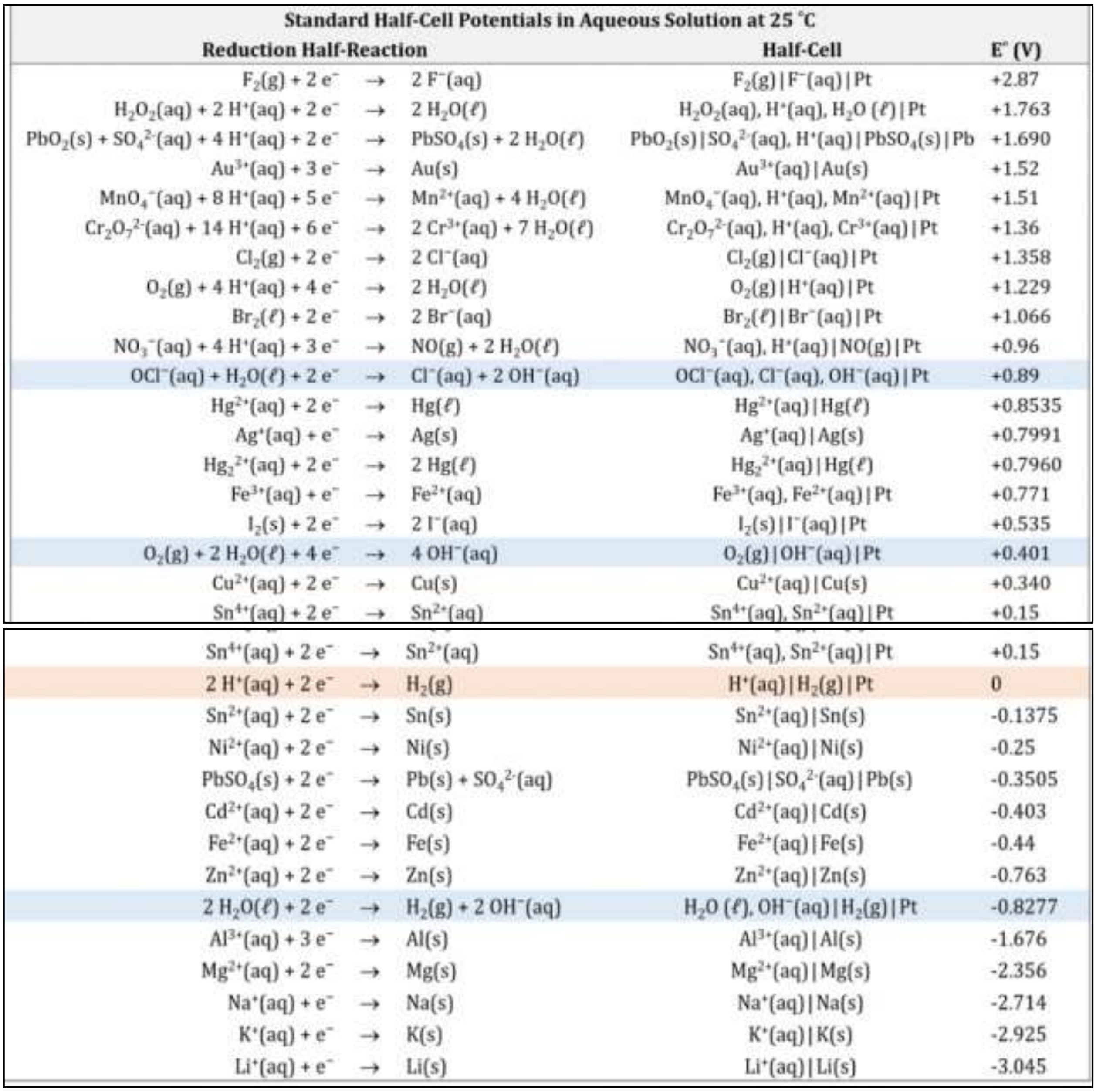
PERIOD \ GROUP	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 **H** Hydrogen 1.008																	2 **He** Helium 4.003
2	3 **Li** Lithium 6.94	4 **Be** Beryllium 9.012											5 **B** Boron 10.81	6 **C** Carbon 12.01	7 **N** Nitrogen 14.01	8 **O** Oxygen 16.00	9 **F** Fluorine 19.00	10 **Ne** Neon 20.18
3	11 **Na** Sodium 22.99	12 **Mg** Magnesium 24.31											13 **Al** Aluminium 26.98	14 **Si** Silicon 28.09	15 **P** Phosphorus 30.97	16 **S** Sulfur 32.06	17 **Cl** Chlorine 35.45	18 **Ar** Argon 39.95
4	19 **K** Potassium 39.10	20 **Ca** Calcium 40.08	21 **Sc** Scandium 44.96	22 **Ti** Titanium 47.88	23 **V** Vanadium 50.94	24 **Cr** Chromium 52.00	25 **Mn** Manganese 54.94	26 **Fe** Iron 55.85	27 **Co** Cobalt 58.93	28 **Ni** Nickel 58.69	29 **Cu** Copper 63.55	30 **Zn** Zinc 65.39	31 **Ga** Gallium 69.72	32 **Ge** Germanium 72.64	33 **As** Arsenic 74.92	34 **Se** Selenium 78.96	35 **Br** Bromine 79.90	36 **Kr** Krypton 83.79
5	37 **Rb** Rubidium 85.47	38 **Sr** Strontium 87.62	39 **Y** Yttrium 88.91	40 **Zr** Zirconium 91.22	41 **Nb** Niobium 92.91	42 **Mo** Molybdenum 95.96	43 **Tc** Technetium (98)	44 **Ru** Ruthenium 101.1	45 **Rh** Rhodium 102.9	46 **Pd** Palladium 106.4	47 **Ag** Silver 107.9	48 **Cd** Cadmium 112.4	49 **In** Indium 114.8	50 **Sn** Tin 118.7	51 **Sb** Antimony 121.8	52 **Te** Tellurium 127.6	53 **I** Iodine 126.9	54 **Xe** Xenon 131.3
6	55 **Cs** Caesium 132.9	56 **Ba** Barium 137.3	**57-71** Lanthanides	72 **Hf** Hafnium 178.5	73 **Ta** Tantalum 180.9	74 **W** Tungsten 183.9	75 **Re** Rhenium 186.2	76 **Os** Osmium 190.2	77 **Ir** Iridium 192.2	78 **Pt** Platinum 195.1	79 **Au** Gold 197.0	80 **Hg** Mercury 200.5	81 **Tl** Thallium 204.38	82 **Pb** Lead 207.2	83 **Bi** Bismuth 209.0	84 **Po** Polonium (209)	85 **At** Astatine (210)	86 **Rn** Radon (222)
7	87 **Fr** Francium (223)	88 **Ra** Radium (226)	**89-103** Actinides	104 **Rf** Rutherfordium (265)	105 **Db** Dubnium (268)	106 **Sg** Seaborgium (271)	107 **Bh** Bohrium (270)	108 **Hs** Hassium (277)	109 **Mt** Meitnerium (276)	110 **Ds** Darmstadtium (281)	111 **Rg** Roentgenium (280)	112 **Cn** Copernicium (285)	113 **Nh** Nihonium (284)	114 **Fl** Flerovium (289)	115 **Mc** Moscovium (288)	116 **Lv** Livermorium (293)	117 **Ts** Tennessine (294)	118 **Og** Oganesson (294)

57 **La** Lanthanum 138.9	58 **Ce** Cerium 140.1	59 **Pr** Praseodymium 140.9	60 **Nd** Neodymium 144.2	61 **Pm** Promethium (145)	62 **Sm** Samarium 150.4	63 **Eu** Europium 152.0	64 **Gd** Gadolinium 157.2	65 **Tb** Terbium 158.9	66 **Dy** Dysprosium 162.5	67 **Ho** Holmium 164.9	68 **Er** Erbium 167.3	69 **Tm** Thulium 168.9	70 **Yb** Ytterbium 173.0	71 **Lu** Lutetium 175.0
89 **Ac** Actinium (227)	90 **Th** Thorium 232.0	91 **Pa** Protactinium 231.0	92 **U** Uranium 238.0	93 **Np** Neptunium (237)	94 **Pu** Plutonium (244)	95 **Am** Americium (243)	96 **Cm** Curium (247)	97 **Bk** Berkelium (247)	98 **Cf** Californium (251)	99 **Es** Einsteinium (252)	100 **Fm** Fermium (257)	101 **Md** Mendelevium (258)	102 **No** Nobelium (259)	103 **Lr** Lawrencium (262)

Table of Solubility Products

Compound	Formula	Temperature	K_{sp}
Aluminium Hydroxide anhydrous	$Al(OH)_3$	20°C	1.9×10^{-33}
Aluminium Hydroxide anhydrous	$Al(OH)_3$	25°C	3×10^{-34}
Aluminium Hydroxide trihydrate	$Al(OH)_3$	20°C	4×10^{-13}
Aluminium Hydroxide trihydrate	$Al(OH)_3$	25°C	3.7×10^{-13}
Aluminium Phosphate	$AlPO_4$	25°C	9.84×10^{-21}
Barium Bromate	$Ba(BrO_3)_2$	25°C	2.43×10^{-4}
Barium Carbonate	$BaCO_3$	16°C	7×10^{-9}
Barium Carbonate	$BaCO_3$	25°C	8.1×10^{-9}
Barium Chromate	$BaCrO_4$	28°C	2.4×10^{-10}
Barium Fluoride	BaF_2	25.8°C	1.73×10^{-6}
Barium Iodate dihydrate	$Ba(IO_3)_2$	25°C	6.5×10^{-10}
Barium Oxalate dihydrate	BaC_2O_4	18°C	1.2×10^{-7}
Barium Sulfate	$BaSO_4$	18°C	0.87×10^{-10}
Barium Sulfate	$BaSO_4$	25°C	1.08×10^{-10}
Barium Sulfate	$BaSO_4$	50°C	1.98×10^{-10}
Beryllium Hydroxide	$Be(OH)_2$	25°C	6.92×10^{-22}
Cadmium Carbonate	$CdCO_3$	25°C	1.0×10^{-12}
Cadmium Hydroxide	$Cd(OH)_2$	25°C	7.2×10^{-15}
Cadmium Oxalate trihydrate	CdC_2O_4	18°C	1.53×10^{-8}
Cadmium Phosphate	$Cd_3(PO_4)_2$	25°C	2.53×10^{-33}
Cadmium sulfide	CdS	18°C	3.6×10^{-29}
Calcium Carbonate calcite	$CaCO_3$	15°C	0.99×10^{-8}
Calcium Carbonate calcite	$CaCO_3$	25°C	0.87×10^{-8}
Calcium Carbonate calcite	$CaCO_3$	18-25°C	4.8×10^{-9}
Calcium Chromate	$CaCrO_4$	18°C	2.3×10^{-2}
Calcium Fluoride	CaF_2	18°C	3.4×10^{-11}
Calcium Fluoride	CaF_2	25°C	3.95×10^{-11}
Calcium Hydroxide	$Ca(OH)_2$	18°C-25°C	8×10^{-6}
Calcium Hydroxide	$Ca(OH)_2$	25°C	5.02×10^{-6}
Calcium Iodate hexahydrate	$Ca(IO_3)_2$	18°C	6.44×10^{-7}
Calcium Oxalate monohydrate	CaC_2O4	18°C	1.78×10^{-9}
Calcium Oxalate monohydrate	CaC_2O4	25°C	2.57×10^{-9}
Calcium Phosphate tribasic	$Ca_3(PO_4)_2$	25°C	2.07×10^{-33}
Calcium Sulfate	$CaSO_4$	10°C	6.1×10^{-5}

C



Standard Half-Cell Potentials in Aqueous Solution at 25 °C

Reduction Half-Reaction			Half-Cell	E° (V)
$F_2(g) + 2\,e^-$	→	$2\,F^-(aq)$	$F_2(g)\,\vert\,F^-(aq)\,\vert\,Pt$	+2.87
$H_2O_2(aq) + 2\,H^+(aq) + 2\,e^-$	→	$2\,H_2O(\ell)$	$H_2O_2(aq), H^+(aq), H_2O\,(\ell)\,\vert\,Pt$	+1.763
$PbO_2(s) + SO_4^{2-}(aq) + 4\,H^+(aq) + 2\,e^-$	→	$PbSO_4(s) + 2\,H_2O(\ell)$	$PbO_2(s)\,\vert\,SO_4^{2-}(aq), H^+(aq)\,\vert\,PbSO_4(s)\,\vert\,Pb$	+1.690
$Au^{3+}(aq) + 3\,e^-$	→	$Au(s)$	$Au^{3+}(aq)\,\vert\,Au(s)$	+1.52
$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^-$	→	$Mn^{2+}(aq) + 4\,H_2O(\ell)$	$MnO_4^-(aq), H^+(aq), Mn^{2+}(aq)\,\vert\,Pt$	+1.51
$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^-$	→	$2\,Cr^{3+}(aq) + 7\,H_2O(\ell)$	$Cr_2O_7^{2-}(aq), H^+(aq), Cr^{3+}(aq)\,\vert\,Pt$	+1.36
$Cl_2(g) + 2\,e^-$	→	$2\,Cl^-(aq)$	$Cl_2(g)\,\vert\,Cl^-(aq)\,\vert\,Pt$	+1.358
$O_2(g) + 4\,H^+(aq) + 4\,e^-$	→	$2\,H_2O(\ell)$	$O_2(g)\,\vert\,H^+(aq)\,\vert\,Pt$	+1.229
$Br_2(\ell) + 2\,e^-$	→	$2\,Br^-(aq)$	$Br_2(\ell)\,\vert\,Br^-(aq)\,\vert\,Pt$	+1.066
$NO_3^-(aq) + 4\,H^+(aq) + 3\,e^-$	→	$NO(g) + 2\,H_2O(\ell)$	$NO_3^-(aq), H^+(aq)\,\vert\,NO(g)\,\vert\,Pt$	+0.96
$OCl^-(aq) + H_2O(\ell) + 2\,e^-$	→	$Cl^-(aq) + 2\,OH^-(aq)$	$OCl^-(aq), Cl^-(aq), OH^-(aq)\,\vert\,Pt$	+0.89
$Hg^{2+}(aq) + 2\,e^-$	→	$Hg(\ell)$	$Hg^{2+}(aq)\,\vert\,Hg(\ell)$	+0.8535
$Ag^+(aq) + e^-$	→	$Ag(s)$	$Ag^+(aq)\,\vert\,Ag(s)$	+0.7991
$Hg_2^{2+}(aq) + 2\,e^-$	→	$2\,Hg(\ell)$	$Hg_2^{2+}(aq)\,\vert\,Hg(\ell)$	+0.7960
$Fe^{3+}(aq) + e^-$	→	$Fe^{2+}(aq)$	$Fe^{3+}(aq), Fe^{2+}(aq)\,\vert\,Pt$	+0.771
$I_2(s) + 2\,e^-$	→	$2\,I^-(aq)$	$I_2(s)\,\vert\,I^-(aq)\,\vert\,Pt$	+0.535
$O_2(g) + 2\,H_2O(\ell) + 4\,e^-$	→	$4\,OH^-(aq)$	$O_2(g)\,\vert\,OH^-(aq)\,\vert\,Pt$	+0.401
$Cu^{2+}(aq) + 2\,e^-$	→	$Cu(s)$	$Cu^{2+}(aq)\,\vert\,Cu(s)$	+0.340
$Sn^{4+}(aq) + 2\,e^-$	→	$Sn^{2+}(aq)$	$Sn^{4+}(aq), Sn^{2+}(aq)\,\vert\,Pt$	+0.15
$2\,H^+(aq) + 2\,e^-$	→	$H_2(g)$	$H^+(aq)\,\vert\,H_2(g)\,\vert\,Pt$	0
$Sn^{2+}(aq) + 2\,e^-$	→	$Sn(s)$	$Sn^{2+}(aq)\,\vert\,Sn(s)$	-0.1375
$Ni^{2+}(aq) + 2\,e^-$	→	$Ni(s)$	$Ni^{2+}(aq)\,\vert\,Ni(s)$	-0.25
$PbSO_4(s) + 2\,e^-$	→	$Pb(s) + SO_4^{2-}(aq)$	$PbSO_4(s)\,\vert\,SO_4^{2-}(aq)\,\vert\,Pb(s)$	-0.3505
$Cd^{2+}(aq) + 2\,e^-$	→	$Cd(s)$	$Cd^{2+}(aq)\,\vert\,Cd(s)$	-0.403
$Fe^{2+}(aq) + 2\,e^-$	→	$Fe(s)$	$Fe^{2+}(aq)\,\vert\,Fe(s)$	-0.44
$Zn^{2+}(aq) + 2\,e^-$	→	$Zn(s)$	$Zn^{2+}(aq)\,\vert\,Zn(s)$	-0.763
$2\,H_2O(\ell) + 2\,e^-$	→	$H_2(g) + 2\,OH^-(aq)$	$H_2O\,(\ell), OH^-(aq)\,\vert\,H_2(g)\,\vert\,Pt$	-0.8277
$Al^{3+}(aq) + 3\,e^-$	→	$Al(s)$	$Al^{3+}(aq)\,\vert\,Al(s)$	-1.676
$Mg^{2+}(aq) + 2\,e^-$	→	$Mg(s)$	$Mg^{2+}(aq)\,\vert\,Mg(s)$	-2.356
$Na^+(aq) + e^-$	→	$Na(s)$	$Na^+(aq)\,\vert\,Na(s)$	-2.714
$K^+(aq) + e^-$	→	$K(s)$	$K^+(aq)\,\vert\,K(s)$	-2.925
$Li^+(aq) + e^-$	→	$Li(s)$	$Li^+(aq)\,\vert\,Li(s)$	-3.045

References to the literature used

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