STUFF TO REVIEW FROM GENERAL CHEMISTRY



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Stuff to Review from General Chemistry

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Licensing

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CHAPTER OVERVIEW

1: Atoms, Molecules, and Ions

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General Chemistry

This chapter will describe some of the fundamental chemical principles related to the composition of matter, including those central to the concept of molecular identity.

1.1: Prelude to Atoms
1.2: Early Ideas in Atomic Theory
1.3: Evolution of Atomic Theory
1.4: Atomic Structure and Symbolism
1.5: Chemical Formulas
1.6: The Periodic Table
1.7: Molecular and Ionic Compounds
1.8: Chemical Nomenclature
1.E: Atoms, Molecules, and Ions (Exercises)

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Thumbnail: Spinning Buckminsterfullerene (C_{60}). Image used with permission (CC BY-SA 3.0; unported; Sponk).

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1.1: Prelude to Atoms

Your overall health and susceptibility to disease depends upon the complex interaction between your genetic makeup and environmental exposure, with the outcome difficult to predict. Early detection of biomarkers, substances that indicate an organism's disease or physiological state, could allow diagnosis and treatment before a condition becomes serious or irreversible. Recent studies have shown that your exhaled breath can contain molecules that may be biomarkers for recent exposure to environmental contaminants or for pathological conditions ranging from asthma to lung cancer.

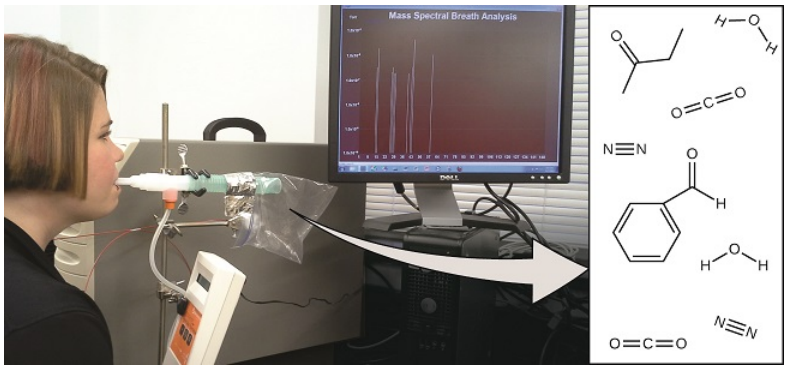


Figure **1.1.1**: Analysis of molecules in an exhaled breath can provide valuable information, leading to early diagnosis of diseases or detection of environmental exposure to harmful substances. (credit: modification of work by Paul Flowers)

A person is shown blowing into a tube connected to a plastic bag. There is a computer screen displaying data that reads "Mass Spectral Breath Analysis." An arrow from the plastic bag points to an illustration of different molecular compounds contained in the person's exhalation

Scientists are working to develop biomarker "fingerprints" that could be used to diagnose a specific disease based on the amounts and identities of certain molecules in a patient's exhaled breath. An essential concept underlying this goal is that of a molecule's identity, which is determined by the numbers and types of atoms it contains, and how they are bonded together. This chapter will describe some of the fundamental chemical principles related to the composition of matter, including those central to the concept of molecular identity.

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1.2: Early Ideas in Atomic Theory

Learning Objectives

By the end of this section, you will be able to:

- State the postulates of Dalton's atomic theory
- Use postulates of Dalton's atomic theory to explain the laws of definite and multiple proportions

The language used in chemistry is seen and heard in many disciplines, ranging from medicine to engineering to forensics to art. The language of chemistry includes its own vocabulary as well as its own form of shorthand. Chemical symbols are used to represent atoms and elements. Chemical formulas depict molecules as well as the composition of compounds. Chemical equations provide information about the quality and quantity of the changes associated with chemical reactions.

This chapter will lay the foundation for our study of the language of chemistry. The concepts of this foundation include the atomic theory, the composition and mass of an atom, the variability of the composition of isotopes, ion formation, chemical bonds in ionic and covalent compounds, the types of chemical reactions, and the naming of compounds. We will also introduce one of the most powerful tools for organizing chemical knowledge: the periodic table.

Atomic Theory through the Nineteenth Century

The earliest recorded discussion of the basic structure of matter comes from ancient Greek philosophers, the scientists of their day. In the fifth century BC, Leucippus and Democritus argued that all matter was composed of small, finite particles that they called *atomos*, a term derived from the Greek word for "indivisible." They thought of atoms as moving particles that differed in shape and size, and which could join together. Later, Aristotle and others came to the conclusion that matter consisted of various combinations of the four "elements"—fire, earth, air, and water—and could be infinitely divided. Interestingly, these philosophers thought about atoms and "elements" as philosophical concepts, but apparently never considered performing experiments to test their ideas.

The Aristotelian view of the composition of matter held sway for over two thousand years, until English schoolteacher John Dalton helped to revolutionize chemistry with his hypothesis that the behavior of matter could be explained using an atomic theory. First published in 1807, many of Dalton's hypotheses about the microscopic features of matter are still valid in modern atomic theory. Here are the postulates of Dalton's atomic theory.

1. Matter is composed of exceedingly small particles called atoms. An atom is the smallest unit of an element that can participate in a chemical change.
2. An element consists of only one type of atom, which has a mass that is characteristic of the element and is the same for all atoms of that element (Figure **1.2.1**). A macroscopic sample of an element contains an incredibly large number of atoms, all of which have identical chemical properties.

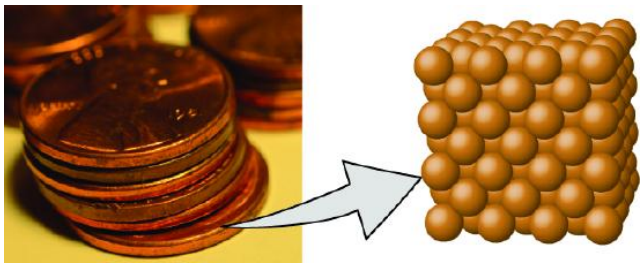


Figure **1.2.1**: A pre-1982 copper penny (left) contains approximately 3×10^{22} copper atoms (several dozen are represented as brown spheres at the right), each of which has the same chemical properties. (credit: modification of work by "slgckgc"/Flickr)

The left image shows a photograph of a stack of pennies. The right image calls out an area of one of the pennies, which is made up of many sphere-shaped copper atoms. The atoms are densely organized.

3. Atoms of one element differ in properties from atoms of all other elements.
4. A compound consists of atoms of two or more elements combined in a small, whole-number ratio. In a given compound, the numbers of atoms of each of its elements are always present in the same ratio (Figure **1.2.2**).

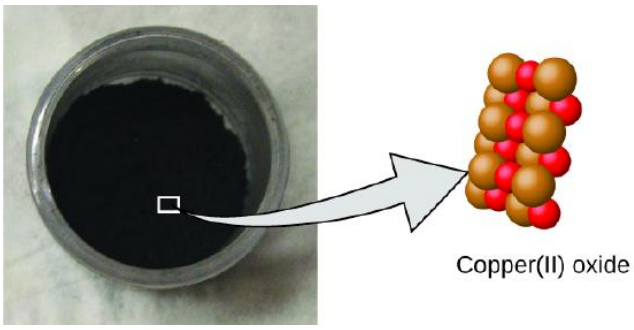


Figure 1.2.2: Copper(II) oxide, a powdery, black compound, results from the combination of two types of atoms—copper (brown spheres) and oxygen (red spheres)—in a 1:1 ratio. (credit: modification of work by "Chemicalinterest"/Wikimedia Commons)

The left image shows a container with a black, powdery compound. The right image calls out the molecular structure of the powder which contains copper atoms that are clustered together with an equal number of oxygen atoms.

5. *Atoms are neither created nor destroyed during a chemical change, but are instead rearranged to yield substances that are different from those present before the change (Figure* 1.2.3*).*

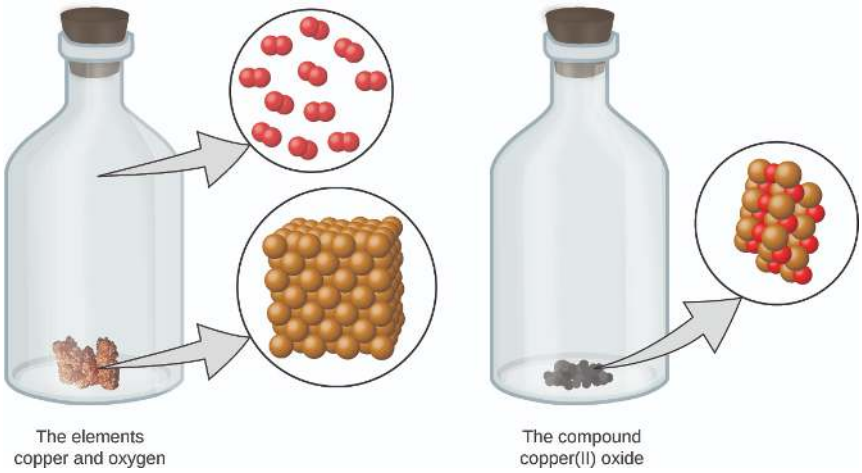


Figure 1.2.3: When the elements copper (a shiny, red-brown solid, shown here as brown spheres) and oxygen (a clear and colorless gas, shown here as red spheres) react, their atoms rearrange to form a compound containing copper and oxygen (a powdery, black solid). (credit copper: modification of work by Copper [images-of-elements.com]).

The left stoppered bottle contains copper and oxygen. There is a callout which shows that copper is made up of many sphere-shaped atoms. The atoms are densely organized. The open space of the bottle contains oxygen gas, which is made up of bonded pairs of oxygen atoms that are evenly spaced. The right stoppered bottle shows the compound copper two oxide. A callout from the powder shows a molecule of copper two oxide, which contains copper atoms that are clustered together with an equal number of oxygen atoms.

Dalton's atomic theory provides a microscopic explanation of the many macroscopic properties of matter that you've learned about. For example, if an element such as copper consists of only one kind of atom, then it cannot be broken down into simpler substances, that is, into substances composed of fewer types of atoms. And if atoms are neither created nor destroyed during a chemical change, then the total mass of matter present when matter changes from one type to another will remain constant (the law of conservation of matter).

Example 1.2.1: Testing Dalton's Atomic Theory

In the following drawing, the green spheres represent atoms of a certain element. The purple spheres represent atoms of another element. If the spheres touch, they are part of a single unit of a compound. Does the following chemical change represented by these symbols violate any of the ideas of Dalton's atomic theory? If so, which one?



This equation shows that the starting materials of the reaction are two bonded, green spheres, which are being combined with two smaller, bonded purple spheres. The product of the change is one purple sphere that is bonded to one green sphere.

Solution

The starting materials consist of two green spheres and two purple spheres. The products consist of only one green sphere and one purple sphere. This violates Dalton's postulate that atoms are neither created nor destroyed during a chemical change, but are merely redistributed. (In this case, atoms appear to have been destroyed.)

? Exercise 1.2.1

In the following drawing, the green spheres represent atoms of a certain element. The purple spheres represent atoms of another element. If the spheres touch, they are part of a single unit of a compound. Does the following chemical change represented by these symbols violate any of the ideas of Dalton's atomic theory? If so, which one



This equation shows that the starting materials of the reaction are two sets of bonded, green spheres which are each being combined with two smaller, bonded purple spheres. The products of the change are two molecules that each contain one purple sphere bonded between two green spheres.

Answer

The starting materials consist of four green spheres and two purple spheres. The products consist of four green spheres and two purple spheres. This does not violate any of Dalton's postulates: Atoms are neither created nor destroyed, but are redistributed in small, whole-number ratios.

Dalton knew of the experiments of French chemist Joseph Proust, who demonstrated that *all samples of a pure compound contain the same elements in the same proportion by mass*. This statement is known as the law of definite proportions or the law of constant composition. The suggestion that the numbers of atoms of the elements in a given compound always exist in the same ratio is consistent with these observations. For example, when different samples of isooctane (a component of gasoline and one of the standards used in the octane rating system) are analyzed, they are found to have a carbon-to-hydrogen mass ratio of 5.33:1, as shown in Table **1.2.1**.

Table **1.2.1**: Constant Composition of Isooctane

Sample	Carbon	Hydrogen	Mass Ratio
A	14.82 g	2.78 g	$\frac{14.82\text{ g carbon}}{2.78\text{ g hydrogen}} = \frac{5.33\text{ g carbon}}{1.00\text{ g hydrogen}}$
B	22.33 g	4.19 g	$\frac{22.33\text{ g carbon}}{4.19\text{ g hydrogen}} = \frac{5.33\text{ g carbon}}{1.00\text{ g hydrogen}}$
C	19.40 g	3.64 g	$\frac{19.40\text{ g carbon}}{3.63\text{ g hydrogen}} = \frac{5.33\text{ g carbon}}{1.00\text{ g hydrogen}}$

It is worth noting that although all samples of a particular compound have the same mass ratio, the converse is not true in general. That is, samples that have the same mass ratio are not necessarily the same substance. For example, there are many compounds other than isooctane that also have a carbon-to-hydrogen mass ratio of 5.33:1.00.

Dalton also used data from Proust, as well as results from his own experiments, to formulate another interesting law. The law of multiple proportions states that *when two elements react to form more than one compound, a fixed mass of one element will react*

with masses of the other element in a ratio of small, whole numbers. For example, copper and chlorine can form a green, crystalline solid with a mass ratio of 0.558 g chlorine to 1 g copper, as well as a brown crystalline solid with a mass ratio of 1.116 g chlorine to 1 g copper. These ratios by themselves may not seem particularly interesting or informative; however, if we take a ratio of these ratios, we obtain a useful and possibly surprising result: a small, whole-number ratio.

$$\frac{\frac{1.116\ \text{g Cl}}{1\ \text{g Cu}}}{\frac{0.558\ \text{g Cl}}{1\ \text{g Cu}}} = \frac{2}{1}$$

This 2-to-1 ratio means that the brown compound has twice the amount of chlorine per amount of copper as the green compound.

This can be explained by atomic theory if the copper-to-chlorine ratio in the brown compound is 1 copper atom to 2 chlorine atoms, and the ratio in the green compound is 1 copper atom to 1 chlorine atom. The ratio of chlorine atoms (and thus the ratio of their masses) is therefore 2 to 1 (Figure **1.2.4**).

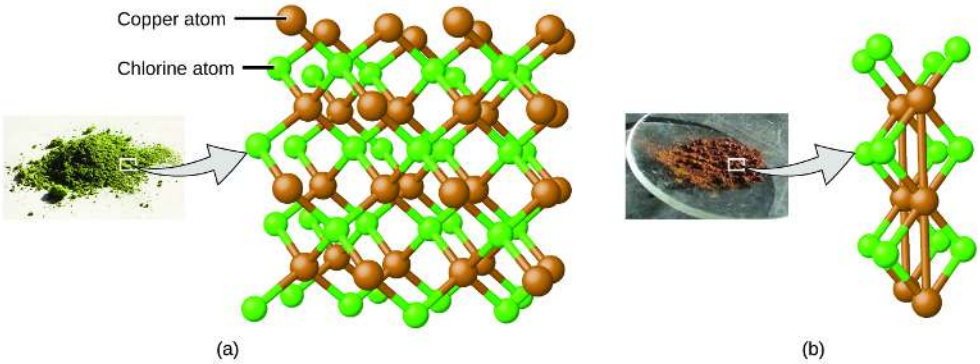


Figure **1.2.4**: Compared to the copper chlorine compound in (a), where copper is represented by brown spheres and chlorine by green spheres, the copper chlorine compound in (b) has twice as many chlorine atoms per copper atom. (credit a: modification of work by "Benjah-bmm27"/Wikimedia Commons; credit b: modification of work by "Walkerma"/Wikimedia Commons)

Figure A shows a pile of green powder. A callout shows that the green powder is made up of a lattice of copper atoms interspersed with chlorine atoms. The atoms are color coded brown for copper and green for chlorine. The number of copper atoms is equal to the number of chlorine atoms in the molecule. Figure B shows a pile of brown powder. A callout shows that the brown powder is also made up of copper and chlorine atoms similar to the molecule shown in figure A.

Example **1.2.2**: Laws of Definite and Multiple Proportions

A sample of compound A (a clear, colorless gas) is analyzed and found to contain 4.27 g carbon and 5.69 g oxygen. A sample of compound B (also a clear, colorless gas) is analyzed and found to contain 5.19 g carbon and 13.84 g oxygen. Are these data an example of the law of definite proportions, the law of multiple proportions, or neither? What do these data tell you about substances A and B?

Solution

In compound A, the mass ratio of carbon to oxygen is:

$$\frac{1.33\ \text{g O}}{1\ \text{g C}}$$

In compound B, the mass ratio of carbon to oxygen is:

$$\frac{2.67\ \text{g O}}{1\ \text{g C}}$$

The ratio of these ratios is:

$$\frac{\frac{1.33\ \text{g O}}{1\ \text{g C}}}{\frac{2.67\ \text{g O}}{1\ \text{g C}}} = \frac{1}{2}$$

This supports the law of multiple proportions. This means that A and B are different compounds, with A having one-half as much carbon per amount of oxygen (or twice as much oxygen per amount of carbon) as B. A possible pair of compounds that would fit this relationship would be A = CO_2 and B = CO.

? Exercise 1.2.1

A sample of compound X (a clear, colorless, combustible liquid with a noticeable odor) is analyzed and found to contain 14.13 g carbon and 2.96 g hydrogen. A sample of compound Y (a clear, colorless, combustible liquid with a noticeable odor that is slightly different from X's odor) is analyzed and found to contain 19.91 g carbon and 3.34 g hydrogen. Are these data an example of the law of definite proportions, the law of multiple proportions, or neither? What do these data tell you about substances X and Y?

Answer

In compound X, the mass ratio of carbon to hydrogen is $\frac{14.13\ \text{g C}}{2.96\ \text{g H}}$.

In compound Y, the mass ratio of carbon to oxygen is $\frac{19.91\ \text{g C}}{3.34\ \text{g H}}$.

The ratio of these ratios is

$$\frac{\frac{14.13\ \text{g C}}{2.96\ \text{g H}}}{\frac{19.91\ \text{g C}}{3.34\ \text{g H}}} = \frac{4.77\ \text{g C/g H}}{5.96\ \text{g C/g H}} = 0.800 = \frac{4}{5}.$$

This small, whole-number ratio supports the law of multiple proportions. This means that X and Y are different compounds.

Summary

The ancient Greeks proposed that matter consists of extremely small particles called atoms. Dalton postulated that each element has a characteristic type of atom that differs in properties from atoms of all other elements, and that atoms of different elements can combine in fixed, small, whole-number ratios to form compounds. Samples of a particular compound all have the same elemental proportions by mass. When two elements form different compounds, a given mass of one element will combine with masses of the other element in a small, whole-number ratio. During any chemical change, atoms are neither created nor destroyed.

Glossary

Dalton's atomic theory
: set of postulates that established the fundamental properties of atoms

law of constant composition
: (also, law of definite proportions) all samples of a pure compound contain the same elements in the same proportions by mass

law of multiple proportions
: when two elements react to form more than one compound, a fixed mass of one element will react with masses of the other element in a ratio of small whole numbers

law of definite proportions
: (also, law of constant composition) all samples of a pure compound contain the same elements in the same proportions by mass

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1.3: Evolution of Atomic Theory

Learning Objectives

- Outline milestones in the development of modern atomic theory
- Summarize and interpret the results of the experiments of Thomson, Millikan, and Rutherford
- Describe the three subatomic particles that compose atoms
- Introduce the term isotopes

In the two centuries since Dalton developed his ideas, scientists have made significant progress in furthering our understanding of atomic theory. Much of this came from the results of several seminal experiments that revealed the details of the internal structure of atoms. Here, we will discuss some of those key developments, with an emphasis on application of the scientific method, as well as understanding how the experimental evidence was analyzed. While the historical persons and dates behind these experiments can be quite interesting, it is most important to understand the concepts resulting from their work.

Atomic Theory after the Nineteenth Century

If matter were composed of atoms, what were atoms composed of? Were they the smallest particles, or was there something smaller? In the late 1800s, a number of scientists interested in questions like these investigated the electrical discharges that could be produced in low-pressure gases, with the most significant discovery made by English physicist J. J. Thomson using a cathode ray tube. This apparatus consisted of a sealed glass tube from which almost all the air had been removed; the tube contained two metal electrodes. When high voltage was applied across the electrodes, a visible beam called a cathode ray appeared between them. This beam was deflected toward the positive charge and away from the negative charge, and was produced in the same way with identical properties when different metals were used for the electrodes. In similar experiments, the ray was simultaneously deflected by an applied magnetic field, and measurements of the extent of deflection and the magnetic field strength allowed Thomson to calculate the charge-to-mass ratio of the cathode ray particles. The results of these measurements indicated that these particles were much lighter than atoms (Figure **1.3.1**).

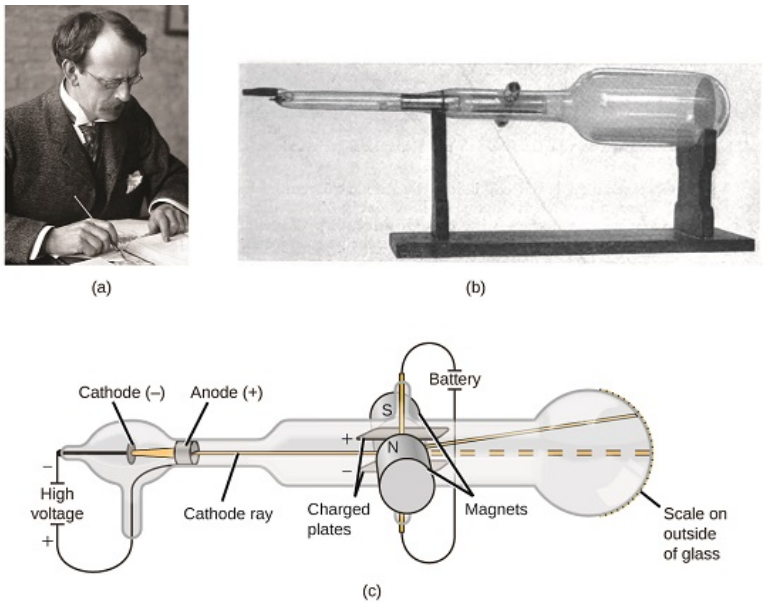
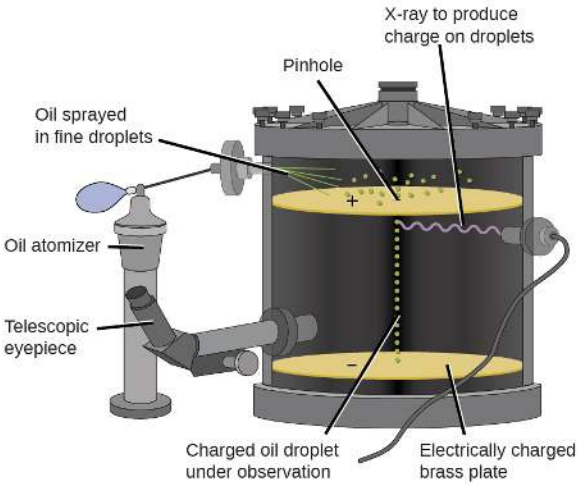


Figure **1.3.1**: (a) J. J. Thomson produced a visible beam in a cathode ray tube. (b) This is an early cathode ray tube, invented in 1897 by Ferdinand Braun. (c) In the cathode ray, the beam (shown in yellow) comes from the cathode and is accelerated past the anode toward a fluorescent scale at the end of the tube. Simultaneous deflections by applied electric and magnetic fields permitted Thomson to calculate the mass-to-charge ratio of the particles composing the cathode ray. (credit a: modification of work by Nobel Foundation; credit b: modification of work by Eugen Nesper; credit c: modification of work by “Kurzon”/Wikimedia Commons).

Based on his observations, here is what Thomson proposed and why: The particles are attracted by positive (+) charges and repelled by negative (−) charges, so they must be negatively charged (like charges repel and unlike charges attract); they are less

massive than atoms and indistinguishable, regardless of the source material, so they must be fundamental, subatomic constituents of all atoms. Although controversial at the time, Thomson's idea was gradually accepted, and his cathode ray particle is what we now call an electron, a negatively charged, subatomic particle with a mass more than one thousand-times less that of an atom. The term "electron" was coined in 1891 by Irish physicist George Stoney, from "*electr*ic i*on*."

In 1909, more information about the electron was uncovered by American physicist Robert A. Millikan via his "oil drop" experiments. Millikan created microscopic oil droplets, which could be electrically charged by friction as they formed or by using X-rays. These droplets initially fell due to gravity, but their downward progress could be slowed or even reversed by an electric field lower in the apparatus. By adjusting the electric field strength and making careful measurements and appropriate calculations, Millikan was able to determine the charge on individual drops (Figure **1.3.2**).



Oil drop	Charge in coulombs (C)
A	4.8×10^{-19} C
B	3.2×10^{-19} C
C	6.4×10^{-19} C
D	1.6×10^{-19} C
E	4.8×10^{-19} C

Figure **1.3.2**: Millikan's experiment measured the charge of individual oil drops. The tabulated data are examples of a few possible values.

Looking at the charge data that Millikan gathered, you may have recognized that the charge of an oil droplet is always a multiple of a specific charge, 1.6×10^{-19} C. Millikan concluded that this value must therefore be a fundamental charge—the charge of a single electron—with his measured charges due to an excess of one electron (1 times 1.6×10^{-19} C), two electrons (2 times 1.6×10^{-19} C), three electrons (3 times 1.6×10^{-19} C), and so on, on a given oil droplet. Since the charge of an electron was now known due to Millikan's research, and the charge-to-mass ratio was already known due to Thomson's research (1.759×10^{11} C/kg), it only required a simple calculation to determine the mass of the electron as well.

$$\textbf{Mass of electron} = 1.602 \times 10^{-19} \cancel{\text{C}} \times \frac{1 \text{ kg}}{1.759 \times 10^{11} \cancel{\text{C}}} = 9.107 \times 10^{-31} \text{ kg} \tag{2.3.1}$$

Scientists had now established that the atom was not indivisible as Dalton had believed, and due to the work of Thomson, Millikan, and others, the charge and mass of the negative, subatomic particles—the electrons—were known. However, the positively charged part of an atom was not yet well understood. In 1904, Thomson proposed the "plum pudding" model of atoms, which described a positively charged mass with an equal amount of negative charge in the form of electrons embedded in it, since all atoms are electrically neutral. A competing model had been proposed in 1903 by Hantaro Nagaoka, who postulated a Saturn-like atom, consisting of a positively charged sphere surrounded by a halo of electrons (Figure **1.3.3**).

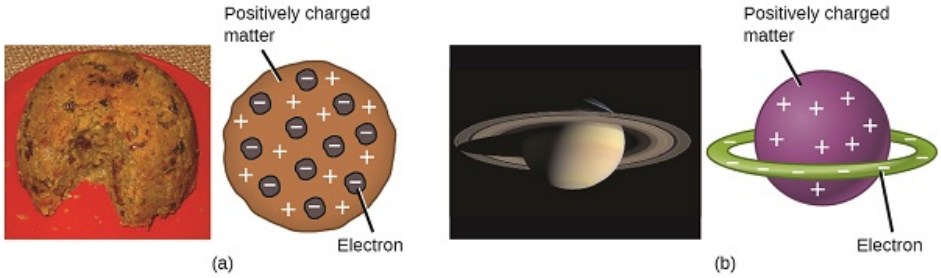


Figure **1.3.3**: (a) Thomson suggested that atoms resembled plum pudding, an English dessert consisting of moist cake with embedded raisins ("plums"). (b) Nagaoka proposed that atoms resembled the planet Saturn, with a ring of electrons surrounding a positive "planet." (credit a: modification of work by "Man vyi"/Wikimedia Commons; credit b: modification of work by "NASA"/Wikimedia Commons).

The next major development in understanding the atom came from Ernest Rutherford, a physicist from New Zealand who largely spent his scientific career in Canada and England. He performed a series of experiments using a beam of high-speed, positively charged alpha particles (α particles) that were produced by the radioactive decay of radium; α particles consist of two protons and two neutrons (you will learn more about radioactive decay in the chapter on nuclear chemistry). Rutherford and his colleagues Hans Geiger (later famous for the Geiger counter) and Ernest Marsden aimed a beam of α particles, the source of which was embedded in a lead block to absorb most of the radiation, at a very thin piece of gold foil and examined the resultant scattering of the α particles using a luminescent screen that glowed briefly where hit by an α particle.

What did they discover? Most particles passed right through the foil without being deflected at all. However, some were diverted slightly, and a very small number were deflected almost straight back toward the source (Figure **1.3.4**). Rutherford described finding these results: "It was quite the most incredible event that has ever happened to me in my life. It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you"[1] (p. 68).

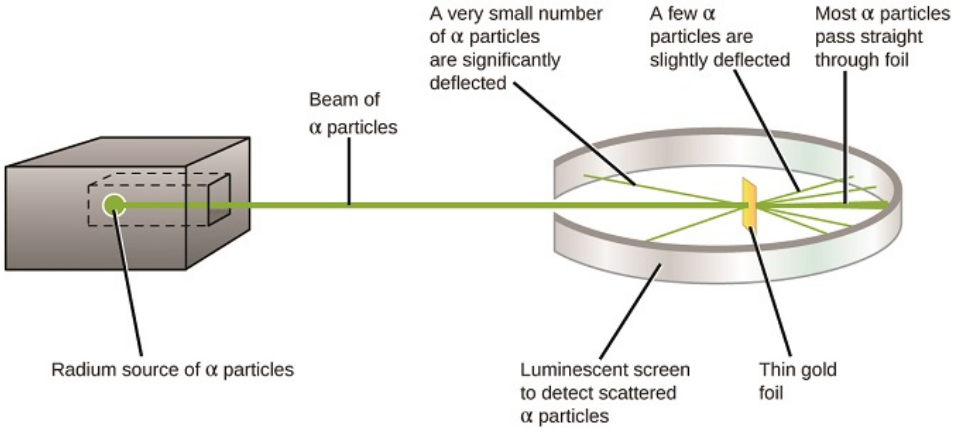


Figure **1.3.4**: Geiger and Rutherford fired α particles at a piece of gold foil and detected where those particles went, as shown in this schematic diagram of their experiment. Most of the particles passed straight through the foil, but a few were deflected slightly and a very small number were significantly deflected.

Here is what Rutherford deduced: Because most of the fast-moving α particles passed through the gold atoms undeflected, they must have traveled through essentially empty space inside the atom. Alpha particles are positively charged, so deflections arose when they encountered another positive charge (like charges repel each other). Since like charges repel one another, the few positively charged α particles that changed paths abruptly must have hit, or closely approached, another body that also had a highly concentrated, positive charge. Since the deflections occurred a small fraction of the time, this charge only occupied a small amount of the space in the gold foil. Analyzing a series of such experiments in detail, Rutherford drew two conclusions:

1. The volume occupied by an atom must consist of a large amount of empty space.
2. A small, relatively heavy, positively charged body, the nucleus, must be at the center of each atom.

This analysis led Rutherford to propose a model in which an atom consists of a very small, positively charged nucleus, in which most of the mass of the atom is concentrated, surrounded by the negatively charged electrons, so that the atom is electrically neutral (Figure **1.3.5**).

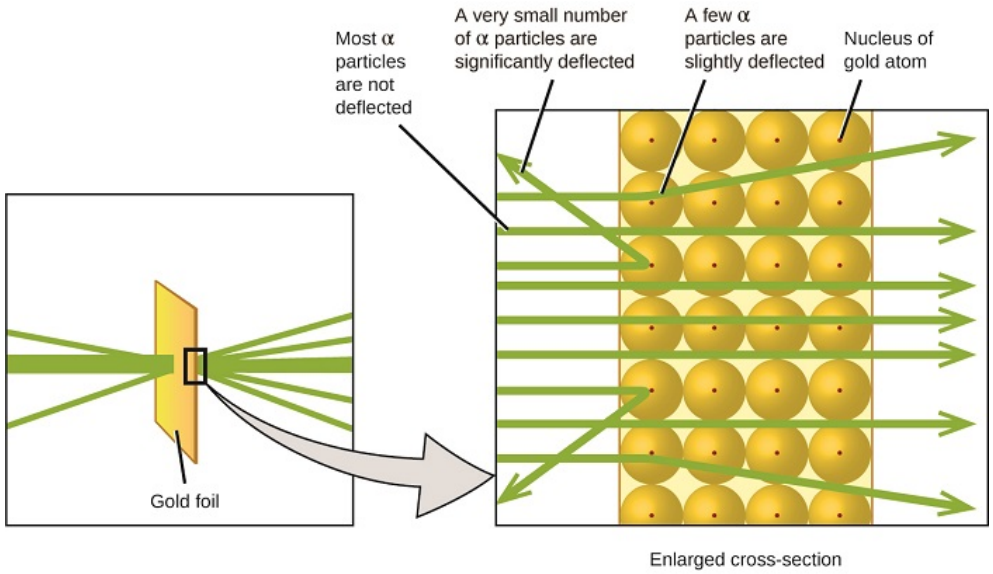


Figure **1.3.5**: The α particles are deflected only when they collide with or pass close to the much heavier, positively charged gold nucleus. Because the nucleus is very small compared to the size of an atom, very few α particles are deflected. Most pass through the relatively large region occupied by electrons, which are too light to deflect the rapidly moving particles.

After many more experiments, Rutherford also discovered that the nuclei of other elements contain the hydrogen nucleus as a "building block," and he named this more fundamental particle the proton, the positively charged, subatomic particle found in the nucleus. With one addition, which you will learn next, this nuclear model of the atom, proposed over a century ago, is still used today.

PhET: Rutherford Scattering

Another important finding was the discovery of isotopes. During the early 1900s, scientists identified several substances that appeared to be new elements, isolating them from radioactive ores. For example, a "new element" produced by the radioactive decay of thorium was initially given the name mesothorium. However, a more detailed analysis showed that mesothorium was chemically identical to radium (another decay product), despite having a different atomic mass. This result, along with similar findings for other elements, led the English chemist Frederick Soddy to realize that an element could have types of atoms with different masses that were chemically indistinguishable. These different types are called isotopes—atoms of the same element that differ in mass. Soddy was awarded the Nobel Prize in Chemistry in 1921 for this discovery.

One puzzle remained: The nucleus was known to contain almost all of the mass of an atom, with the number of protons only providing half, or less, of that mass. Different proposals were made to explain what constituted the remaining mass, including the existence of neutral particles in the nucleus. As you might expect, detecting uncharged particles is very challenging, and it was not until 1932 that James Chadwick found evidence of neutrons, uncharged, subatomic particles with a mass approximately the same as that of protons. The existence of the neutron also explained isotopes: They differ in mass because they have different numbers of neutrons, but they are chemically identical because they have the same number of protons. This will be explained in more detail later in this chapter.

Summary

Although no one has actually seen the inside of an atom, experiments have demonstrated much about atomic structure. Thomson's cathode ray tube showed that atoms contain small, negatively charged particles called electrons. Millikan discovered that there is a fundamental electric charge—the charge of an electron. Rutherford's gold foil experiment showed that atoms have a small, dense, positively charged nucleus; the positively charged particles within the nucleus are called protons. Chadwick discovered that the nucleus also contains neutral particles called neutrons. Soddy demonstrated that atoms of the same element can differ in mass; these are called isotopes.

Footnotes

1. Ernest Rutherford, “The Development of the Theory of Atomic Structure,” ed. J. A. Ratcliffe, in *Background to Modern Science*, eds. Joseph Needham and Walter Pagel, (Cambridge, UK: Cambridge University Press, 1938), 61–74. Accessed September 22, 2014, https://ia600508.us.archive.org/3/it...e032734mbp.pdf.

Glossary

alpha particle (α particle)
positively charged particle consisting of two protons and two neutrons

electron
negatively charged, subatomic particle of relatively low mass located outside the nucleus

isotopes
atoms that contain the same number of protons but different numbers of neutrons

neutron
uncharged, subatomic particle located in the nucleus

proton
positively charged, subatomic particle located in the nucleus

nucleus
massive, positively charged center of an atom made up of protons and neutrons

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1.4: Atomic Structure and Symbolism

Learning Objectives

- Write and interpret symbols that depict the atomic number, mass number, and charge of an atom or ion
- Define the atomic mass unit and average atomic mass
- Calculate average atomic mass and isotopic abundance

The development of modern atomic theory revealed much about the inner structure of atoms. It was learned that an atom contains a very small nucleus composed of positively charged protons and uncharged neutrons, surrounded by a much larger volume of space containing negatively charged electrons. The nucleus contains the majority of an atom's mass because protons and neutrons are much heavier than electrons, whereas electrons occupy almost all of an atom's volume. The diameter of an atom is on the order of 10^{-10} m, whereas the diameter of the nucleus is roughly 10^{-15} m—about 100,000 times smaller. For a perspective about their relative sizes, consider this: If the nucleus were the size of a blueberry, the atom would be about the size of a football stadium (Figure **1.4.1**).



Figure **1.4.1**: If an atom could be expanded to the size of a football stadium, the nucleus would be the size of a single blueberry. (credit middle: modification of work by "babyknight"/Wikimedia Commons; credit right: modification of work by Paxson Woelber).

The diagram on the left shows a picture of an atom with a nucleus. The central figure shows a photograph of an American football stadium. The figure on the right shows a photograph of a handful of blueberries.

Atoms—and the protons, neutrons, and electrons that compose them—are extremely small. For example, a carbon atom weighs less than 2×10^{-23} g, and an electron has a charge of less than 2×10^{-19} C (coulomb). When describing the properties of tiny objects such as atoms, we use appropriately small units of measure, such as the atomic mass unit (amu) and the fundamental unit of charge (e). The amu was originally defined based on hydrogen, the lightest element, then later in terms of oxygen. Since 1961, it has been defined with regard to the most abundant isotope of carbon, atoms of which are assigned masses of exactly 12 amu. (This isotope is known as "carbon-12" as will be discussed later in this module.) Thus, one amu is exactly $\mathbf{1/12}$ of the mass of one carbon-12 atom: 1 amu = 1.6605×10^{-24} g. (The Dalton (Da) and the unified atomic mass unit (u) are alternative units that are equivalent to the amu.) The fundamental unit of charge (also called the elementary charge) equals the magnitude of the charge of an electron (e) with e = 1.602×10^{-19} C.

A proton has a mass of 1.0073 amu and a charge of 1+. A neutron is a slightly heavier particle with a mass 1.0087 amu and a charge of zero; as its name suggests, it is neutral. The electron has a charge of 1− and is a much lighter particle with a mass of about 0.00055 amu (it would take about 1800 electrons to equal the mass of one proton. The properties of these fundamental particles are summarized in Table **1.4.1**. (An observant student might notice that the sum of an atom's subatomic particles does not equal the atom's actual mass: The total mass of six protons, six neutrons, and six electrons is 12.0993 amu, slightly larger than the 12.00 amu of an actual carbon-12 atom. This "missing" mass is known as the mass defect, and you will learn about it in the chapter on nuclear chemistry.)

Table **1.4.1**: Properties of Subatomic Particles

Name	Location	Charge (C)	Unit Charge	Mass (amu)	Mass (g)
electron	outside nucleus	-1.602×10^{-19}	1−	0.00055	0.00091×10^{-24}
proton	nucleus	1.602×10^{-19}	1+	1.00727	1.67262×10^{-24}
neutron	nucleus	0	0	1.00866	1.67493×10^{-24}

The number of protons in the nucleus of an atom is its **atomic number** (Z). This is the defining trait of an element: Its value determines the identity of the atom. For example, any atom that contains six protons is the element carbon and has the atomic number 6, regardless of how many neutrons or electrons it may have. A neutral atom must contain the same number of positive and negative charges, so the number of protons equals the number of electrons. Therefore, the atomic number also indicates the number of electrons in an atom. The total number of protons and neutrons in an atom is called its mass number (A). The number of neutrons is therefore the difference between the mass number and the atomic number: A – Z = number of neutrons.

$$\begin{aligned} \text{atomic number (Z)} &= \text{number of protons} \\ \text{mass number (A)} &= \text{number of protons} + \text{number of neutrons} \\ \text{A} - \text{Z} &= \text{number of neutrons} \end{aligned}$$

Atoms are electrically neutral if they contain the same number of positively charged protons and negatively charged electrons. When the numbers of these subatomic particles are *not* equal, the atom is electrically charged and is called an ion. The charge of an atom is defined as follows:

$$\text{Atomic charge} = \text{number of protons} - \text{number of electrons}$$

As will be discussed in more detail later in this chapter, atoms (and molecules) typically acquire charge by gaining or losing electrons. An atom that gains one or more electrons will exhibit a negative charge and is called an anion. Positively charged atoms called cations are formed when an atom loses one or more electrons. For example, a neutral sodium atom (Z = 11) has 11 electrons. If this atom loses one electron, it will become a cation with a 1+ charge (11 − 10 = 1+). A neutral oxygen atom (Z = 8) has eight electrons, and if it gains two electrons it will become an anion with a 2− charge (8 − 10 = 2−).

Example 1.4.1: Composition of an Atom

Iodine is an essential trace element in our diet; it is needed to produce thyroid hormone. Insufficient iodine in the diet can lead to the development of a goiter, an enlargement of the thyroid gland (Figure 1.4.2).



(a)



(b)

Figure **1.4.2**: (a) Insufficient iodine in the diet can cause an enlargement of the thyroid gland called a goiter. (b) The addition of small amounts of iodine to salt, which prevents the formation of goiters, has helped eliminate this concern in the US where salt consumption is high. (credit a: modification of work by "Almazi"/Wikimedia Commons; credit b: modification of work by Mike Mozart)

Figure A shows a photo of a person who has a very swollen thyroid in his or her neck. Figure B shows a photo of a canister of Morton iodized salt.

The addition of small amounts of iodine to table salt (iodized salt) has essentially eliminated this health concern in the United States, but as much as 40% of the world's population is still at risk of iodine deficiency. The iodine atoms are added as anions, and each has a 1− charge and a mass number of 127. Determine the numbers of protons, neutrons, and electrons in one of these iodine anions.

Solution

The atomic number of iodine (53) tells us that a neutral iodine atom contains 53 protons in its nucleus and 53 electrons outside its nucleus. Because the sum of the numbers of protons and neutrons equals the mass number, 127, the number of neutrons is 74 (127 − 53 = 74). Since the iodine is added as a 1− anion, the number of electrons is 54 [53 – (1–) = 54].

? Exercise **1.4.1**

An ion of platinum has a mass number of 195 and contains 74 electrons. How many protons and neutrons does it contain, and what is its charge?

Answer

78 protons; 117 neutrons; charge is 4+

Chemical Symbols

A chemical symbol is an abbreviation that we use to indicate an element or an atom of an element. For example, the symbol for mercury is Hg (Figure **1.4.3**). We use the same symbol to indicate one atom of mercury (microscopic domain) or to label a container of many atoms of the element mercury (macroscopic domain).



Figure **1.4.3**: The symbol Hg represents the element mercury regardless of the amount; it could represent one atom of mercury or a large amount of mercury. from Wikipedia (user: Materialscientist).

The symbols for several common elements and their atoms are listed in Table **1.4.2**. Some symbols are derived from the common name of the element; others are abbreviations of the name in another language. Symbols have one or two letters, for example, H for hydrogen and Cl for chlorine. To avoid confusion with other notations, only the first letter of a symbol is capitalized. For example, Co is the symbol for the element cobalt, but CO is the notation for the compound carbon monoxide, which contains atoms of the elements carbon (C) and oxygen (O). All known elements and their symbols are in the periodic table.

Table **1.4.2**: Some Common Elements and Their Symbols

Element	Symbol	Element	Symbol
aluminum	Al	iron	Fe (from *ferrum*)
bromine	Br	lead	Pb (from *plumbum*)
calcium	Ca	magnesium	Mg
carbon	C	mercury	Hg (from *hydrargyrum*)
chlorine	Cl	nitrogen	N
chromium	Cr	oxygen	O
cobalt	Co	potassium	K (from *kalium*)
copper	Cu (from *cuprum*)	silicon	Si
fluorine	F	silver	Ag (from *argentum*)
gold	Au (from *aurum*)	sodium	Na (from *natrium*)
helium	He	sulfur	S
hydrogen	H	tin	Sn (from *stannum*)
iodine	I	zinc	Zn

Traditionally, the discoverer (or discoverers) of a new element names the element. However, until the name is recognized by the International Union of Pure and Applied Chemistry (IUPAC), the recommended name of the new element is based on the Latin word(s) for its atomic number. For example, element 106 was called unnilhexium (Unh), element 107 was called unnilseptium (Uns), and element 108 was called unniloctium (Uno) for several years. These elements are now named after scientists or locations; for example, element 106 is now known as *seaborgium* (Sg) in honor of Glenn Seaborg, a Nobel Prize winner who was active in the discovery of several heavy elements.

Isotopes

The symbol for a specific isotope of any element is written by placing the mass number as a superscript to the left of the element symbol (Figure **1.4.4**). The atomic number is sometimes written as a subscript preceding the symbol, but since this number defines the element's identity, as does its symbol, it is often omitted. For example, magnesium exists as a mixture of three isotopes, each with an atomic number of 12 and with mass numbers of 24, 25, and 26, respectively. These isotopes can be identified as ^{24}Mg, ^{25}Mg, and ^{26}Mg. These isotope symbols are read as "element, mass number" and can be symbolized consistent with this reading. For instance, ^{24}Mg is read as "magnesium 24," and can be written as "magnesium-24" or "Mg-24." ^{25}Mg is read as "magnesium 25," and can be written as "magnesium-25" or "Mg-25." All magnesium atoms have 12 protons in their nucleus. They differ only because a ^{24}Mg atom has 12 neutrons in its nucleus, a ^{25}Mg atom has 13 neutrons, and a ^{26}Mg has 14 neutrons.

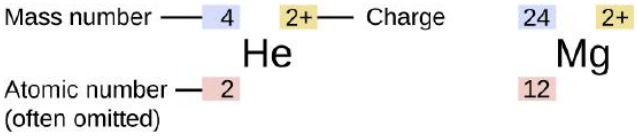


Figure **1.4.4**: The symbol for an atom indicates the element via its usual two-letter symbol, the mass number as a left superscript, the atomic number as a left subscript (sometimes omitted), and the charge as a right superscript.

This diagram shows the symbol for helium, "H e." The number to the upper left of the symbol is the mass number, which is 4. The number to the upper right of the symbol is the charge which is positive 2. The number to the lower left of the symbol is the atomic number, which is 2. This number is often omitted. Also shown is "M g" which stands for magnesium It has a mass number of 24, a charge of positive 2, and an atomic number of 12.

Information about the naturally occurring isotopes of elements with atomic numbers 1 through 10 is given in Table **1.4.2**. Note that in addition to standard names and symbols, the isotopes of hydrogen are often referred to using common names and accompanying symbols. Hydrogen-2, symbolized ^{2}H, is also called deuterium and sometimes symbolized D. Hydrogen-3, symbolized ^{3}H, is also called tritium and sometimes symbolized T.

Table **1.4.2**: Nuclear Compositions of Atoms of the Very Light Elements

Element	Symbol	Atomic Number	Number of Protons	Number of Neutrons	Mass (amu)	% Natural Abundance
hydrogen	$^{1}_{1}\mathrm{H}$ (protium)	1	1	0	1.0078	99.989
	$^{2}_{1}\mathrm{H}$ (deuterium)	1	1	1	2.0141	0.0115
	$^{3}_{1}\mathrm{H}$ (tritium)	1	1	2	3.01605	— (trace)
helium	$^{3}_{2}\mathrm{He}$	2	2	1	3.01603	0.00013
	$^{4}_{2}\mathrm{He}$	2	2	2	4.0026	100
lithium	$^{6}_{3}\mathrm{Li}$	3	3	3	6.0151	7.59
	$^{7}_{3}\mathrm{Li}$	3	3	4	7.0160	92.41
beryllium	$^{9}_{4}\mathrm{Be}$	4	4	5	9.0122	100
boron	$^{10}_{5}\mathrm{B}$	5	5	5	10.0129	19.9
	$^{11}_{5}\mathrm{B}$	5	5	6	11.0093	80.1
carbon	$^{12}_{6}\mathrm{C}$	6	6	6	12.0000	98.89
	$^{13}_{6}\mathrm{C}$	6	6	7	13.0034	1.11
	$^{14}_{6}\mathrm{C}$	6	6	8	14.0032	— (trace)
nitrogen	$^{14}_{7}\mathrm{N}$	7	7	7	14.0031	99.63
	$^{15}_{7}\mathrm{N}$	7	7	8	15.0001	0.37
oxygen	$^{16}_{8}\mathrm{O}$	8	8	8	15.9949	99.757
	$^{17}_{8}\mathrm{O}$	8	8	9	16.9991	0.038
	$^{18}_{8}\mathrm{O}$	8	8	10	17.9992	0.205
fluorine	$^{19}_{9}\mathrm{F}$	9	9	10	18.9984	100
neon	$^{20}_{10}\mathrm{Ne}$	10	10	10	19.9924	90.48
	$^{21}_{10}\mathrm{Ne}$	10	10	11	20.9938	0.27
	$^{22}_{10}\mathrm{Ne}$	10	10	12	21.9914	9.25

Atomic Mass

Because each proton and each neutron contribute approximately one amu to the mass of an atom, and each electron contributes far less, the atomic mass of a single atom is approximately equal to its mass number (a whole number). However, the average masses of atoms of most elements are not whole numbers because most elements exist naturally as mixtures of two or more isotopes.

The mass of an element shown in a periodic table or listed in a table of atomic masses is a weighted, average mass of all the isotopes present in a naturally occurring sample of that element. This is equal to the sum of each individual isotope's mass multiplied by its fractional abundance.

$$\text{average mass} = \sum_i (\text{fractional abundance} \times \text{isotopic mass})_i$$

For example, the element boron is composed of two isotopes: About 19.9% of all boron atoms are ^{10}B with a mass of 10.0129 amu, and the remaining 80.1% are ^{11}B with a mass of 11.0093 amu. The average atomic mass for boron is calculated to be:

$$\begin{aligned}\text{boron average mass} &= (0.199 \times 10.0129\ \text{amu}) + (0.801 \times 11.0093\ \text{amu}) \\ &= 1.99\ \text{amu} + 8.82\ \text{amu} \\ &= 10.81\ \text{amu}\end{aligned}$$

It is important to understand that no single boron atom weighs exactly 10.8 amu; 10.8 amu is the average mass of all boron atoms, and individual boron atoms weigh either approximately 10 amu or 11 amu.

✔ Example 1.4.2: Calculation of Average Atomic Mass

A meteorite found in central Indiana contains traces of the noble gas neon picked up from the solar wind during the meteorite's trip through the solar system. Analysis of a sample of the gas showed that it consisted of 91.84% ^{20}Ne (mass 19.9924 amu), 0.47% ^{21}Ne (mass 20.9940 amu), and 7.69% ^{22}Ne (mass 21.9914 amu). What is the average mass of the neon in the solar wind?

Solution

$$\begin{aligned}\text{average mass} &= (0.9184 \times 19.9924\ \text{amu}) + (0.0047 \times 20.9940\ \text{amu}) + (0.0769 \times 21.9914\ \text{amu}) \\ &= (18.36 + 0.099 + 1.69)\ \text{amu} \\ &= 20.15\ \text{amu}\end{aligned}$$

The average mass of a neon atom in the solar wind is 20.15 amu. (The average mass of a terrestrial neon atom is 20.1796 amu. This result demonstrates that we may find slight differences in the natural abundance of isotopes, depending on their origin.)

? Exercise 1.4.2

A sample of magnesium is found to contain 78.70% of ^{24}Mg atoms (mass 23.98 amu), 10.13% of ^{25}Mg atoms (mass 24.99 amu), and 11.17% of ^{26}Mg atoms (mass 25.98 amu). Calculate the average mass of a Mg atom.

Answer

24.31 amu

We can also do variations of this type of calculation, as shown in the next example.

✔ Example 1.4.3: Calculation of Percent Abundance

Naturally occurring chlorine consists of ^{35}Cl (mass 34.96885 amu) and ^{37}Cl (mass 36.96590 amu), with an average mass of 35.453 amu. What is the percent composition of Cl in terms of these two isotopes?

Solution

The average mass of chlorine is the fraction that is ^{35}Cl times the mass of ^{35}Cl plus the fraction that is ^{37}Cl times the mass of ^{37}Cl.

$$\text{average mass} = (\text{fraction of } ^{35}\text{Cl} \times \text{mass of } ^{35}\text{Cl}) + (\text{fraction of } ^{37}\text{Cl} \times \text{mass of } ^{37}\text{Cl})$$

If we let x represent the fraction that is ^{35}Cl, then the fraction that is ^{37}Cl is represented by $1.00 - x$.

(The fraction that is ^{35}Cl + the fraction that is ^{37}Cl must add up to 1, so the fraction of ^{37}Cl must equal 1.00 − the fraction of ^{35}Cl.)

Substituting this into the average mass equation, we have:

$$\begin{aligned}35.453\ \text{amu} &= (x \times 34.96885\ \text{amu}) + [(1.00 - x) \times 36.96590\ \text{amu}] \\ 35.453 &= 34.96885x + 36.96590 - 36.96590x \\ 1.99705x &= 1.513 \\ x &= \frac{1.513}{1.99705} = 0.7576\end{aligned}$$

So solving yields: $x = 0.7576$, which means that $1.00 - 0.7576 = 0.2424$. Therefore, chlorine consists of 75.76% ^{35}Cl and 24.24% ^{37}Cl.

? Exercise 1.4.3

Naturally occurring copper consists of ^{63}Cu (mass 62.9296 amu) and ^{65}Cu (mass 64.9278 amu), with an average mass of 63.546 amu. What is the percent composition of Cu in terms of these two isotopes?

Answer

69.15% Cu-63 and 30.85% Cu-65

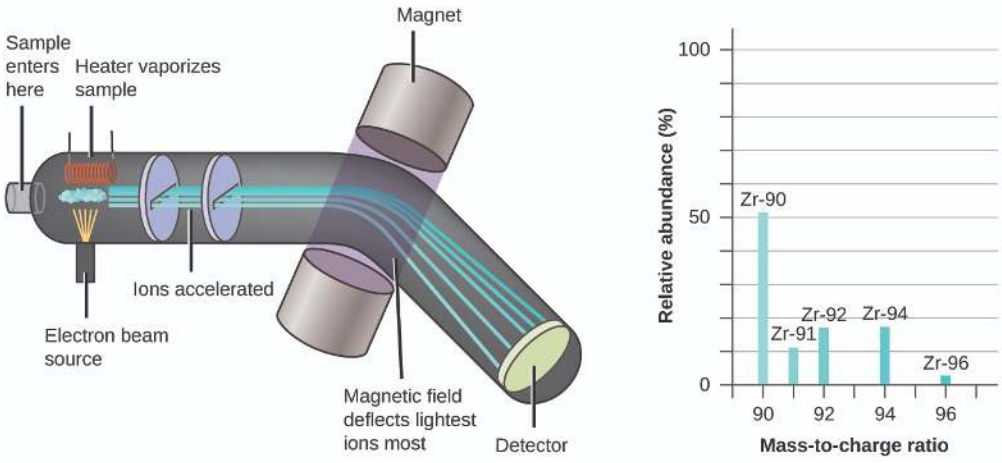


Figure **1.4.5**: Analysis of zirconium in a mass spectrometer produces a mass spectrum with peaks showing the different isotopes of Zr.

The left diagram shows how a mass spectrometer works. The graph to the right of the spectrometer shows a mass spectrum of zirconium. The relative abundance, as a percentage from 0 to 100, is graphed on the y axis, and the mass to charge ratio is graphed on the x axis. The sample contains five different isomers of zirconium.

The occurrence and natural abundances of isotopes can be experimentally determined using an instrument called a mass spectrometer. Mass spectrometry (MS) is widely used in chemistry, forensics, medicine, environmental science, and many other fields to analyze and help identify the substances in a sample of material. In a typical mass spectrometer (Figure **1.4.5**), the sample is vaporized and exposed to a high-energy electron beam that causes the sample's atoms (or molecules) to become electrically charged, typically by losing one or more electrons. These cations then pass through a (variable) electric or magnetic field that deflects each cation's path to an extent that depends on both its mass and charge (similar to how the path of a large steel ball bearing rolling past a magnet is deflected to a lesser extent that that of a small steel BB). The ions are detected, and a plot of the relative number of ions generated versus their mass-to-charge ratios (a *mass spectrum*) is made. The height of each vertical feature or peak in a mass spectrum is proportional to the fraction of cations with the specified mass-to-charge ratio. Since its initial use during the development of modern atomic theory, MS has evolved to become a powerful tool for chemical analysis in a wide range of applications.



Video* 1.4.1: Watch this video from the Royal Society for Chemistry for a brief description of the rudiments of mass spectrometry.*

Summary

An atom consists of a small, positively charged nucleus surrounded by electrons. The nucleus contains protons and neutrons; its diameter is about 100,000 times smaller than that of the atom. The mass of one atom is usually expressed in atomic mass units (amu), which is referred to as the atomic mass. An amu is defined as exactly $\mathbf{1/12}$ of the mass of a carbon-12 atom and is equal to 1.6605×10^{-24} g.

Protons are relatively heavy particles with a charge of 1+ and a mass of 1.0073 amu. Neutrons are relatively heavy particles with no charge and a mass of 1.0087 amu. Electrons are light particles with a charge of 1− and a mass of 0.00055 amu. The number of protons in the nucleus is called the atomic number (Z) and is the property that defines an atom's elemental identity. The sum of the numbers of protons and neutrons in the nucleus is called the mass number and, expressed in amu, is approximately equal to the mass of the atom. An atom is neutral when it contains equal numbers of electrons and protons.

Isotopes of an element are atoms with the same atomic number but different mass numbers; isotopes of an element, therefore, differ from each other only in the number of neutrons within the nucleus. When a naturally occurring element is composed of several isotopes, the atomic mass of the element represents the average of the masses of the isotopes involved. A chemical symbol identifies the atoms in a substance using symbols, which are one-, two-, or three-letter abbreviations for the atoms.

Key Equations

- $\textbf{average mass} = \sum_i (\textbf{fractional abundance} \times \textbf{isotopic mass})_i$

Glossary

anion
negatively charged atom or molecule (contains more electrons than protons)

atomic mass
average mass of atoms of an element, expressed in amu

atomic mass unit (amu)
(also, unified atomic mass unit, u, or Dalton, Da) unit of mass equal to $\frac{1}{12}$ of the mass of a ^{12}C atom

atomic number (Z)
number of protons in the nucleus of an atom

cation
positively charged atom or molecule (contains fewer electrons than protons)

chemical symbol

one-, two-, or three-letter abbreviation used to represent an element or its atoms

Dalton (Da)

alternative unit equivalent to the atomic mass unit

fundamental unit of charge

(also called the elementary charge) equals the magnitude of the charge of an electron (e) with $e = 1.602 \times 10^{-19}$ C

ion

electrically charged atom or molecule (contains unequal numbers of protons and electrons)

mass number (A)

sum of the numbers of neutrons and protons in the nucleus of an atom

unified atomic mass unit (u)

alternative unit equivalent to the atomic mass unit

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1.5: Chemical Formulas

Learning Objectives

- Symbolize the composition of molecules using molecular formulas and empirical formulas
- Represent the bonding arrangement of atoms within molecules using structural formulas

A molecular formula is a representation of 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 C atom and four H atoms, indicating the number of atoms in the molecule (Figure **1.5.1**). 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, simply know that the lines are an indication of 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.

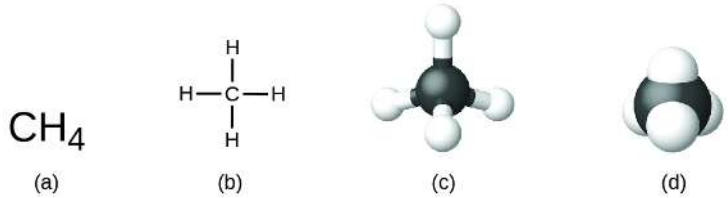


Figure **1.5.1**: A methane molecule can be represented as (a) a molecular formula, (b) a structural formula, (c) a ball-and-stick model, and (d) a space-filling model. Carbon and hydrogen atoms are represented by black and white spheres, respectively.

Figure A shows C H subscript 4. Figure B shows a carbon atom that is bonded to four hydrogen atoms at right angles: one above, one to the left, one to the right, and one below. Figure C shows a 3-D, ball-and-stick model of the carbon atom bonded to four hydrogen atoms. Figure D shows a space-filling model of a carbon atom with hydrogen atoms partially embedded into the surface of the carbon atom.

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 **1.5.2**).

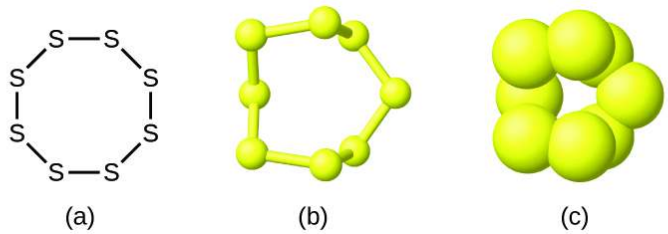


Figure **1.5.2**: A molecule of sulfur is composed of eight sulfur atoms and is therefore written as S_8. It can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. Sulfur atoms are represented by yellow spheres.

Figure A shows eight sulfur atoms, symbolized with the letter S, that are bonded to each other to form an octagon. Figure B shows a 3-D, ball-and-stick model of the arrangement of the sulfur atoms. The shape is clearly not octagonal as it is represented in the structural formula. Figure C is a space-filling model that shows each sulfur atom is partially embedded into the sulfur atom it bonds with.

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. H_2 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 **1.5.3**).

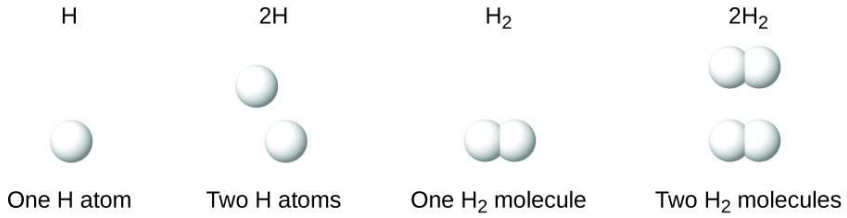


Figure **1.5.3**: The symbols H, 2H, H_2, and $2H_2$ represent very different entities.

This figure shows four diagrams. The diagram for H shows a single, white sphere and is labeled one H atom. The diagram for 2 H shows two white spheres that are not bonded together. It is labeled 2 H atoms. The diagram for H subscript 2 shows two white spheres bonded together. It is labeled one H subscript 2 molecule. The diagram for 2 H subscript 2 shows two sets of bonded, white spheres. It is labeled 2 H subscript 2 molecules.

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 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 **1.5.4**).

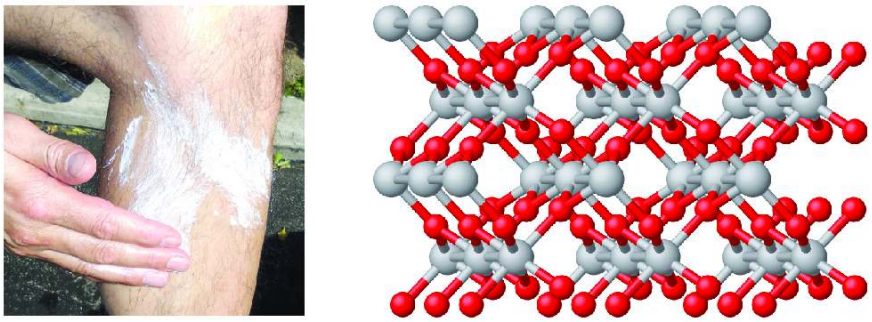


Figure **1.5.4**: (a) The white compound titanium dioxide provides effective protection from the sun. (b) A crystal of titanium dioxide, TiO_2, contains titanium and oxygen in a ratio of 1 to 2. The titanium atoms are gray and the oxygen atoms are red. (credit a: modification of work by “osseous”/Flickr).

Figure A shows a photo of a person applying suntan lotion to his or her lower leg. Figure B shows a 3-D ball-and-stick model of the molecule titanium dioxide, which involves a complicated interlocking of many titanium and oxygen atoms. The titanium atoms in the molecule are shown as silver spheres and the oxygen atoms are shown as red spheres. There are twice as many oxygen atoms as titanium atoms in the molecule.

As discussed previously, we can describe a compound with a molecular formula, in which the subscripts indicate the *actual numbers of atoms* of each element in a molecule of the compound. In many cases, the molecular formula of a substance is derived from experimental determination of both its empirical formula and its molecular mass (the sum of atomic masses for all atoms composing the molecule). For example, it can be determined experimentally that benzene contains two elements, carbon (C) and hydrogen (H), and that for every carbon atom in benzene, there is one hydrogen atom. Thus, the empirical formula is CH. An experimental determination of the molecular mass reveals that a molecule of benzene contains six carbon atoms and six hydrogen atoms, so the molecular formula for benzene is C_6H_6 (Figure **1.5.5**).

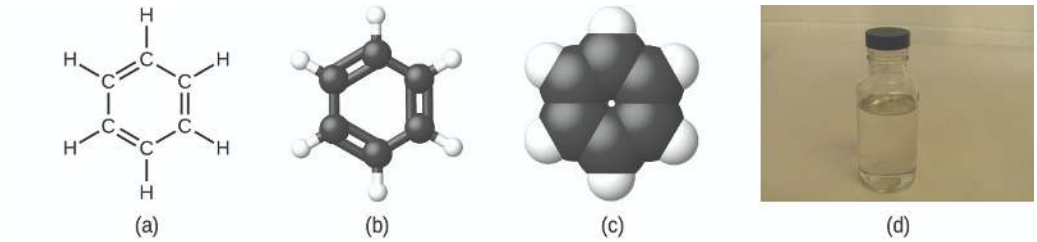


Figure **1.5.5**: Benzene, C_6H_6, is produced during oil refining and has many industrial uses. A benzene molecule can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. (d) Benzene is a clear liquid. (credit d: modification of work by Sahar Atwa).

Figure A shows that benzene is composed of six carbons shaped like a hexagon. Every other bond between the carbon atoms is a double bond. Each carbon also has a single bonded hydrogen atom. Figure B shows a 3-D, ball-and-stick drawing of benzene. The six carbon atoms are black spheres while the six hydrogen atoms are smaller, white spheres. Figure C is a space-filling model of benzene which shows that most of the interior space is occupied by the carbon atoms. The hydrogen atoms are embedded in the outside surface of the carbon atoms. Figure d shows a small vial filled with benzene which appears to be clear.

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 **1.5.6**) 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.

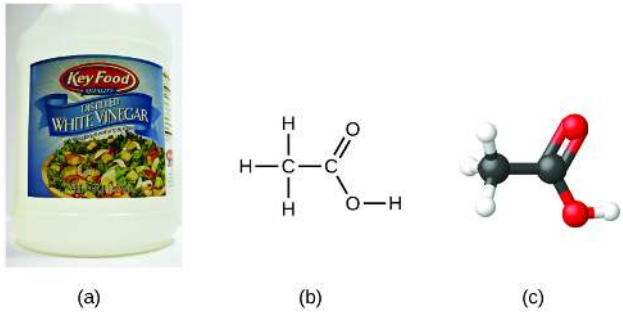


Figure **1.5.6**: (a) Vinegar contains acetic acid, $C_2H_4O_2$, which has an empirical formula of CH_2O. It can be represented as (b) a structural formula and (c) as a ball-and-stick model. (credit a: modification of work by "HomeSpot HQ"/Flickr)

Figure A shows a jug of distilled, white vinegar. Figure B shows a structural formula for acetic acid which contains two carbon atoms connected by a single bond. The left carbon atom forms single bonds with three hydrogen atoms. The right carbon atom forms a double bond with an oxygen atom. The right carbon atom also forms a single bond with an oxygen atom. This oxygen forms a single bond with a hydrogen atom. Figure C shows a 3-D ball-and-stick model of acetic acid.

✔ Example 1.5.1: Empirical and Molecular Formulas

Molecules of glucose (blood sugar) contain 6 carbon atoms, 12 hydrogen atoms, and 6 oxygen atoms. What are the molecular and empirical formulas of glucose?

Solution

The molecular formula is $C_6H_{12}O_6$ because one molecule actually contains 6 C, 12 H, and 6 O atoms. The simplest whole-number ratio of C to H to O atoms in glucose is 1:2:1, so the empirical formula is CH_2O.

? Exercise 1.5.1

A molecule of metaldehyde (a pesticide used for snails and slugs) contains 8 carbon atoms, 16 hydrogen atoms, and 4 oxygen atoms. What are the molecular and empirical formulas of metaldehyde?

Answer

Molecular formula, $C_8H_{16}O_4$; empirical formula, C_2H_4O

It is important to be aware that it may be possible for the same atoms to be arranged in different ways: Compounds with the same molecular formula may have different atom-to-atom bonding and therefore different structures. For example, could there be another compound with the same formula as acetic acid, $C_2H_4O_2$? And if so, what would be the structure of its molecules?

If you predict that another compound with the formula $C_2H_4O_2$ could exist, then you demonstrated good chemical insight and are correct. Two C atoms, four H atoms, and two O atoms can also be arranged to form methyl formate, which is used in manufacturing, as an insecticide, and for quick-drying finishes. Methyl formate molecules have one of the oxygen atoms between the two carbon atoms, differing from the arrangement in acetic acid molecules. Acetic acid and methyl formate are examples of isomers—compounds with the same chemical formula but different molecular structures (Figure **1.5.7**). Note that this small difference in the arrangement of the atoms has a major effect on their respective chemical properties. You would certainly not want to use a solution of methyl formate as a substitute for a solution of acetic acid (vinegar) when you make salad dressing.

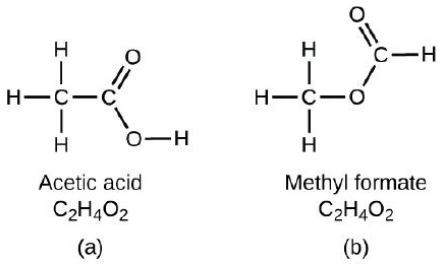


Figure **1.5.7**: Molecules of (a) acetic acid and methyl formate (b) are structural isomers; they have the same formula ($C_2H_4O_2$) but different structures (and therefore different chemical properties).

Figure A shows a structural diagram of acetic acid, C subscript 2 H subscript 4 O subscript 2. Acetic acid contains two carbon atoms connected by a single bond. The left carbon atom forms single bonds with three hydrogen atoms. The carbon on the right forms a double bond with an oxygen atom. The right carbon atom also forms a single bond to an oxygen atom which forms a single bond with a hydrogen atom. Figure B shows a structural diagram of methyl formate, C subscript 2 H subscript 4 O subscript 2. This molecule contains a carbon atom which forms single bonds with three hydrogen atoms, and a single bond with an oxygen atom. The oxygen atom forms a single bond with another carbon atom which forms a double bond with another oxygen atom and a single bond with a hydrogen atom.

Many types of isomers exist (Figure **1.5.8**). Acetic acid and methyl formate are structural isomers, compounds in which the molecules differ in how the atoms are connected to each other. There are also various types of spatial isomers, in which the relative orientations of the atoms in space can be different. For example, the compound carvone (found in caraway seeds, spearmint, and mandarin orange peels) consists of two isomers that are mirror images of each other. *S*-(+)-carvone smells like caraway, and *R*-(−)-carvone smells like spearmint.

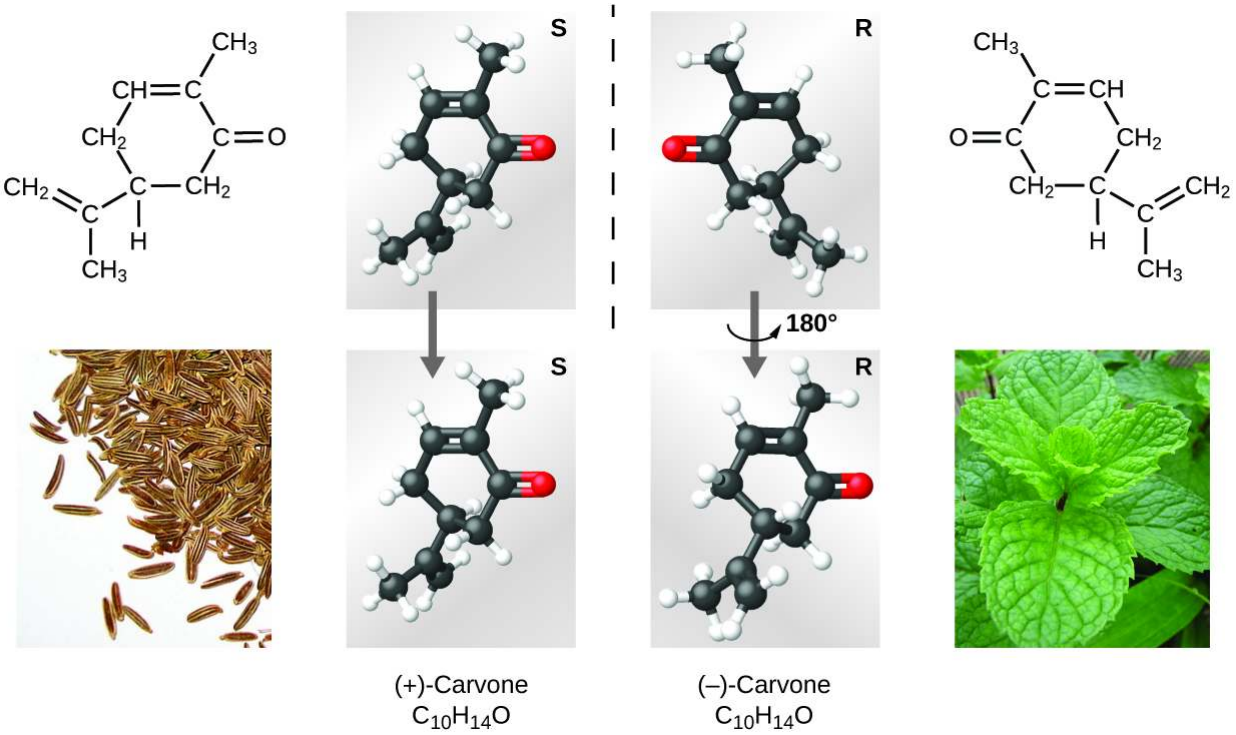


Figure **1.5.8**: Molecules of carvone are spatial isomers; they only differ in the relative orientations of the atoms in space. (credit bottom left: modification of work by "Miansari66"/Wikimedia Commons; credit bottom right: modification of work by Forest & Kim Starr)

Summary

A molecular formula uses chemical symbols and subscripts to indicate the exact numbers of different atoms in a molecule or compound. An empirical formula gives the simplest, whole-number ratio of atoms in a compound. A structural formula indicates the bonding arrangement of the atoms in the molecule. Ball-and-stick and space-filling models show the geometric arrangement of atoms in a molecule. Isomers are compounds with the same molecular formula but different arrangements of atoms.

Glossary

empirical formula
formula showing the composition of a compound given as the simplest whole-number ratio of atoms

isomers
compounds with the same chemical formula but different structures

molecular formula
formula indicating the composition of a molecule of a compound and giving the actual number of atoms of each element in a molecule of the compound.

spatial isomers
compounds in which the relative orientations of the atoms in space differ

structural isomer
one of two substances that have the same molecular formula but different physical and chemical properties because their atoms are bonded differently

structural formula

shows the atoms in a molecule and how they are connected

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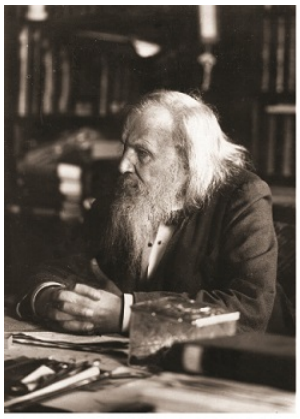
1.6: The Periodic Table

Learning Objectives

- State the periodic law and explain the organization of elements in the periodic table
- Predict the general properties of elements based on their location within the periodic table
- Identify metals, nonmetals, and metalloids by their properties and/or location on the periodic table

As early chemists worked to purify ores and discovered more elements, they realized that various elements could be grouped together 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 also are 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 are 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.

Dimitri Mendeleev in Russia (1869) and Lothar Meyer in Germany (1870) independently recognized that there was a periodic relationship among the properties of the elements known at that time. Both published tables with the elements arranged according to increasing atomic mass. But Mendeleev went one step further than Meyer: He used his table to predict the existence of elements that would have the properties similar to aluminum and silicon, but were yet unknown. The discoveries of gallium (1875) and germanium (1886) provided great support for Mendeleev's work. Although Mendeleev and Meyer had a long dispute over priority, Mendeleev's contributions to the development of the periodic table are now more widely recognized (Figure **1.6.1**).



(a)

Reihen	Gruppo I. — R²O	Gruppo II. — RO	Gruppo III. — R²O³	Gruppo IV. RH⁴ RO²	Gruppo V. RH³ R²O⁵	Gruppo VI. RH² RO³	Gruppo VII. RH R²O⁷	Gruppo VIII. — RO⁴
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	—=68	—=72	As=75	Se=78	Br=80	
6	Rb=86	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=231	—	U=240	—	— — — —

(b)

Figure **1.6.1**: (a) Dimitri Mendeleev is widely credited with creating (b) the first periodic table of the elements. (credit a: modification of work by Serge Lachinov; credit b: modification of work by “Den fjättrade ankan”/Wikimedia Commons)

Figure A shows a photograph of Dimitri Mendeleev. Figure B shows the first periodic table developed by Mendeleev, which had eight groups and twelve periods. In the first group (—, R superscript plus sign 0) is the following information: H = 1, L i = 7, N a = 23, K = 39, (C u = 63), R b = 85, (A g = 108), C a = 183, (—),—, (A u = 199) —. Note that each of these entries corresponds to one of the twelve periods respectively. The second group (—, R 0) contains the following information: (not entry for period 1) B o = 9, 4, M g = 24, C a = 40, Z n = 65, S r = 87, C d = 112, B a = 187, —, —, H g = 200, —. Note the ach of these entries corresponds to one of the twelve periods respectively. Group three (—, R superscript one 0 superscript nine) contains the information: (no entry for period 1), B = 11, A l = 27, 8. — = 44, — = 68, ? Y t = 88, I n = 113, ? D I = 138, —, ? E r = 178, T l = 204, —. Note that each of these entries corresponds to one of the twelve periods respectively. Group four (RH superscript four, R0 superscript eight) contains the following information: (no entry for period 1), C = 12, B i = 28, T i = 48, — = 72, Z r = 90, S n = 118, ? C o = 140, ? L a = 180, P b = 207, T h = 231. Note that each of these entries corresponds to one of the twelve periods respectively. Group five (R H superscript two, R superscript two 0 superscript five) contains the following information: (no entry for period 1), N = 14, P = 31, V = 51, A s = 75, N b = 94, S b = 122, —, —, T a = 182, B l = 208, —. Note that each of these entries corresponds to one of the twelve periods respectively. Group six (R H superscript two, R 0 superscript three) contains the following information: (no entry for period 1), O = 16, S = 32, C r = 52, S o = 78, M o = 96, T o = 125, —, —, W = 184, —, U = 240. Note that each of these entries corresponds to one of the twelve periods respectively. Group seven (R H , R superscript plus sing, 0 superscript 7) contains the following information: (no entry for period 1), F = 19, C l = 35, 5, M n = 55, B r = 80, — = 100, J = 127, —, —, —, —, —. Note that each of these entries corresponds to one of the twelve periods respectively. Group 8 (—, R 0 superscript four) contains the following information: (no entry for periods 1, 2, 3), in period 4: F o = 56, C o = 59, N i = 59, C u = 63, no entry for period five, in period 6: R u = 104, R h = 104, P d = 106, A g = 108, no entries for periods 7, 8 , or 9, in period 10: O s = 195, I r = 197, P t = 198, A u = 199, no entries for periods 11 or 12.

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 **1.6.2**). 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.

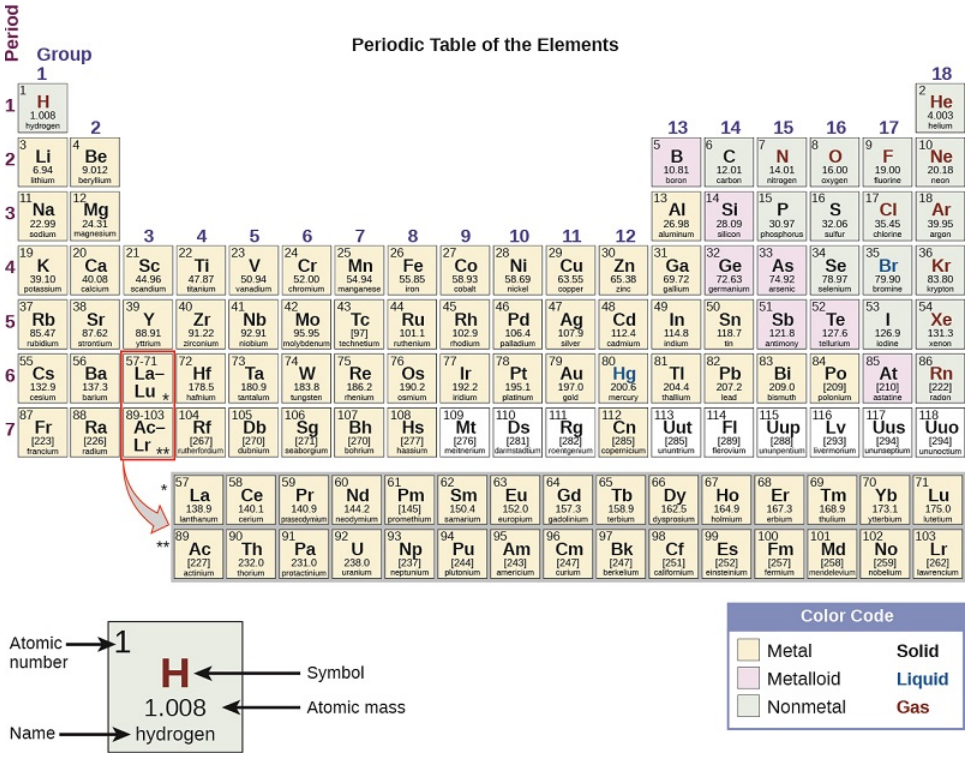


Figure 1.6.2: Elements in the periodic table are organized according to their properties.

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The Periodic Table of Elements is shown. The 18 columns are labeled “Group” and the 7 rows are labeled “Period.” Below the table to the right is a box labeled “Color Code” with different colors for metals, metalloids, and nonmetals, as well as solids, liquids, and gases. To the left of this box is an enlarged picture of the upper-left most box on the table. The number 1 is in its upper-left hand corner and is labeled “Atomic number.” The letter “H” is in the middle in red indicating that it is a gas. It is labeled “Symbol.” Below that is the number 1.008 which is labeled “Atomic Mass.” Below that is the word hydrogen which is labeled “name.” The color of the box indicates that it is a nonmetal. Each element will be described in this order: atomic number; name; symbol; whether it is a metal, metalloid, or nonmetal; whether it is a solid, liquid, or gas; and atomic mass. Beginning at the top left of the table, or period 1, group 1, is a box containing “1; hydrogen; H; nonmetal; gas; and 1.008.” There is only one other element box in period 1, group 18, which contains “2; helium; H e; nonmetal; gas; and 4.003.” Period 2, group 1 contains “3; lithium; L i; metal; solid; and 6.94” Group 2 contains “4; beryllium; B e; metal; solid; and 9.012.” Groups 3 through 12 are skipped and group 13 contains “5; boron; B; metalloid; solid; 10.81.” Group 14 contains “6; carbon; C; nonmetal; solid; and 12.01.” Group 15 contains “7; nitrogen; N; nonmetal; gas; and 14.01.” Group 16 contains “8; oxygen; O; nonmetal; gas; and 16.00.” Group 17 contains “9; fluorine; F; nonmetal; gas; and 19.00.” Group 18 contains “10; neon; N e; nonmetal; gas; and 20.18.” Period 3, group 1 contains “11; sodium; N a; metal; solid; and 22.99.” Group 2 contains “12; magnesium; M g; metal; solid; and 24.31.” Groups 3 through 12 are skipped again in period 3 and group 13 contains “13; aluminum; A l; metal; solid; and 26.98.” Group 14 contains “14; silicon; S i; metalloid; solid; and 28.09.” Group 15 contains “15; phosphorous; P; nonmetal; solid; and 30.97.” Group 16 contains “16; sulfur; S; nonmetal; solid; and 32.06.” Group 17 contains “17; chlorine; C l; nonmetal; gas; and 35.45.” Group 18 contains “18; argon; A r; nonmetal; gas; and 39.95.” Period 4, group 1 contains “19; potassium; K; metal; solid; and 39.10.” Group 2 contains “20; calcium; C a; metal; solid; and 40.08.” Group 3 contains “21; scandium; S c; metal; solid; and 44.96.” Group 4 contains “22; titanium; T i; metal; solid; and 47.87.” Group 5 contains “23; vanadium; V; metal; solid; and 50.94.” Group 6 contains “24; chromium; C r; metal; solid; and 52.00.” Group 7 contains “25; manganese; M n; metal; solid; and 54.94.” Group 8 contains “26; iron; F e; metal; solid; and 55.85.” Group 9 contains “27; cobalt; C o; metal; solid; and 58.93.” Group 10 contains “28; nickel; N i; metal; solid; and 58.69.” Group 11 contains “29; copper; C u; metal; solid; and 63.55.” Group 12 contains “30; zinc; Z n; metal; solid; and 65.38.” Group 13 contains “31; gallium; G a; metal; solid; and 69.72.” Group 14 contains “32; germanium; G e; metalloid; solid; and 72.63.” Group 15 contains “33; arsenic; A s; metalloid; solid; and 74.92.” Group 16 contains “34; selenium; S e; nonmetal; solid; and 78.97.” Group 17 contains “35; bromine; B r; nonmetal; liquid; and 79.90.” Group 18 contains “36; krypton; K r; nonmetal; gas; and 83.80.” Period 5, group 1 contains “37; rubidium; R b; metal; solid; and 85.47.” Group 2 contains “38; strontium; S r; metal; solid; and 87.62.” Group 3 contains “39; yttrium; Y; metal; solid; and 88.91.” Group 4 contains “40; zirconium; Z r; metal; solid; and 91.22.” Group 5 contains “41; niobium; N b; metal; solid; and 92.91.” Group 6 contains “42; molybdenum; M o; metal; solid; and 95.95.” Group 7 contains “43; technetium; T c; metal; solid; and 97.” Group 8 contains “44; ruthenium; R u; metal; solid; and 101.1.” Group 9 contains “45; rhodium; R h; metal; solid; and 102.9.” Group 10 contains “46; palladium; P d; metal; solid; and 106.4.” Group 11 contains “47; silver; A g; metal; solid; and 107.9.” Group 12 contains “48; cadmium; C d; metal; solid; and 112.4.” Group 13 contains “49; indium; I n; metal; solid; and 114.8.” Group 14 contains “50; tin; S n; metal; solid; and 118.7.” Group 15 contains “51; antimony; S b; metalloid; solid; and 121.8.” Group 16 contains “52; tellurium; T e; metalloid; solid; and 127.6.” Group 17 contains “53; iodine; I; nonmetal; solid; and 126.9.” Group 18 contains “54; xenon; X e; nonmetal; gas; and 131.3.” Period 6, group 1 contains “55; cesium; C s; metal; solid; and 132.9.” Group 2 contains “56; barium; B a; metal; solid; and 137.3.” Group 3 breaks the pattern. The box has a large arrow pointing to a row of elements below the table with atomic numbers ranging from 57-71. In sequential order by atomic number, the first box in this row contains “57; lanthanum; L a; metal; solid; and 138.9.” To its right, the next is “58; cerium; C e; metal; solid; and 140.1.” Next is “59; praseodymium; P r; metal; solid; and 140.9.” Next is “60; neodymium; N d; metal; solid; and 144.2.” Next is “61; promethium; P m; metal; solid; and 145.” Next is “62; samarium; S m; metal; solid; and 150.4.” Next is “63; europium; E u; metal; solid; and 152.0.” Next is “64; gadolinium; G d; metal; solid; and 157.3.” Next is “65; terbium; T b; metal; solid; and 158.9.” Next is “66; dysprosium; D y; metal; solid; and 162.5.” Next is “67; holmium; H o; metal; solid; and 164.9.” Next is “68; erbium; E r; metal; solid; and 167.3.” Next is “69; thulium; T m; metal; solid; and 168.9.” Next is “70; ytterbium; Y b; metal; solid; and 173.1.” The last in this special row is “71; lutetium; L u; metal; solid; and 175.0.” Continuing in period 6, group 4 contains “72; hafnium; H f; metal; solid; and 178.5.” Group 5 contains “73; tantalum; T a; metal; solid; and 180.9.” Group 6 contains “74; tungsten; W; metal; solid; and 183.8.” Group 7 contains “75; rhenium; R e; metal; solid; and 186.2.” Group 8 contains “76; osmium; O s; metal; solid; and 190.2.” Group 9 contains “77; iridium; I r; metal; solid; and 192.2.” Group 10 contains “78; platinum; P t; metal; solid; and 195.1.” Group 11 contains “79; gold; A u; metal; solid; and 197.0.” Group 12 contains “80; mercury; H g; metal; liquid; and 200.6.” Group 13 contains “81; thallium; T l; metal; solid; and 204.4.” Group 14 contains “82; lead; P b; metal; solid; and 207.2.” Group 15 contains “83; bismuth; B i; metal; solid; and 209.0.” Group 16 contains “84; polonium; P o; metal; solid; and 209.” Group 17 contains “85; astatine; A t; metalloid; solid; and 210.” Group 18 contains “86; radon; R n; nonmetal; gas; and 222.” Period 7, group 1 contains “87; francium; F r; metal; solid; and 223.” Group 2 contains “88; radium; R a; metal; solid; and 226.” Group 3 breaks the pattern much like what occurs in period 6. A large arrow points from the box in period 7, group 3 to a special row containing the elements with atomic numbers ranging from 89-103, just below the row which contains atomic numbers 57-71. In sequential order by atomic number, the first box in this row contains “89; actinium; A c; metal; solid; and 227.” To its right, the next is “90; thorium; T h; metal; solid; and 232.0.” Next is “91; protactinium; P a; metal; solid; and 231.0.” Next is “92; uranium; U; metal; solid; and 238.0.” Next is “93; neptunium; N p; metal; solid; and N p.” Next is “94; plutonium; P u; metal; solid; and 244.” Next is “95; americium; A m; metal; solid; and 243.” Next is “96; curium; C m; metal; solid; and 247.” Next is “97; berkelium; B k; metal; solid; and 247.” Next is “98; californium; C f; metal; solid; and 251.” Next is “99; einsteinium; E s; metal; solid; and 252.” Next is “100; fermium; F m; metal; solid; and 257.” Next is “101; mendelevium; M d; metal; solid; and 258.” Next is “102; nobelium; N o; metal; solid; and 259.” The last in this special row is “103; lawrencium; L r; metal; solid; and 262.” Continuing in period 7, group 4 contains “104; rutherfordium; R f; metal; solid; and 267.” Group 5 contains “105; dubnium; D b; metal; solid; and 270.” Group 6 contains “106; seaborgium; S g; metal; solid; and 271.” Group 7 contains “107; bohrium; B h; metal; solid; and 270.” Group 8 contains “108; hassium; H s; metal; solid; and 277.” Group 9 contains “109; meitnerium; M t; not

indicated; solid; and 276.” Group 10 contains “110; darmstadtium; D s; not indicated; solid; and 281.” Group 11 contains “111; roentgenium; R g; not indicated; solid; and 282.” Group 12 contains “112; copernicium; C n; metal; liquid; and 285.” Group 13 contains “113; ununtrium; U u t; not indicated; solid; and 285.” Group 14 contains “114; flerovium; F l; not indicated; solid; and 289.” Group 15 contains “115; ununpentium; U u p; not indicated; solid; and 288.” Group 16 contains “116; livermorium; L v; not indicated; solid; and 293.” Group 17 contains “117; ununseptium; U u s; not indicated; solid; and 294.” Group 18 contains “118; ununoctium; U u o; not indicated; solid; and 294.”

Many elements differ dramatically in their chemical and physical properties, but some elements are similar in their behaviors. For example, many elements appear shiny, are malleable (able to be deformed without breaking) and ductile (can be drawn into wires), and conduct heat and electricity well. Other elements are not shiny, malleable, or ductile, and are poor conductors of heat and electricity. We can sort the elements into large classes with common properties: metals (elements that are shiny, malleable, good conductors of heat and electricity—shaded yellow); nonmetals (elements that appear dull, poor conductors of heat and electricity—shaded green); and metalloids (elements that conduct heat and electricity moderately well, and possess some properties of metals and some properties of nonmetals—shaded purple).

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 **1.6.3**). 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 the 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 1 and group 17 elements. For that reason, hydrogen may be shown at the top of both groups, or by itself.

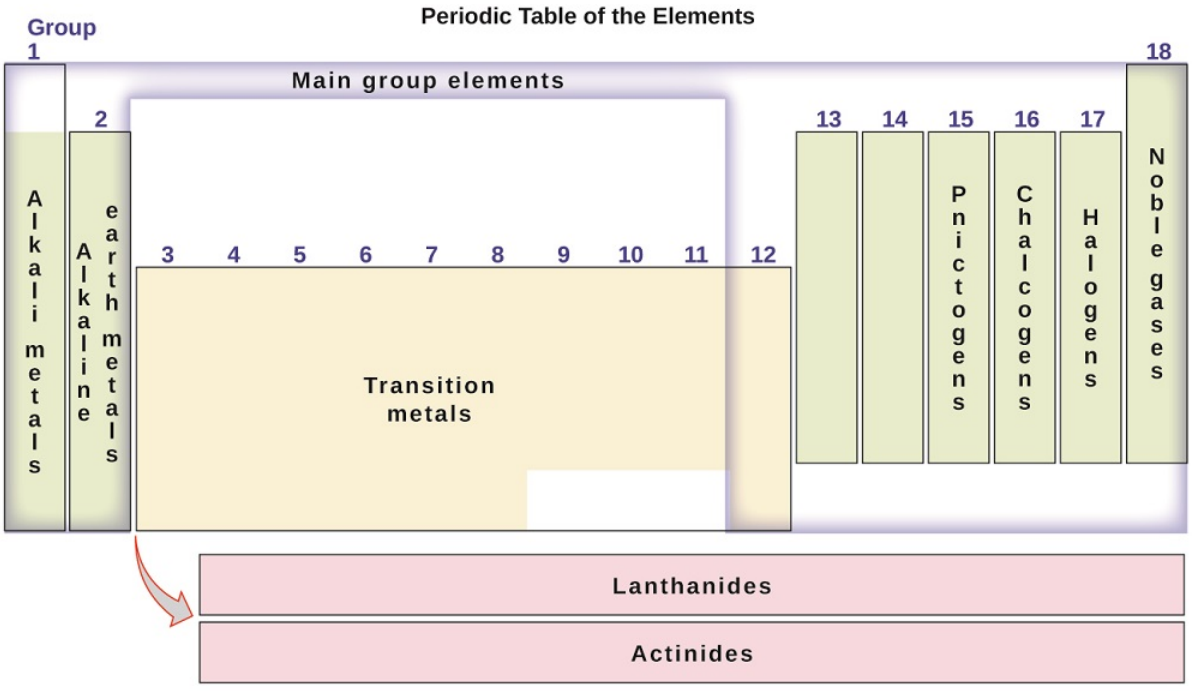


Figure **1.6.3**: The periodic table organizes elements with similar properties into groups.

This diagram combines the groups and periods of the periodic table based on their similar properties. Group 1 contains the alkali metals, group 2 contains the earth alkaline metals, group 15 contains the pnictogens, group 16 contains the chalcogens, group 17 contains the halogens and group 18 contains the noble gases. The main group elements consist of groups 1, 2, and 12 through 18. Therefore, most of the transition metals, which are contained in groups 3 through 11, are not main group elements. The lanthanides and actinides are called out at the bottom of the periodic table.

Example 1.6.1: Naming Groups of Elements

Atoms of each of the following elements are essential for life. Give the group name for the following elements:

a. chlorine
b. calcium
c. sodium
d. sulfur

Solution

The family names are as follows:

a. halogen
b. alkaline earth metal
c. alkali metal
d. chalcogen

Exercise 1.6.1

Give the group name for each of the following elements:

a. krypton
b. selenium
c. barium
d. lithium

Answer a

noble gas

Answer b

chalcogen

Answer c

alkaline earth metal

Answer d

alkali metal

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.

Summary

The discovery of the periodic recurrence of similar properties among the elements led to the formulation of the periodic table, in which the elements are arranged in order of increasing atomic number in rows known as periods and columns known as groups. Elements in the same group of the periodic table have similar chemical properties. Elements can be classified as metals, metalloids, and nonmetals, or as a main-group elements, transition metals, and inner transition metals. Groups are numbered 1–18 from left to right. The elements in group 1 are known as the alkali metals; those in group 2 are the alkaline earth metals; those in 15 are the pnictogens; those in 16 are the chalcogens; those in 17 are the halogens; and those in 18 are the noble gases.

Glossary

actinide
inner transition metal in the bottom of the bottom two rows of the periodic table

alkali metal
element in group 1

alkaline earth metal
element in group 2

chalcogen
element in group 16

group
vertical column of the periodic table

halogen
element in group 17

inert gas
(also, noble gas) element in group 18

inner transition metal
(also, lanthanide or actinide) element in the bottom two rows; if in the first row, also called lanthanide, or if in the second row, also called actinide

lanthanide
inner transition metal in the top of the bottom two rows of the periodic table

main-group element
(also, representative element) element in columns 1, 2, and 12–18

metal
element that is shiny, malleable, good conductor of heat and electricity

metalloid
element that conducts heat and electricity moderately well, and possesses some properties of metals and some properties of nonmetals

noble gas
(also, inert gas) element in group 18

nonmetal
element that appears dull, poor conductor of heat and electricity

period
(also, series) horizontal row of the periodic table

periodic law
properties of the elements are periodic function of their atomic numbers.

periodic table
table of the elements that places elements with similar chemical properties close together

pnictogen

element in group 15

representative element

(also, main-group element) element in columns 1, 2, and 12–18

transition metal

element in columns 3–11

series

(also, period) horizontal row of the period table

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1.7: Molecular and Ionic Compounds

Learning Objectives

- Define ionic and molecular (covalent) compounds
- Predict the type of compound formed from elements based on their location within the periodic table
- Determine formulas for simple ionic compounds

In ordinary chemical reactions, the nucleus of each atom (and thus the identity of the element) remains unchanged. Electrons, however, can be added to atoms by transfer from other atoms, lost by transfer to other atoms, or shared with other atoms. The transfer and sharing of electrons among atoms govern the chemistry of the elements. During the formation of some compounds, atoms gain or lose electrons, and form electrically charged particles called ions (Figure **1.7.1**).

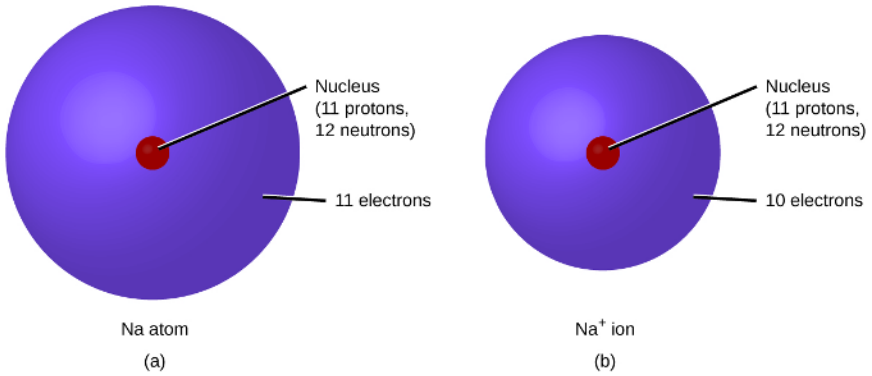


Figure **1.7.1**: (a) A sodium atom (Na) has equal numbers of protons and electrons (11) and is uncharged. (b) A sodium cation (Na^+) has lost an electron, so it has one more proton (11) than electrons (10), giving it an overall positive charge, signified by a superscripted plus sign.

Figure A shows a sodium atom which has a nucleus containing 11 protons, 12 neutrons, and 11 electrons. Figure B shows a sodium ion. Its nucleus contains 11 protons, 12 neutrons, and 11 electrons.

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 calcium atom, with 20 protons and 20 electrons, readily loses two electrons. This results in a cation with 20 protons, 18 electrons, and a 2+ charge. It has the same number of electrons as atoms of the preceding noble gas, argon, and is symbolized Ca^{2+}. The name of a metal ion is the same as the name of the metal atom from which it forms, so Ca^{2+} is called a calcium 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 bromine atom, with 35 protons and 35 electrons, can gain one electron to provide it with 36 electrons. This results in an anion with 35 protons, 36 electrons, and a 1− charge. It has the same number of electrons as atoms of the next noble gas, krypton, and is symbolized Br^-. (A discussion of the theory supporting the favored status of noble gas electron numbers reflected in these predictive rules for ion formation is provided in a later chapter of this text.)

Note the usefulness of the periodic table in predicting likely ion formation and charge (Figure **1.7.2**). Moving from the far left to the right on the periodic table, main-group elements tend to form cations with a charge equal to the group number. That is, group 1 elements form 1+ ions; group 2 elements form 2+ ions, and so on. Moving from the far right to the left on the periodic table, elements often form anions with a negative charge equal to the number of groups moved left from the noble gases. For example, group 17 elements (one group left of the noble gases) form 1− ions; group 16 elements (two groups left) form 2− ions, and so on. This trend can be used as a guide in many cases, but its predictive value decreases when moving toward the center of the periodic

table. In fact, transition metals and some other metals often exhibit variable charges that are not predictable by their location in the table. For example, copper can form ions with a 1+ or 2+ charge, and iron can form ions with a 2+ or 3+ charge.

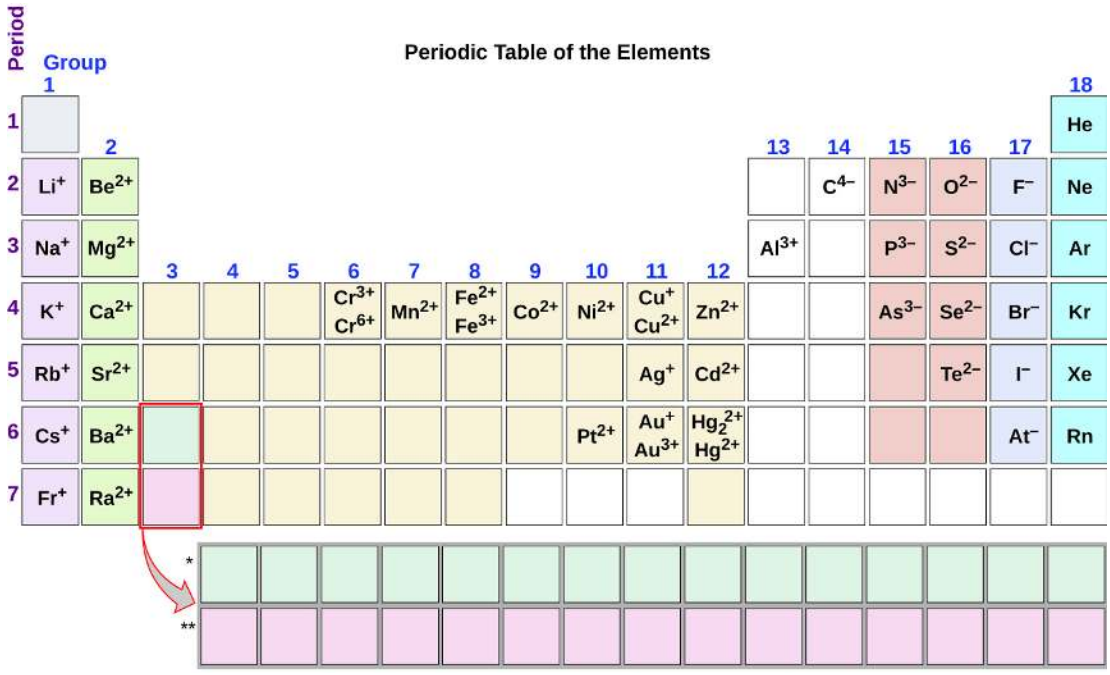


Figure 1.7.2: Some elements exhibit a regular pattern of ionic charge when they form ions.

This periodic table shows the charges of ions corresponding with the group number. Starting with a charge of positive one for group 1, positive 2 for group 2, and negative 4, 3, 2, and 1 for groups 14, 15, 16, and 17 respectively. Noble gases on the far right do not have any charges. Some of the ions of transition metals are shown, with multiple charges existing for certain metals.

Example 1.7.1: Composition of Ions

An ion found in some compounds used as antiperspirants contains 13 protons and 10 electrons. What is its symbol?

Solution

Because the number of protons remains unchanged when an atom forms an ion, the atomic number of the element must be 13. Knowing this lets us use the periodic table to identify the element as Al (aluminum). The Al atom has lost three electrons and thus has three more positive charges (13) than it has electrons (10). This is the aluminum cation, Al^{3+}.

Exercise 1.7.1

Give the symbol and name for the ion with 34 protons and 36 electrons.

Answer

Se^{2-}, the selenide ion

Example 1.7.2: Formation of Ions

Magnesium and nitrogen react to form an ionic compound. Predict which forms an anion, which forms a cation, and the charges of each ion. Write the symbol for each ion and name them.

Solution

Magnesium's position in the periodic table (group 2) tells us that it is a metal. Metals form positive ions (cations). A magnesium atom must lose two electrons to have the same number electrons as an atom of the previous noble gas, neon. Thus, a magnesium atom will form a cation with two fewer electrons than protons and a charge of 2+. The symbol for the ion is Mg^{2+}, and it is called a magnesium ion.

Nitrogen's position in the periodic table (group 15) reveals that it is a nonmetal. Nonmetals form negative ions (anions). A nitrogen atom must gain three electrons to have the same number of electrons as an atom of the following noble gas, neon. Thus, a nitrogen atom will form an anion with three more electrons than protons and a charge of 3−. The symbol for the ion is N^{3-}, and it is called a nitride ion.

? Exercise 1.7.2

Aluminum and carbon react to form an ionic compound. Predict which forms an anion, which forms a cation, and the charges of each ion. Write the symbol for each ion and name them.

Answer

Al will form a cation with a charge of 3+: Al^{3+}, an aluminum ion. Carbon will form an anion with a charge of 4−: C^{4-}, a carbide ion.

The ions that we have discussed so far are called monatomic ions, that is, they 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 **1.7.1**. Oxyanions are polyatomic ions that contain one or more oxygen atoms. At this point in your study of chemistry, 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.

Table **1.7.1**: Common Polyatomic Ions

Name	Formula	Related Acid	Formula
ammonium	NH_4^+		
hydronium	H_3O^+		
oxide	O^{2-}		
peroxide	O_2^{2-}		
hydroxide	OH^-		
acetate	CH_3COO^-	acetic acid	CH_3COOH
cyanide	CN^-	hydrocyanic acid	HCN
azide	N_3^-	hydrazoic acid	HN_3
carbonate	CO_3^{2-}	carbonic acid	H_2CO_3
bicarbonate	HCO_3^-		
nitrate	NO_3^-	nitric acid	HNO_3
nitrite	NO_2^-	nitrous acid	HNO_2
sulfate	SO_4^{2-}	sulfuric acid	H_2SO_4
hydrogen sulfate	HSO_4^-		
sulfite	SO_3^{2-}	sulfurous acid	H_2SO_3
hydrogen sulfite	HSO_3^-		
phosphate	PO_4^{3-}	phosphoric acid	H_3PO_4
hydrogen phosphate	HPO_4^{2-}		
dihydrogen phosphate	$H_2PO_4^-$		
perchlorate	ClO_4^-	perchloric acid	$HClO_4$
chlorate	ClO_3^-	chloric acid	$HClO_3$
chlorite	ClO_2^-	chlorous acid	$HClO_2$
hypochlorite	ClO^-	hypochlorous acid	$HClO$
chromate	CrO_4^{2-}	chromic acid	H_2CrO_4
dichromate	$Cr_2O_7^{2-}$	dichromic acid	$H_2Cr_2O_7$
permanganate	MnO_4^-	permanganic acid	$HMnO_4$

Note that there is a system for naming some polyatomic ions; *-ate* and *-ite* are suffixes 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) on the basis of 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 sodium cation, Na^+, and each chlorine atom in a sample of chlorine gas (group 17) accepts one electron to form a chloride anion, Cl^-, the resulting compound, NaCl, is composed of sodium ions and chloride ions in the ratio of one Na^+ ion for each Cl^- ion. Similarly, each calcium atom (group 2) can give up two electrons and transfer one to each of two chlorine atoms to form $CaCl_2$, which is composed of Ca^{2+} and Cl^- ions in the ratio of one Ca^{2+} ion to two Cl^- 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 compounds that are ionic: When a metal is combined with one or more nonmetals, the compound is usually ionic. This guideline works well for predicting ionic compound formation for most of the compounds typically encountered in an introductory chemistry course. 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 are able to move freely through the liquid (Figure **1.7.3**).

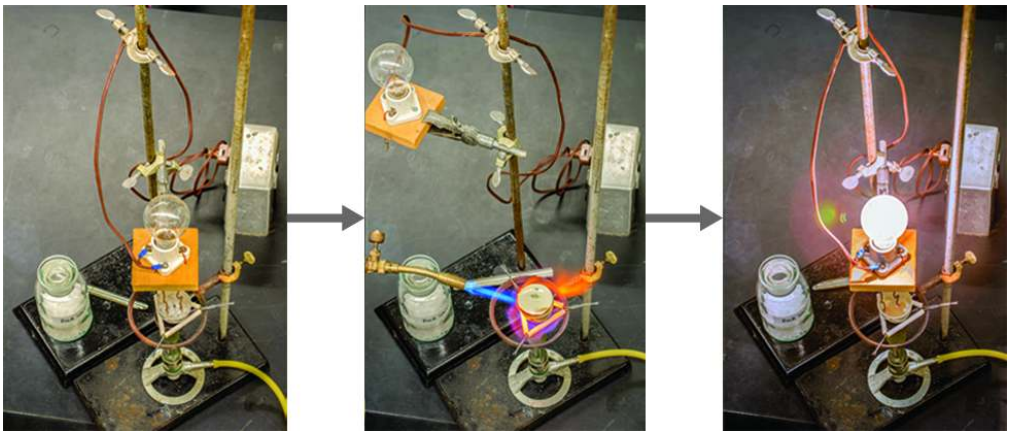


Figure **1.7.3**: Sodium chloride melts at 801 °C and conducts electricity when molten. (credit: modification of work by Mark Blaser and Matt Evans)

This figure shows three photos connected by right-facing arrows. The first shows a light bulb as part of a complex lab equipment setup. The light bulb is not lit. The second photo shows a substances being heated or set on fire. The third shows the light bulb again which is lit.

In every ionic compound, the total number of positive charges of the cations equals the total number of negative charges of the anions. Thus, ionic compounds are electrically neutral overall, even though they contain positive and negative ions. We can use this observation to help us write the formula of an ionic compound. The formula of an ionic compound must have a ratio of ions such that the numbers of positive and negative charges are equal.

Example **1.7.3**: Predicting the Formula of an Ionic Compound

The gemstone sapphire (Figure **1.7.4**) is mostly a compound of aluminum and oxygen that contains aluminum cations, Al^{3+}, and oxygen anions, O^{2-}. What is the formula of this compound?



Figure **1.7.4**: Although pure aluminum oxide is colorless, trace amounts of iron and titanium give blue sapphire its characteristic color. (credit: modification of work by Stanislav Doronenko)

Solution Because the ionic compound must be electrically neutral, it must have the same number of positive and negative charges. Two aluminum ions, each with a charge of 3+, would give us six positive charges, and three oxide ions, each with a charge of 2−, would give us six negative charges. The formula would be Al_2O_3.

? Exercise 1.7.3

Predict the formula of the ionic compound formed between the sodium cation, Na^+, and the sulfide anion, S^{2-}.

Answer

Na_2S

Many ionic compounds contain polyatomic ions (Table **1.7.1**) as the cation, the anion, or both. As with simple ionic compounds, these compounds must also be electrically neutral, so their formulas can be predicted by treating the polyatomic ions as discrete units. We use parentheses in a formula to indicate a group of atoms that behave as a unit. For example, the formula for calcium phosphate, one of the minerals in our bones, is $Ca_3(PO_4)_2$. This formula indicates that there are three calcium ions (Ca^{2+}) for every two phosphate ($\mathbf{PO_4^{3-}}$) groups. The $\mathbf{PO_4^{3-}}$ groups are discrete units, each consisting of one phosphorus atom and four oxygen atoms, and having an overall charge of 3−. The compound is electrically neutral, and its formula shows a total count of three Ca, two P, and eight O atoms.

✓ Example 1.7.4: Predicting the Formula of a Compound with a Polyatomic Anion

Baking powder contains calcium dihydrogen phosphate, an ionic compound composed of the ions Ca^{2+} and $\mathbf{H_2PO_4^-}$. What is the formula of this compound?

Solution

The positive and negative charges must balance, and this ionic compound must be electrically neutral. Thus, we must have two negative charges to balance the 2+ charge of the calcium ion. This requires a ratio of one Ca^{2+} ion to two $\mathbf{H_2PO_4^-}$ ions. We designate this by enclosing the formula for the dihydrogen phosphate ion in parentheses and adding a subscript 2. The formula is $Ca(H_2PO_4)_2$.

? Exercise 1.7.4

Predict the formula of the ionic compound formed between the lithium ion and the peroxide ion, $\mathbf{O_2^{2-}}$ (Hint: Use the periodic table to predict the sign and the charge on the lithium ion.)

Answer

Li_2O_2

Because an ionic compound is not made up of single, discrete molecules, it may not be properly symbolized using a *molecular* formula. Instead, ionic compounds must be symbolized by a formula indicating the *relative numbers* of its constituent ions. For compounds containing only monatomic ions (such as NaCl) and for many compounds containing polyatomic ions (such as $CaSO_4$), these formulas are just the empirical formulas introduced earlier in this chapter. However, the formulas for some ionic compounds containing polyatomic ions are not empirical formulas. For example, the ionic compound sodium oxalate is comprised of Na^+ and

$C_2O_4^{2-}$ ions combined in a 2:1 ratio, and its formula is written as $Na_2C_2O_4$. The subscripts in this formula are not the smallest-possible whole numbers, as each can be divided by 2 to yield the empirical formula, $NaCO_2$. This is not the accepted formula for sodium oxalate, however, as it does not accurately represent the compound's polyatomic anion, $C_2O_4^{2-}$.

Molecular Compounds

Many compounds do not contain ions but instead consist solely of discrete, neutral molecules. These molecular compounds (covalent compounds) result when atoms share, rather than transfer (gain or lose), electrons. Covalent bonding is an important and extensive concept in chemistry, and it will be treated in considerable detail in a later chapter of this text. We can often identify molecular compounds on the basis of 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 compounds that are covalent. While we can use the positions of a compound's elements in the periodic table to predict whether it is ionic or covalent at this point in our study of chemistry, you should be aware that this is a very simplistic approach that does not account for a number of interesting exceptions. Shades of gray exist between ionic and molecular compounds, and you'll learn more about those later.

✔ Example 1.7.5: Predicting the Type of Bonding in Compounds

Predict whether the following compounds are ionic or molecular:

a. KI, the compound used as a source of iodine in table salt
b. H_2O_2, the bleach and disinfectant hydrogen peroxide
c. $CHCl_3$, the anesthetic chloroform
d. Li_2CO_3, a source of lithium in antidepressants

Solution

a. Potassium (group 1) is a metal, and iodine (group 17) is a nonmetal; KI is predicted to be ionic.
b. Hydrogen (group 1) is a nonmetal, and oxygen (group 16) is a nonmetal; H_2O_2 is predicted to be molecular.
c. Carbon (group 14) is a nonmetal, hydrogen (group 1) is a nonmetal, and chlorine (group 17) is a nonmetal; $CHCl_3$ is predicted to be molecular.
d. Lithium (group 1) is a metal, and carbonate is a polyatomic ion; Li_2CO_3 is predicted to be ionic.

? Exercise 1.7.5

Using the periodic table, predict whether the following compounds are ionic or covalent:

a. SO_2
b. CaF_2
c. N_2H_4
d. $Al_2(SO_4)_3$

Answer a

molecular

Answer b

ionic

Answer c

molecular

Answer d

ionic

Summary

Metals (particularly those in groups 1 and 2) tend to lose the number of electrons that would leave them with the same number of electrons as in the preceding noble gas in the periodic table. By this means, a positively charged ion is formed. Similarly, nonmetals (especially those in groups 16 and 17, and, to a lesser extent, those in Group 15) can gain the number of electrons needed to provide atoms with the same number of electrons as in the next noble gas in the periodic table. Thus, nonmetals tend to form negative ions. Positively charged ions are called cations, and negatively charged ions are called anions. Ions can be either monatomic (containing only one atom) or polyatomic (containing more than one atom).

Compounds that contain ions are called ionic compounds. Ionic compounds generally form from metals and nonmetals. Compounds that do not contain ions, but instead consist of atoms bonded tightly together in molecules (uncharged groups of atoms that behave as a single unit), are called covalent compounds. Covalent compounds usually form from two or more nonmetals.

Glossary

covalent bond
attractive force between the nuclei of a molecule's atoms and pairs of electrons between the atoms

covalent compound
(also, molecular compound) composed of molecules formed by atoms of two or more different elements

ionic bond
electrostatic forces of attraction between the oppositely charged ions of an ionic compound

ionic compound
compound composed of cations and anions combined in ratios, yielding an electrically neutral substance

molecular compound
(also, covalent compound) composed of molecules formed by atoms of two or more different elements

monatomic ion
ion composed of a single atom

polyatomic ion
ion composed of more than one atom

oxyanion
polyatomic anion composed of a central atom bonded to oxygen atoms

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1.8: Chemical Nomenclature

Learning Objectives

- Derive names for common types of inorganic compounds using a systematic approach.
- Describe how to name binary covalent compounds including acids and oxyacids.

Nomenclature, a collection of rules for naming things, is important in science and in many other situations. This module describes an approach that is used to name simple ionic and molecular compounds, such as NaCl, $CaCO_3$, and N_2O_4. The simplest of these are binary compounds, those containing only two elements, but we will also consider how to name ionic compounds containing polyatomic ions, and one specific, very important class of compounds known as acids (subsequent chapters in this text will focus on these compounds in great detail). We will limit our attention here to inorganic compounds, compounds that are composed principally of elements other than carbon, and will follow the nomenclature guidelines proposed by IUPAC. The rules for organic compounds, in which carbon is the principle element, will be treated in a later chapter on organic chemistry.

Ionic Compounds

To name an inorganic compound, we need to consider the answers to several questions. First, is the compound ionic or molecular? If the compound is ionic, does the metal form ions of only one type (fixed charge) or more than one type (variable charge)? Are the ions monatomic or polyatomic? If the compound is molecular, does it contain hydrogen? If so, does it also contain oxygen? From the answers we derive, we place the compound in an appropriate category and then name it accordingly. We will begin with the nomenclature rules for ionic compounds.

Compounds Containing Only Monatomic Ions

The name of a binary compound containing monatomic ions consists of the name of the cation (the name of the metal) followed by the name of the anion (the name of the nonmetallic element with its ending replaced by the suffix *–ide*). Some examples are given in Table **1.8.2**.

Table **1.8.1**: Names of Some Ionic Compounds

NaCl, sodium chloride	Na_2O, sodium oxide
KBr, potassium bromide	CdS, cadmium sulfide
CaI_2, calcium iodide	Mg_3N_2, magnesium nitride
CsF, cesium fluoride	Ca_3P_2, calcium phosphide
LiCl, lithium chloride	Al_4C_3, aluminum carbide

Compounds Containing Polyatomic Ions

Compounds containing polyatomic ions are named similarly to those containing only monatomic ions, except there is no need to change to an *–ide* ending, since the suffix is already present in the name of the anion. Examples are shown in Table **1.8.2**.

CL, ammonium chloride, C a S O subscript 4 calcium sulfate, and M g subscript 3 (P O subscript 4) subscript 2 magnesium phosphate." data-quail-id="54" data-mt-width="1246">

Table **1.8.2**: Names of Some Polyatomic Ionic Compounds

$KC_2H_3O_2$, potassium acetate	$(NH_4)Cl$, ammonium chloride
$NaHCO_3$, sodium bicarbonate	$CaSO_4$, calcium sulfate
$Al_2(CO_3)_3$, aluminum carbonate	$Mg_3(PO_4)_2$, magnesium phosphate

Ionic Compounds in Your Cabinets

Every day you encounter and use a large number of ionic compounds. Some of these compounds, where they are found, and what they are used for are listed in Table **1.8.3**. Look at the label or ingredients list on the various products that you use during the next few days, and see if you run into any of those in this table, or find other ionic compounds that you could now name or write as a formula.

Table **1.8.3**: Everyday Ionic Compounds

Ionic Compound	Name	Use
NaCl	sodium chloride	ordinary table salt
KI	potassium iodide	added to “iodized” salt for thyroid health
NaF	sodium fluoride	ingredient in toothpaste
$NaHCO_3$	sodium bicarbonate	baking soda; used in cooking (and in antacids)
Na_2CO_3	sodium carbonate	washing soda; used in cleaning agents
NaOCl	sodium hypochlorite	active ingredient in household bleach
$CaCO_3$	calcium carbonate	ingredient in antacids
$Mg(OH)_2$	magnesium hydroxide	ingredient in antacids
$Al(OH)_3$	aluminum hydroxide	ingredient in antacids
NaOH	sodium hydroxide	lye; used as drain cleaner
K_3PO_4	potassium phosphate	food additive (many purposes)
$MgSO_4$	magnesium sulfate	added to purified water
Na_2HPO_4	sodium hydrogen phosphate	anti-caking agent; used in powdered products
Na_2SO_3	sodium sulfite	preservative

Compounds Containing a Metal Ion with a Variable Charge

Most of the transition metals can form two or more cations with different charges. Compounds of these metals with nonmetals are named with the same method as compounds in the first category, except the charge of the metal ion is specified by a Roman numeral in parentheses after the name of the metal. The charge of the metal ion is determined from the formula of the compound and the charge of the anion. For example, consider binary ionic compounds of iron and chlorine. Iron typically exhibits a charge of either 2+ or 3+, and the two corresponding compound formulas are $FeCl_2$ and $FeCl_3$. The simplest name, “iron chloride,” will, in this case, be ambiguous, as it does not distinguish between these two compounds. In cases like this, the charge of the metal ion is included as a Roman numeral in parentheses immediately following the metal name. These two compounds are then unambiguously named iron(II) chloride and iron(III) chloride, respectively. Other examples are provided in Table **1.8.4**.

Table **1.8.4**: Names of Some Transition Metal Ionic Compounds

Transition Metal Ionic Compound	Name
$FeCl_3$	iron(III) chloride
Hg_2O	mercury(I) oxide
HgO	mercury(II) oxide
$Cu_3(PO_4)_2$	copper(II) phosphate

Out-of-date nomenclature used the suffixes *–ic* and *–ous* to designate metals with higher and lower charges, respectively: Iron(III) chloride, $FeCl_3$, was previously called ferric chloride, and iron(II) chloride, $FeCl_2$, was known as ferrous chloride. Though this naming convention has been largely abandoned by the scientific community, it remains in use by some segments of industry. For example, you may see the words *stannous fluoride* on a tube of toothpaste. This represents the formula SnF_2, which is more properly named tin(II) fluoride. The other fluoride of tin is SnF_4, which was previously called stannic fluoride but is now named tin(IV) fluoride.

Example 1.8.1: Naming Ionic Compounds

Name the following ionic compounds, which contain a metal that can have more than one ionic charge:

a. Fe_2S_3
b. CuSe
c. GaN
d. $CrCl_3$
e. $Ti_2(SO_4)_3$

Solution

The anions in these compounds have a fixed negative charge (S^{2-}, Se^{2-} , N^{3-}, Cl^-, and SO_4^{2-}), and the compounds must be neutral. Because the total number of positive charges in each compound must equal the total number of negative charges, the positive ions must be Fe^{3+}, Cu^{2+}, Ga^{3+}, Cr^{3+}, and Ti^{3+}. These charges are used in the names of the metal ions:

a. iron(III) sulfide
b. copper(II) selenide
c. gallium(III) nitride
d. chromium(III) chloride
e. titanium(III) sulfate

Exercise 1.8.1

Write the formulas of the following ionic compounds:

a. chromium(III) phosphide
b. mercury(II) sulfide
c. manganese(II) phosphate
d. copper(I) oxide
e. chromium(VI) fluoride

Answer a

CrP

Answer b

HgS

Answer c

$Mn_3(PO_4)_2$

Answer d

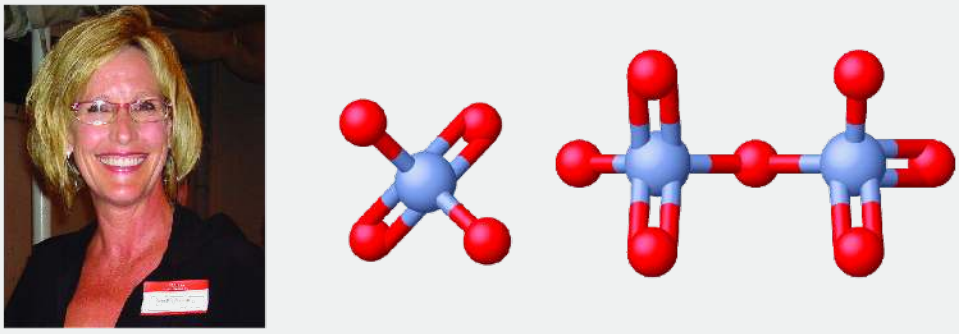
Cu_2O

Answer e

CrF_6

Erin Brokovich and Chromium Contamination

In the early 1990s, legal file clerk Erin Brockovich (Figure **1.8.2**) discovered a high rate of serious illnesses in the small town of Hinckley, California. Her investigation eventually linked the illnesses to groundwater contaminated by Cr(VI) used by Pacific Gas & Electric (PG&E) to fight corrosion in a nearby natural gas pipeline. As dramatized in the film *Erin Brokovich* (for which Julia Roberts won an Oscar), Erin and lawyer Edward Masry sued PG&E for contaminating the water near Hinckley in 1993. The settlement they won in 1996—$333 million—was the largest amount ever awarded for a direct-action lawsuit in the US at that time.



(a) (b)

Figure **1.8.2**: (a) Erin Brockovich found that Cr(VI), used by PG&E, had contaminated the Hinckley, California, water supply. (b) The Cr(VI) ion is often present in water as the polyatomic ions chromate, CrO_4^{2-} (left), and dichromate, $Cr_2O_7^{2-}$ (right).

Chromium compounds are widely used in industry, such as for chrome plating, in dye-making, as preservatives, and to prevent corrosion in cooling tower water, as occurred near Hinckley. In the environment, chromium exists primarily in either the Cr(III) or Cr(VI) forms. Cr(III), an ingredient of many vitamin and nutritional supplements, forms compounds that are not very soluble in water, and it has low toxicity. Cr(VI), on the other hand, is much more toxic and forms compounds that are reasonably soluble in water. Exposure to small amounts of Cr(VI) can lead to damage of the respiratory, gastrointestinal, and immune systems, as well as the kidneys, liver, blood, and skin.

Despite cleanup efforts, Cr(VI) groundwater contamination remains a problem in Hinckley and other locations across the globe. A 2010 study by the Environmental Working Group found that of 35 US cities tested, 31 had higher levels of Cr(VI) in their tap water than the public health goal of 0.02 parts per billion set by the California Environmental Protection Agency.

Molecular (Covalent) Compounds

The bonding characteristics of inorganic molecular compounds are different from ionic compounds, and they are named using a different system as well. The charges of cations and anions dictate their ratios in ionic compounds, so specifying the names of the ions provides sufficient information to determine chemical formulas. However, because covalent bonding allows for significant variation in the combination ratios of the atoms in a molecule, the names for molecular compounds must explicitly identify these ratios.

Compounds Composed of Two Elements

When two nonmetallic elements form a molecular compound, several combination ratios are often possible. For example, carbon and oxygen can form the compounds CO and CO_2. Since these are different substances with different properties, they cannot both have the same name (they cannot both be called carbon oxide). To deal with this situation, we use a naming method that is somewhat similar to that used for ionic compounds, but with added prefixes to specify the numbers of atoms of each element. The name of the more metallic element (the one farther to the left and/or bottom of the periodic table) is first, followed by the name of the more nonmetallic element (the one farther to the right and/or top) with its ending changed to the suffix *–ide*. The numbers of atoms of each element are designated by the Greek prefixes shown in Table **1.8.5**.

Table **1.8.5**: Nomenclature Prefixes

Number	Prefix		Number	Prefix
1 (sometimes omitted)	mono-		6	hexa-
2	di-		7	hepta-
3	tri-		8	octa-
4	tetra-		9	nona-
5	penta-		10	deca-

When only one atom of the first element is present, the prefix *mono-* is usually deleted from that part. Thus, **CO** is named carbon monoxide, and **CO_2** is called carbon dioxide. When two vowels are adjacent, the *a* in the Greek prefix is usually dropped. Some other examples are shown in Table **1.8.6**.

Table **1.8.6**: Names of Some Molecular Compounds Composed of Two Elements

Compound	Name		Compound	Name
SO_2	sulfur dioxide		BCl_3	boron trichloride
SO_3	sulfur trioxide		SF_6	sulfur hexafluoride
NO_2	nitrogen dioxide		PF_5	phosphorus pentafluoride
N_2O_4	dinitrogen tetroxide		P_4O_{10}	tetraphosphorus decaoxide
N_2O_5	dinitrogen pentoxide		IF_7	iodine heptafluoride

There are a few common names that you will encounter as you continue your study of chemistry. For example, although NO is often called nitric oxide, its proper name is nitrogen monoxide. Similarly, N_2O is known as nitrous oxide even though our rules would specify the name dinitrogen monoxide. (And H_2O is usually called water, not dihydrogen monoxide.) You should commit to memory the common names of compounds as you encounter them.

✔ Example 1.8.2: Naming Covalent Compounds

Name the following covalent compounds:

a. SF_6
b. N_2O_3
c. Cl_2O_7
d. P_4O_6

Solution

Because these compounds consist solely of nonmetals, we use prefixes to designate the number of atoms of each element:

a. sulfur hexafluoride
b. dinitrogen trioxide
c. dichlorine heptoxide
d. tetraphosphorus hexoxide

? Exercise 1.8.2

Write the formulas for the following compounds:

a. phosphorus pentachloride
b. dinitrogen monoxide

c. iodine heptafluoride
d. carbon tetrachloride

Answer a

PCl_5

Answer b

N_2O

Answer c

IF_7

Answer d

CCl_4

Binary Acids

Some compounds containing hydrogen are members of an important class of substances known as acids. The chemistry of these compounds is explored in more detail in later chapters of this text, but for now, it will suffice to note that many acids release hydrogen ions, H^+, when dissolved in water. To denote this distinct chemical property, a mixture of water with an acid is given a name derived from the compound's name. If the compound is a binary acid (comprised of hydrogen and one other nonmetallic element):

1. The word "hydrogen" is changed to the prefix *hydro-*
2. The other nonmetallic element name is modified by adding the suffix *-ic*
3. The word "acid" is added as a second word

For example, when the gas **HCl** (hydrogen chloride) is dissolved in water, the solution is called *hydrochloric acid*. Several other examples of this nomenclature are shown in Table **1.8.7**.

Table **1.8.7**: Names of Some Simple Acids

Name of Gas	Name of Acid
HF(*g*), hydrogen fluoride	HF(*aq*), hydrofluoric acid
HCl(*g*), hydrogen chloride	HCl(*aq*), hydrochloric acid
HBr(*g*), hydrogen bromide	HBr(*aq*), hydrobromic acid
HI(*g*), hydrogen iodide	HI(*aq*), hydroiodic acid
H_2S(*g*), hydrogen sulfide	H_2S(*aq*), hydrosulfuric acid

Oxyacids

Many compounds containing three or more elements (such as organic compounds or coordination compounds) are subject to specialized nomenclature rules that you will learn later. However, we will briefly discuss the important compounds known as oxyacids, compounds that contain hydrogen, oxygen, and at least one other element, and are bonded in such a way as to impart acidic properties to the compound (you will learn the details of this in a later chapter). Typical oxyacids consist of hydrogen combined with a polyatomic, oxygen-containing ion. To name oxyacids:

1. Omit "hydrogen"
2. Start with the root name of the anion
3. Replace *–ate* with *–ic*, or *–ite* with *–ous*
4. Add "acid"

For example, consider H_2CO_3 (which you might be tempted to call “hydrogen carbonate”). To name this correctly, “hydrogen” is omitted; the *–ate* of carbonate is replace with *–ic*; and acid is added—so its name is carbonic acid. Other examples are given in Table **1.8.8**. There are some exceptions to the general naming method (e.g., H_2SO_4 is called sulfuric acid, not sulfic acid, and H_2SO_3 is sulfurous, not sulfous, acid).

Table **1.8.8**: Names of Common Oxyacids

Formula	Anion Name	Acid Name
$HC_2H_3O_2$	acetate	acetic acid
HNO_3	nitrate	nitric acid
HNO_2	nitrite	nitrous acid
$HClO_4$	perchlorate	perchloric acid
H_2CO_3	carbonate	carbonic acid
H_2SO_4	sulfate	sulfuric acid
H_2SO_3	sulfite	sulfurous acid
H_3PO_4	phosphate	phosphoric acid

Summary

Chemists use nomenclature rules to clearly name compounds. Ionic and molecular compounds are named using somewhat-different methods. Binary ionic compounds typically consist of a metal and a nonmetal. The name of the metal is written first, followed by the name of the nonmetal with its ending changed to *–ide*. For example, K_2O is called potassium oxide. If the metal can form ions with different charges, a Roman numeral in parentheses follows the name of the metal to specify its charge. Thus, $FeCl_2$ is iron(II) chloride and $FeCl_3$ is iron(III) chloride. Some compounds contain polyatomic ions; the names of common polyatomic ions should be memorized. Molecular compounds can form compounds with different ratios of their elements, so prefixes are used to specify the numbers of atoms of each element in a molecule of the compound. Examples include SF_6, sulfur hexafluoride, and N_2O_4, dinitrogen tetroxide. Acids are an important class of compounds containing hydrogen and having special nomenclature rules. Binary acids are named using the prefix *hydro-*, changing the *–ide* suffix to *–ic*, and adding “acid;” HCl is hydrochloric acid. Oxyacids are named by changing the ending of the anion (*-ate* to *–ic*, and *-ite* to *-ous*) and adding “acid;” H_2CO_3 is carbonic acid.

Glossary

binary acid
: compound that contains hydrogen and one other element, bonded in a way that imparts acidic properties to the compound (ability to release H^+ ions when dissolved in water)

binary compound
: compound containing two different elements.

oxyacid
: compound that contains hydrogen, oxygen, and one other element, bonded in a way that imparts acidic properties to the compound (ability to release H^+ ions when dissolved in water)

nomenclature
: system of rules for naming objects of interest

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1.E: Atoms, Molecules, and Ions (Exercises)

2.1: Early Ideas in Atomic Theory

In the following drawing, the green spheres represent atoms of a certain element. The purple spheres represent atoms of another element. If the spheres of different elements touch, they are part of a single unit of a compound. The following chemical change represented by these spheres may violate one of the ideas of Dalton's atomic theory. Which one?


This equation contains the starting materials of a single, green sphere plus two smaller, purple spheres bonded together. When the starting materials are added together the products of the change are one purple sphere bonded with one green sphere plus one purple sphere bonded with one green sphere.

The starting materials consist of one green sphere and two purple spheres. The products consist of two green spheres and two purple spheres. This violates Dalton's postulate that that atoms are not created during a chemical change, but are merely redistributed.

Which postulate of Dalton's theory is consistent with the following observation concerning the weights of reactants and products? When 100 grams of solid calcium carbonate is heated, 44 grams of carbon dioxide and 56 grams of calcium oxide are produced.

Identify the postulate of Dalton's theory that is violated by the following observations: 59.95% of one sample of titanium dioxide is titanium; 60.10% of a different sample of titanium dioxide is titanium.

This statement violates Dalton's fourth postulate: In a given compound, the numbers of atoms of each type (and thus also the percentage) always have the same ratio.

Samples of compound X, Y, and Z are analyzed, with results shown here.

Compound	Description	Mass of Carbon	Mass of Hydrogen
X	clear, colorless, liquid with strong odor	1.776 g	0.148 g
Y	clear, colorless, liquid with strong odor	1.974 g	0.329 g
Z	clear, colorless, liquid with strong odor	7.812 g	0.651 g

Do these data provide example(s) of the law of definite proportions, the law of multiple proportions, neither, or both? What do these data tell you about compounds X, Y, and Z?

2.2: Evolution of Atomic Theory

Exercises

1. The existence of isotopes violates one of the original ideas of Dalton's atomic theory. Which one?
2. How are electrons and protons similar? How are they different?
3. How are protons and neutrons similar? How are they different?
4. Predict and test the behavior of α particles fired at a "plum pudding" model atom.
    a. Predict the paths taken by α particles that are fired at atoms with a Thomson's plum pudding model structure. Explain why you expect the α particles to take these paths.
    b. If α particles of higher energy than those in (a) are fired at plum pudding atoms, predict how their paths will differ from the lower-energy α particle paths. Explain your reasoning.
    c. Now test your predictions from (a) and (b). Open the Rutherford Scattering simulation and select the "Plum Pudding Atom" tab. Set "Alpha Particles Energy" to "min," and select "show traces." Click on the gun to start firing α particles. Does this match your prediction from (a)? If not, explain why the actual path would be that shown in the simulation. Hit the pause button, or "Reset All." Set "Alpha Particles Energy" to "max," and start firing α particles. Does this match your prediction from (b)? If not, explain the effect of increased energy on the actual paths as shown in the simulation.
5. Predict and test the behavior of α particles fired at a Rutherford atom model.

a. (a) Predict the paths taken by α particles that are fired at atoms with a Rutherford atom model structure. Explain why you expect the α particles to take these paths.
b. (b) If α particles of higher energy than those in (a) are fired at Rutherford atoms, predict how their paths will differ from the lower-energy α particle paths. Explain your reasoning.
c. (c) Predict how the paths taken by the α particles will differ if they are fired at Rutherford atoms of elements other than gold. What factor do you expect to cause this difference in paths, and why?
d. (d) Now test your predictions from (a), (b), and (c). Open the Rutherford Scattering simulation and select the "Rutherford Atom" tab. Due to the scale of the simulation, it is best to start with a small nucleus, so select "20" for both protons and neutrons, "min" for energy, show traces, and then start firing α particles. Does this match your prediction from (a)? If not, explain why the actual path would be that shown in the simulation. Pause or reset, set energy to "max," and start firing α particles. Does this match your prediction from (b)? If not, explain the effect of increased energy on the actual path as shown in the simulation. Pause or reset, select "40" for both protons and neutrons, "min" for energy, show traces, and fire away. Does this match your prediction from (c)? If not, explain why the actual path would be that shown in the simulation. Repeat this with larger numbers of protons and neutrons. What generalization can you make regarding the type of atom and effect on the path of α particles? Be clear and specific.

Solutions

1 Dalton originally thought that all atoms of a particular element had identical properties, including mass. Thus, the concept of isotopes, in which an element has different masses, was a violation of the original idea. To account for the existence of isotopes, the second postulate of his atomic theory was modified to state that atoms of the same element must have identical chemical properties.

2 Both are subatomic particles that reside in an atom's nucleus. Both have approximately the same mass. Protons are positively charged, whereas neutrons are uncharged.

3 Both are subatomic particles that reside in an atom's nucleus. Both have approximately the same mass. Protons are positively charged, whereas neutrons are uncharged.

4. (a) The plum pudding model indicates that the positive charge is spread uniformly throughout the atom, so we expect the α particles to (perhaps) be slowed somewhat by the positive-positive repulsion, but to follow straight-line paths (i.e., not to be deflected) as they pass through the atoms. (b) Higher-energy α particles will be traveling faster (and perhaps slowed less) and will also follow straight-line paths through the atoms. (c) The α particles followed straight-line paths through the plum pudding atom. There was no apparent slowing of the α particles as they passed through the atoms.

5. (a) The Rutherford atom has a small, positively charged nucleus, so most α particles will pass through empty space far from the nucleus and be undeflected. Those α particles that pass near the nucleus will be deflected from their paths due to positive-positive repulsion. The more directly toward the nucleus the α particles are headed, the larger the deflection angle will be. (b) Higher-energy α particles that pass near the nucleus will still undergo deflection, but the faster they travel, the less the expected angle of deflection. (c) If the nucleus is smaller, the positive charge is smaller and the expected deflections are smaller—both in terms of how closely the α particles pass by the nucleus undeflected and the angle of deflection. If the nucleus is larger, the positive charge is larger and the expected deflections are larger—more α particles will be deflected, and the deflection angles will be larger. (d) The paths followed by the α particles match the predictions from (a), (b), and (c).

2.3: Atomic Structure and Symbolism

In what way are isotopes of a given element always different? In what way(s) are they always the same?

Write the symbol for each of the following ions:

1. (a) the ion with a 1+ charge, atomic number 55, and mass number 133
2. (b) the ion with 54 electrons, 53 protons, and 74 neutrons
3. (c) the ion with atomic number 15, mass number 31, and a 3− charge
4. (d) the ion with 24 electrons, 30 neutrons, and a 3+ charge

1.

(a) $^{133}Cs^{+}$; (b) $^{127}I^{-}$; (c) $^{31}P^{3-}$; (d) $^{57}Co^{3+}$

Write the symbol for each of the following ions:

1. (a) the ion with a 3+ charge, 28 electrons, and a mass number of 71
2. (b) the ion with 36 electrons, 35 protons, and 45 neutrons
3. (c) the ion with 86 electrons, 142 neutrons, and a 4+ charge
4. (d) the ion with a 2+ charge, atomic number 38, and mass number 87

Open the Build an Atom simulation and click on the Atom icon.

1. (a) Pick any one of the first 10 elements that you would like to build and state its symbol.
2. (b) Drag protons, neutrons, and electrons onto the atom template to make an atom of your element. State the numbers of protons, neutrons, and electrons in your atom, as well as the net charge and mass number.
3. (c) Click on "Net Charge" and "Mass Number," check your answers to (b), and correct, if needed.
4. (d) Predict whether your atom will be stable or unstable. State your reasoning.
5. (e) Check the "Stable/Unstable" box. Was your answer to (d) correct? If not, first predict what you can do to make a stable atom of your element, and then do it and see if it works. Explain your reasoning.

(a) Carbon-12, ^{12}C; (b) This atom contains six protons and six neutrons. There are six electrons in a neutral ^{12}C atom. The net charge of such a neutral atom is zero, and the mass number is 12. (c) The preceding answers are correct. (d) The atom will be stable since C-12 is a stable isotope of carbon. (e) The preceding answer is correct. Other answers for this exercise are possible if a different element of isotope is chosen.

Open the Build an Atom simulation

(a) Drag protons, neutrons, and electrons onto the atom template to make a neutral atom of Oxygen-16 and give the isotope symbol for this atom.

(b) Now add two more electrons to make an ion and give the symbol for the ion you have created.

Open the Build an Atom simulation

(a) Drag protons, neutrons, and electrons onto the atom template to make a neutral atom of Lithium-6 and give the isotope symbol for this atom.

(b) Now remove one electron to make an ion and give the symbol for the ion you have created.

(a) Lithium-6 contains three protons, three neutrons, and three electrons. The isotope symbol is ^{6}Li or $^{6}_{3}Li$. (b) $^{6}Li^{+}$ or $^{6}_{3}Li^{+}$

Determine the number of protons, neutrons, and electrons in the following isotopes that are used in medical diagnoses:

(a) atomic number 9, mass number 18, charge of 1−

(b) atomic number 43, mass number 99, charge of 7+

(c) atomic number 53, atomic mass number 131, charge of 1−

(d) atomic number 81, atomic mass number 201, charge of 1+

(e) Name the elements in parts (a), (b), (c), and (d).

The following are properties of isotopes of two elements that are essential in our diet. Determine the number of protons, neutrons and electrons in each and name them.

(a) atomic number 26, mass number 58, charge of 2+

(b) atomic number 53, mass number 127, charge of 1−

(a) Iron, 26 protons, 24 electrons, and 32 neutrons; (b) iodine, 53 protons, 54 electrons, and 74 neutrons

Give the number of protons, electrons, and neutrons in neutral atoms of each of the following isotopes:

(a) $^{10}_{5}B$

(b) $^{199}_{80}Hg$

(c) $^{63}_{29}Cu$

(d) $^{13}_{6}C$

(e) $^{77}_{34}Se$

Give the number of protons, electrons, and neutrons in neutral atoms of each of the following isotopes:

(a) $^{7}_{3}Li$

(b) $^{125}_{52}Te$

(c) $^{109}_{47}Ag$

(d) $^{15}_{7}N$

(e) $^{31}_{15}P$

(a) 3 protons, 3 electrons, 4 neutrons; (b) 52 protons, 52 electrons, 73 neutrons; (c) 47 protons, 47 electrons, 62 neutrons; (d) 7 protons, 7 electrons, 8 neutrons; (e) 15 protons, 15 electrons, 16 neutrons

Click on the site and select the “Mix Isotopes” tab, hide the “Percent Composition” and “Average Atomic Mass” boxes, and then select the element boron.

(a) Write the symbols of the isotopes of boron that are shown as naturally occurring in significant amounts.

(b) Predict the relative amounts (percentages) of these boron isotopes found in nature. Explain the reasoning behind your choice.

(c) Add isotopes to the black box to make a mixture that matches your prediction in (b). You may drag isotopes from their bins or click on “More” and then move the sliders to the appropriate amounts.

(d) Reveal the “Percent Composition” and “Average Atomic Mass” boxes. How well does your mixture match with your prediction? If necessary, adjust the isotope amounts to match your prediction.

(e) Select “Nature’s” mix of isotopes and compare it to your prediction. How well does your prediction compare with the naturally occurring mixture? Explain. If necessary, adjust your amounts to make them match “Nature’s” amounts as closely as possible.

Repeat Exercise using an element that has three naturally occurring isotopes.

Let us use neon as an example. Since there are three isotopes, there is no way to be sure to accurately predict the abundances to make the total of 20.18 amu average atomic mass. Let us guess that the abundances are 9% Ne-22, 91% Ne-20, and only a trace of Ne-21. The average mass would be 20.18 amu. Checking the nature’s mix of isotopes shows that the abundances are 90.48% Ne-20, 9.25% Ne-22, and 0.27% Ne-21, so our guessed amounts have to be slightly adjusted.

An element has the following natural abundances and isotopic masses: 90.92% abundance with 19.99 amu, 0.26% abundance with 20.99 amu, and 8.82% abundance with 21.99 amu. Calculate the average atomic mass of this element.

Average atomic masses listed by IUPAC are based on a study of experimental results. Bromine has two isotopes ^{79}Br and ^{81}Br, whose masses (78.9183 and 80.9163 amu) and abundances (50.69% and 49.31%) were determined in earlier experiments. Calculate the average atomic mass of bromine based on these experiments.

79.904 amu

Variations in average atomic mass may be observed for elements obtained from different sources. Lithium provides an example of this. The isotopic composition of lithium from naturally occurring minerals is 7.5% ^{6}Li and 92.5% ^{7}Li, which have masses of 6.01512 amu and 7.01600 amu, respectively. A commercial source of lithium, recycled from a military source, was 3.75% ^{6}Li (and the rest ^{7}Li). Calculate the average atomic mass values for each of these two sources.

The average atomic masses of some elements may vary, depending upon the sources of their ores. Naturally occurring boron consists of two isotopes with accurately known masses (^{10}B, 10.0129 amu and ^{11}B, 11.0931 amu). The actual atomic mass of boron can vary from 10.807 to 10.819, depending on whether the mineral source is from Turkey or the United States. Calculate the percent abundances leading to the two values of the average atomic masses of boron from these two countries.

Turkey source: 0.2649 (of 10.0129 amu isotope); US source: 0.2537 (of 10.0129 amu isotope)

The ^{18}O:^{16}O abundance ratio in some meteorites is greater than that used to calculate the average atomic mass of oxygen on earth. Is the average mass of an oxygen atom in these meteorites greater than, less than, or equal to that of a terrestrial oxygen atom?

2.4: Chemical Formulas

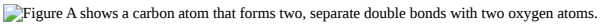
Explain why the symbol for an atom of the element oxygen and the formula for a molecule of oxygen differ.

The symbol for the element oxygen, O, represents both the element and one atom of oxygen. A molecule of oxygen, O_2, contains two oxygen atoms; the subscript 2 in the formula must be used to distinguish the diatomic molecule from two single oxygen atoms.

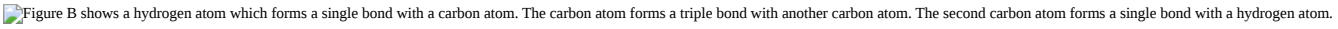
Explain why the symbol for the element sulfur and the formula for a molecule of sulfur differ.

Write the molecular and empirical formulas of the following compounds:

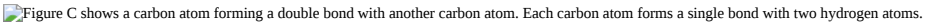
(a)


Figure A shows a carbon atom that forms two, separate double bonds with two oxygen atoms.

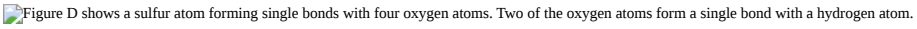
(b)


Figure B shows a hydrogen atom which forms a single bond with a carbon atom. The carbon atom forms a triple bond with another carbon atom. The second carbon atom forms a single bond with a hydrogen atom.

(c)


Figure C shows a carbon atom forming a double bond with another carbon atom. Each carbon atom forms a single bond with two hydrogen atoms.

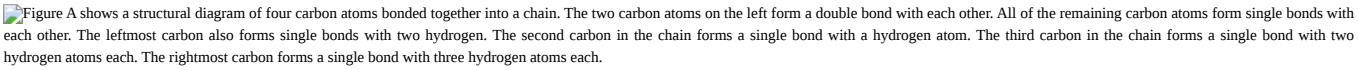
(d)


Figure D shows a sulfur atom forming single bonds with four oxygen atoms. Two of the oxygen atoms form a single bond with a hydrogen atom.

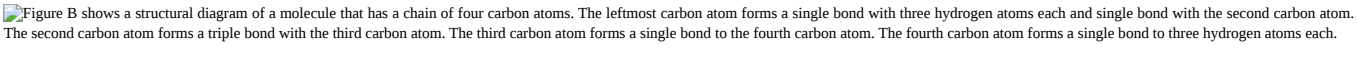
(a) molecular CO_2, empirical CO_2; (b) molecular C_2H_2, empirical CH; (c) molecular C_2H_4, empirical CH_2; (d) molecular H_2SO_4, empirical H_2SO_4

Write the molecular and empirical formulas of the following compounds:

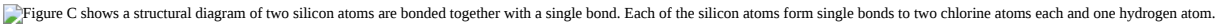
(a)


Figure A shows a structural diagram of four carbon atoms bonded together into a chain. The two carbon atoms on the left form a double bond with each other. All of the remaining carbon atoms form single bonds with each other. The leftmost carbon also forms single bonds with two hydrogen. The second carbon in the chain forms a single bond with a hydrogen atom. The third carbon in the chain forms a single bond with two hydrogen atoms each. The rightmost carbon forms a single bond with three hydrogen atoms each.

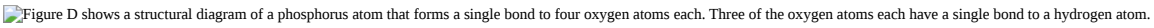
(b)


Figure B shows a structural diagram of a molecule that has a chain of four carbon atoms. The leftmost carbon atom forms a single bond with three hydrogen atoms each and single bond with the second carbon atom. The second carbon atom forms a triple bond with the third carbon atom. The third carbon atom forms a single bond to the fourth carbon atom. The fourth carbon atom forms a single bond to three hydrogen atoms each.

(c)


Figure C shows a structural diagram of two silicon atoms are bonded together with a single bond. Each of the silicon atoms form single bonds to two chlorine atoms each and one hydrogen atom.

(d)


Figure D shows a structural diagram of a phosphorus atom that forms a single bond to four oxygen atoms each. Three of the oxygen atoms each have a single bond to a hydrogen atom.

Determine the empirical formulas for the following compounds:

1. (a) caffeine, $C_8H_{10}N_4O_2$
2. (b) fructose, $C_{12}H_{22}O_{11}$
3. (c) hydrogen peroxide, H_2O_2
4. (d) glucose, $C_6H_{12}O_6$
5. (e) ascorbic acid (vitamin C), $C_6H_8O_6$

(a) $C_4H_5N_2O$; (b) $C_{12}H_{22}O_{11}$; (c) HO; (d) CH_2O; (e) $C_3H_4O_3$

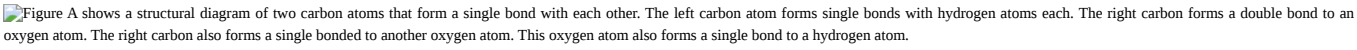
Determine the empirical formulas for the following compounds:

1. (a) acetic acid, $C_2H_4O_2$
2. (b) citric acid, $C_6H_8O_7$
3. (c) hydrazine, N_2H_4

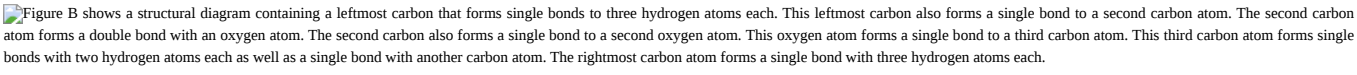
4. (d) nicotine, $C_{10}H_{14}N_2$
5. (e) butane, C_4H_{10}

Write the empirical formulas for the following compounds:

(a)


Figure A shows a structural diagram of two carbon atoms that form a single bond with each other. The left carbon atom forms single bonds with hydrogen atoms each. The right carbon forms a double bond to an oxygen atom. The right carbon also forms a single bonded to another oxygen atom. This oxygen atom also forms a single bond to a hydrogen atom.

(b)


Figure B shows a structural diagram containing a leftmost carbon that forms single bonds to three hydrogen atoms each. This leftmost carbon also forms a single bond to a second carbon atom. The second carbon atom forms a double bond with an oxygen atom. The second carbon also forms a single bond to a second oxygen atom. This oxygen atom forms a single bond to a third carbon atom. This third carbon atom forms single bonds with two hydrogen atoms each as well as a single bond with another carbon atom. The rightmost carbon atom forms a single bond with three hydrogen atoms each.

(a) CH_2O; (b) C_2H_4O

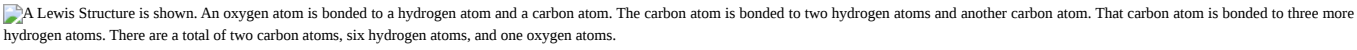
Open the Build a Molecule simulation and select the “Larger Molecules” tab. Select an appropriate atoms “Kit” to build a molecule with two carbon and six hydrogen atoms. Drag atoms into the space above the “Kit” to make a molecule. A name will appear when you have made an actual molecule that exists (even if it is not the one you want). You can use the scissors tool to separate atoms if you would like to change the connections. Click on “3D” to see the molecule, and look at both the space-filling and ball-and-stick possibilities.

1. (a) Draw the structural formula of this molecule and state its name.
2. (b) Can you arrange these atoms in any way to make a different compound?

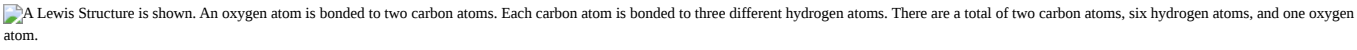
Use the Build a Molecule simulation to repeat Exercise, but build a molecule with two carbons, six hydrogens, and one oxygen.

1. (a) Draw the structural formula of this molecule and state its name.
2. (b) Can you arrange these atoms to make a different molecule? If so, draw its structural formula and state its name.
3. (c) How are the molecules drawn in (a) and (b) the same? How do they differ? What are they called (the type of relationship between these molecules, not their names).

(a) ethanol


A Lewis Structure is shown. An oxygen atom is bonded to a hydrogen atom and a carbon atom. The carbon atom is bonded to two hydrogen atoms and another carbon atom. That carbon atom is bonded to three more hydrogen atoms. There are a total of two carbon atoms, six hydrogen atoms, and one oxygen atoms.

(b) methoxymethane, more commonly known as dimethyl ether


A Lewis Structure is shown. An oxygen atom is bonded to two carbon atoms. Each carbon atom is bonded to three different hydrogen atoms. There are a total of two carbon atoms, six hydrogen atoms, and one oxygen atom.

(c) These molecules have the same chemical composition (types and number of atoms) but different chemical structures. They are structural isomers.

Use the Build a Molecule simulation to repeat Exercise, but build a molecule with three carbons, seven hydrogens, and one chlorine.

a. Draw the structural formula of this molecule and state its name.
b. Can you arrange these atoms to make a different molecule? If so, draw its structural formula and state its name.
c. How are the molecules drawn in (a) and (b) the same? How do they differ? What are they called (the type of relationship between these molecules, not their names)?

2.5: The Periodic Table

Using the periodic table, classify each of the following elements as a metal or a nonmetal, and then further classify each as a main-group (representative) element, transition metal, or inner transition metal:

a. uranium
b. bromine
c. strontium
d. neon
e. gold

f. americium
g. rhodium
h. sulfur
i. carbon
j. potassium

(a) metal, inner transition metal; (b) nonmetal, representative element; (c) metal, representative element; (d) nonmetal, representative element; (e) metal, transition metal; (f) metal, inner transition metal; (g) metal, transition metal; (h) nonmetal, representative element; (i) nonmetal, representative element; (j) metal, representative element

Using the periodic table, classify each of the following elements as a metal or a nonmetal, and then further classify each as a main-group (representative) element, transition metal, or inner transition metal:

1. (a) cobalt
2. (b) europium
3. (c) iodine
4. (d) indium
5. (e) lithium
6. (f) oxygen
7. (g) cadmium
8. (h) terbium
9. (i) rhenium

Using the periodic table, identify the lightest member of each of the following groups:

1. (a) noble gases
2. (b) alkaline earth metals
3. (c) alkali metals
4. (d) chalcogens

(a) He; (b) Be; (c) Li; (d) O

Using the periodic table, identify the heaviest member of each of the following groups:

1. (a) alkali metals
2. (b) chalcogens
3. (c) noble gases
4. (d) alkaline earth metals

1. Use the periodic table to give the name and symbol for each of the following elements:
2. (a) the noble gas in the same period as germanium
3. (b) the alkaline earth metal in the same period as selenium
4. (c) the halogen in the same period as lithium
5. (d) the chalcogen in the same period as cadmium

(a) krypton, Kr; (b) calcium, Ca; (c) fluorine, F; (d) tellurium, Te

Use the periodic table to give the name and symbol for each of the following elements:

1. (a) the halogen in the same period as the alkali metal with 11 protons
2. (b) the alkaline earth metal in the same period with the neutral noble gas with 18 electrons
3. (c) the noble gas in the same row as an isotope with 30 neutrons and 25 protons
4. (d) the noble gas in the same period as gold

Write a symbol for each of the following neutral isotopes. Include the atomic number and mass number for each.

1. (a) the alkali metal with 11 protons and a mass number of 23
2. (b) the noble gas element with and 75 neutrons in its nucleus and 54 electrons in the neutral atom
3. (c) the isotope with 33 protons and 40 neutrons in its nucleus

4. (d) the alkaline earth metal with 88 electrons and 138 neutrons

(a) $^{23}_{11}\mathrm{Na}$; (b) $^{129}_{54}\mathrm{Xe}$; (c) $^{73}_{33}\mathrm{As}$; (d) $^{226}_{88}\mathrm{Ra}$

Write a symbol for each of the following neutral isotopes. Include the atomic number and mass number for each.

1. (a) the chalcogen with a mass number of 125
2. (b) the halogen whose longest-lived isotope is radioactive
3. (c) the noble gas, used in lighting, with 10 electrons and 10 neutrons
4. (d) the lightest alkali metal with three neutrons

2.6: Molecular and Ionic Compounds

Using the periodic table, predict whether the following chlorides are ionic or covalent: KCl, NCl_3, ICl, $MgCl_2$, PCl_5, and CCl_4.

Ionic: KCl, $MgCl_2$; Covalent: NCl_3, ICl, PCl_5, CCl_4

Using the periodic table, predict whether the following chlorides are ionic or covalent: $SiCl_4$, PCl_3, $CaCl_2$, CsCl, $CuCl_2$, and $CrCl_3$.

For each of the following compounds, state whether it is ionic or covalent. If it is ionic, write the symbols for the ions involved:

1. (a) NF_3
2. (b) BaO,
3. (c) $(NH_4)_2CO_3$
4. (d) $Sr(H_2PO_4)_2$
5. (e) IBr
6. (f) Na_2O

(a) covalent; (b) ionic, Ba^{2+}, O^{2-}; (c) ionic, $\mathbf{NH_4}^+$, $\mathbf{CO_3}^{2-}$; (d) ionic, Sr^{2+}, $\mathbf{H_2PO_4}^-$; (e) covalent; (f) ionic, Na^+, O^{2-}

For each of the following compounds, state whether it is ionic or covalent, and if it is ionic, write the symbols for the ions involved:

1. (a) $KClO_4$
2. (b) $MgC_2H_3O_2$
3. (c) H_2S
4. (d) Ag_2S
5. (e) N_2Cl_4
6. (f) $Co(NO_3)_2$

For each of the following pairs of ions, write the symbol for the formula of the compound they will form:

1. (a) Ca^{2+}, S^{2-}
2. (b) $\mathbf{NH_4}^+$, $\mathbf{SO_4}^{2-}$
3. (c) Al^{3+}, Br^-
4. (d) Na^+, $\mathbf{HPO_4}^{2-}$
5. (e) Mg^{2+}, $\mathbf{PO_4}^{3-}$

(a) CaS; (b) $(NH_4)_2CO_3$; (c) $AlBr_3$; (d) Na_2HPO_4; (e) $Mg_3(PO_4)_2$

For each of the following pairs of ions, write the symbol for the formula of the compound they will form:

1. (a) K^+, O^{2-}
2. (b) $\mathbf{NH_4}^+$, $\mathbf{PO_4}^{3-}$
3. (c) Al^{3+}, O^{2-}
4. (d) Na^+, $\mathbf{CO_3}^{2-}$
5. (e) Ba^{2+}, $\mathbf{PO_4}^{3-}$

2.7: Chemical Nomenclature

Name the following compounds:

1. (a) CsCl

2. (b) BaO
3. (c) K_2S
4. (d) $BeCl_2$
5. (e) HBr
6. (f) AlF_3

(a) cesium chloride; (b) barium oxide; (c) potassium sulfide; (d) beryllium chloride; (e) hydrogen bromide; (f) aluminum fluoride

Name the following compounds:

1. (a) NaF
2. (b) Rb_2O
3. (c) BCl_3
4. (d) H_2Se
5. (e) P_4O_6
6. (f) ICl_3

Write the formulas of the following compounds:

1. (a) rubidium bromide
2. (b) magnesium selenide
3. (c) sodium oxide
4. (d) calcium chloride
5. (e) hydrogen fluoride
6. (f) gallium phosphide
7. (g) aluminum bromide
8. (h) ammonium sulfate

(a) RbBr; (b) MgSe; (c) Na_2O; (d) $CaCl_2$; (e) HF; (f) GaP; (g) $AlBr_3$; (h) $(NH_4)_2SO_4$

Write the formulas of the following compounds:

1. (a) lithium carbonate
2. (b) sodium perchlorate
3. (c) barium hydroxide
4. (d) ammonium carbonate
5. (e) sulfuric acid
6. (f) calcium acetate
7. (g) magnesium phosphate
8. (h) sodium sulfite

Write the formulas of the following compounds:

1. (a) chlorine dioxide
2. (b) dinitrogen tetraoxide
3. (c) potassium phosphide
4. (d) silver(I) sulfide
5. (e) aluminum nitride
6. (f) silicon dioxide

(a) ClO_2; (b) N_2O_4; (c) K_3P; (d) Ag_2S; (e) AlN; (f) SiO_2

Write the formulas of the following compounds:

1. (a) barium chloride
2. (b) magnesium nitride
3. (c) sulfur dioxide
4. (d) nitrogen trichloride

5. (e) dinitrogen trioxide
6. (f) tin(IV) chloride

Each of the following compounds contains a metal that can exhibit more than one ionic charge. Name these compounds:

1. (a) Cr_2O_3
2. (b) $FeCl_2$
3. (c) CrO_3
4. (d) $TiCl_4$
5. (e) CoO
6. (f) MoS_2

(a) chromium(III) oxide; (b) iron(II) chloride; (c) chromium(VI) oxide; (d) titanium(IV) chloride; (e) cobalt(II) oxide; (f) molybdenum(IV) sulfide

Each of the following compounds contains a metal that can exhibit more than one ionic charge. Name these compounds:

1. (a) $NiCO_3$
2. (b) MoO_3
3. (c) $Co(NO_3)_2$
4. (d) V_2O_5
5. (e) MnO_2
6. (f) Fe_2O_3

The following ionic compounds are found in common household products. Write the formulas for each compound:

1. (a) potassium phosphate
2. (b) copper(II) sulfate
3. (c) calcium chloride
4. (d) titanium dioxide
5. (e) ammonium nitrate
6. (f) sodium bisulfate (the common name for sodium hydrogen sulfate)

(a) K_3PO_4; (b) $CuSO_4$; (c) $CaCl_2$; (d) TiO_2; (e) NH_4NO_3; (f) $NaHSO_4$

The following ionic compounds are found in common household products. Name each of the compounds:

1. (a) $Ca(H_2PO_4)_2$
2. (b) $FeSO_4$
3. (c) $CaCO_3$
4. (d) MgO
5. (e) $NaNO_2$
6. (f) KI

What are the IUPAC names of the following compounds?

1. (a) manganese dioxide
2. (b) mercurous chloride (Hg_2Cl_2)
3. (c) ferric nitrate [$Fe(NO_3)_3$]
4. (d) titanium tetrachloride
5. (e) cupric bromide ($CuBr_2$)

(a) manganese(IV) oxide; (b) mercury(I) chloride; (c) iron(III) nitrate; (d) titanium(IV) chloride; (e) copper(II) bromide

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CHAPTER OVERVIEW

2: Composition of Substances and Solutions

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General Chemistry

Quantitative aspects of the composition of substances and mixtures are the subject of this chapter.

2.1: Formula Mass and the Mole Concept

2.2: Determining Empirical and Molecular Formulas

2.3: Molarity

2.E: Composition of Substances and Solutions (Exercises)

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2.1: Formula Mass and the Mole Concept

Learning Objectives

- Calculate formula masses for covalent and ionic compounds
- Define the amount unit mole and the related quantity Avogadro's number
- Explain the relation between mass, moles, and numbers of atoms or molecules, and perform calculations deriving these quantities from one another

We can argue that modern chemical science began when scientists started exploring the quantitative as well as the qualitative aspects of chemistry. For example, Dalton's atomic theory was an attempt to explain the results of measurements that allowed him to calculate the relative masses of elements combined in various compounds. Understanding the relationship between the masses of atoms and the chemical formulas of compounds allows us to quantitatively describe the composition of substances.

Formula Mass

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.

Formula Mass for Covalent Substances

For covalent substances, 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. Consider chloroform ($CHCl_3$), a covalent compound once used as a surgical anesthetic and now primarily used in the production of tetrafluoroethylene, the building block for the "anti-stick" polymer, Teflon. The molecular formula of chloroform indicates that a single molecule contains one carbon atom, one hydrogen atom, and three chlorine atoms. The average molecular mass of a chloroform molecule is therefore equal to the sum of the average atomic masses of these atoms. Figure **2.1.1** outlines the calculations used to derive the molecular mass of chloroform, which is 119.37 amu.

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	1	×	12.01	=	12.01
H	1	×	1.008	=	1.008
Cl	3	×	35.45	=	106.35
				Molecular mass	119.37

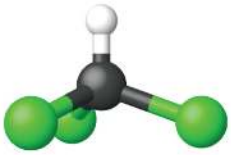


Figure **2.1.1**: The average mass of a chloroform molecule, $CHCl_3$, is 119.37 amu, which is the sum of the average atomic masses of each of its constituent atoms. The model shows the molecular structure of chloroform.

A table and diagram are shown. The table is made up of six columns and five rows. The header row reads: "Element," "Quantity," a blank space, "Average atomic mass (a m u)," a blank space, and "Subtotal (a m u)." The first column contains the symbols "C," "H," "C l" and a blank, merged cell that runs the width of the first five columns. The second column contains the numbers "1," "1," and "3" as well as the merged cell. The third column contains the multiplication symbol in each cell except for the last, merged cell. The fourth column contains the numbers "12.01," "1.008," and "35.45" as well as the merged cell. The fifth column contains the symbol "=" in each cell except for the last, merged cell. The sixth column contains the values "12.01," "1.008," "106.35," and "119.37." There is a thick black line below the number 106.35. The merged cell under the first five columns reads "Molecular mass." To the left of the table is a diagram of a molecule. Three green spheres are attached to a slightly smaller black sphere, which is also attached to a smaller white sphere. The green spheres lie beneath and to the sides of the black sphere while the white sphere is located straight up from the black sphere.

Likewise, the molecular mass of an aspirin molecule, $C_9H_8O_4$, is the sum of the atomic masses of nine carbon atoms, eight hydrogen atoms, and four oxygen atoms, which amounts to 180.15 amu (Figure **2.1.2**).

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	9	×	12.01	=	108.09
H	8	×	1.008	=	8.064
O	4	×	16.00	=	64.00
				Molecular mass	180.15

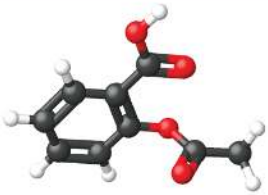


Figure **2.1.2**: The average mass of an aspirin molecule is 180.15 amu. The model shows the molecular structure of aspirin, $C_9H_8O_4$. A table and diagram are shown. The table is made up of six columns and five rows. The header row reads: “Element,” “Quantity,” a blank space, “Average atomic mass (a m u),” a blank space, and “Subtotal (a m u).” The first column contains the symbols “C,” “H,” “O,” and a merged cell. The merged cell runs the length of the first five columns. The second column contains the numbers “9,” “8,” and “4” as well as the merged, cell. The third column contains the multiplication symbol in each cell except for the last, merged cell. The fourth column contains the numbers “12.01,” “1.008,” and “16.00” as well as the merged cell. The fifth column contains the symbol “=” in each cell except for the last, merged cell. The sixth column contains the values: “108.09,” “8.064,” “64.00,” and “180.15.” There is a thick black line below the number 64.00. The merged cell under the first five columns reads “Molecular mass.” To the left of the table is a diagram of a molecule. Six black spheres are located in a six-sided ring and connected by alternating double and single black bonds. Attached to each of the four black spheres is one smaller white sphere. Attached to the farthest right black sphere is a red sphere, connected to two more black spheres, all in a row. Attached to the last black sphere of that row are two more white spheres. Attached to the first black sphere of that row is another red sphere. A black sphere, attached to two red spheres and a white sphere is attached to the black sphere on the top right of the six-sided ring.

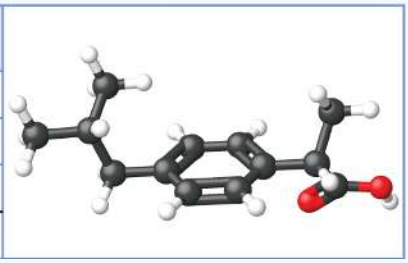
✔ Example 2.1.1: Computing Molecular Mass for a Covalent Compound

Ibuprofen, $C_{13}H_{18}O_2$, is a covalent compound and the active ingredient in several popular nonprescription pain medications, such as Advil and Motrin. What is the molecular mass (amu) for this compound?

Solution

Molecules of this compound are comprised of 13 carbon atoms, 18 hydrogen atoms, and 2 oxygen atoms. Following the approach described above, the average molecular mass for this compound is therefore:

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	13	×	12.01	=	156.13
H	18	×	1.008	=	18.114
O	2	×	16.00	=	32.00
				Molecular mass	206.27



? Exercise 2.1.1

Acetaminophen, $C_8H_9NO_2$, is a covalent compound and the active ingredient in several popular nonprescription pain medications, such as Tylenol. What is the molecular mass (amu) for this compound?

Answer

151.16 amu

Formula Mass for Ionic Compounds

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 sodium chloride, NaCl, the chemical name for common table salt. Sodium chloride is an ionic compound composed of sodium cations, Na^+, and chloride anions, Cl^-, combined in a 1:1 ratio. The formula mass for this compound is

computed as 58.44 amu (Figure **2.1.3**).

Element	Quantity		Average atomic mass (amu)		Subtotal
Na	1	×	22.99	=	22.99
Cl	1	×	35.45	=	35.45
				Formula mass	58.44

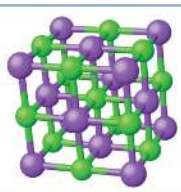


Figure **2.1.3**: Table salt, NaCl, contains an array of sodium and chloride ions combined in a 1:1 ratio. Its formula mass is 58.44 amu.
A table and diagram are shown. The table is made up of six columns and four rows. The header row reads: “Element,” “Quantity,” a blank space, “Average atomic mass (a m u),” a blank space and “Subtotal (a m u).” The first column contains the symbols “N a”, “C l,” and a merged cell. The merged cell runs the length of the first five columns. The second column contains the numbers “1” and “1” as well as the merged cell. The third column contains the multiplication symbol in each cell except for the last, merged cell. The fourth column contains the numbers “22.99” and “35.45” as well as the merged cell. The fifth column contains the symbol “=” in each cell except for the last, merged cell. The sixth column contains the values “22.99,” “35.45,” and “58.44.” There is a thick black line below the number “35.45.” The merged cell under the first five columns reads “Formula mass.” To the left of the table is a diagram of a chemical structure. The diagram shows green and purple spheres placed in an alternating pattern, making up the corners of eight stacked cubes to form one larger cube. The green spheres are slightly smaller than the purple spheres.

Note that the average masses of neutral sodium and chlorine atoms were used in this computation, rather than the masses for sodium cations and chlorine anions. This approach is perfectly acceptable when computing the formula mass of an ionic compound. Even though a sodium cation has a slightly smaller mass than a sodium atom (since it is missing an electron), this difference will be offset by the fact that a chloride anion is slightly more massive than a chloride atom (due to the extra electron). Moreover, the mass of an electron is negligibly small with respect to the mass of a typical atom. Even when calculating the mass of an isolated ion, the missing or additional electrons can generally be ignored, since their contribution to the overall mass is negligible, reflected only in the nonsignificant digits that will be lost when the computed mass is properly rounded. The few exceptions to this guideline are very light ions derived from elements with precisely known atomic masses.

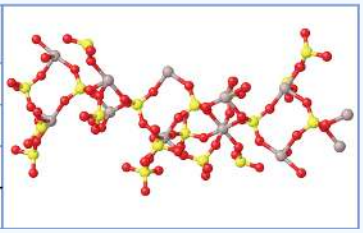
✔ Example 2.1.2: Computing Formula Mass for an Ionic Compound

Aluminum sulfate, $Al_2(SO_4)_3$, is an ionic compound that is used in the manufacture of paper and in various water purification processes. What is the formula mass (amu) of this compound?

Solution

The formula for this compound indicates it contains Al^{3+} and SO_4^{2-} ions combined in a 2:3 ratio. For purposes of computing a formula mass, it is helpful to rewrite the formula in the simpler format, $Al_2S_3O_{12}$. Following the approach outlined above, the formula mass for this compound is calculated as follows:

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
Al	2	×	26.98	=	53.96
S	3	×	32.06	=	96.18
O	12	×	16.00	=	192.00
				Molecular mass	342.14



? Exercise 2.1.2

Calcium phosphate, $Ca_3(PO_4)_2$, is an ionic compound and a common anti-caking agent added to food products. What is the formula mass (amu) of calcium phosphate?

Answer

310.18 amu

The Mole

The identity of a substance is defined not only by the types of atoms or ions it contains, but by the quantity of each type of atom or ion. For example, water, $\mathbf{H_2O}$, and hydrogen peroxide, $\mathbf{H_2O_2}$, are alike in that their respective molecules are composed of hydrogen and oxygen atoms. However, because a hydrogen peroxide molecule contains two oxygen atoms, as opposed to the water molecule, which has only one, the two substances exhibit very different properties. Today, we possess sophisticated instruments that allow the direct measurement of these defining microscopic traits; however, the same traits were originally derived from the measurement of macroscopic properties (the masses and volumes of bulk quantities of matter) using relatively simple tools (balances and volumetric glassware). This experimental approach required the introduction of a new unit for amount of substances, the *mole*, which remains indispensable in modern chemical science.

The 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, number of atoms, molecules, and so forth.

The number of entities composing a mole has been experimentally determined to be $\mathbf{6.02214179 \times 10^{23}}$, a fundamental constant named **Avogadro’s number** (N_A) or the Avogadro constant in honor of Italian scientist Amedeo Avogadro. This constant is properly reported with an explicit unit of “per mole,” a conveniently rounded version being $\mathbf{6.022 \times 10^{23}/mol}$.

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) (Figure **2.1.4**).

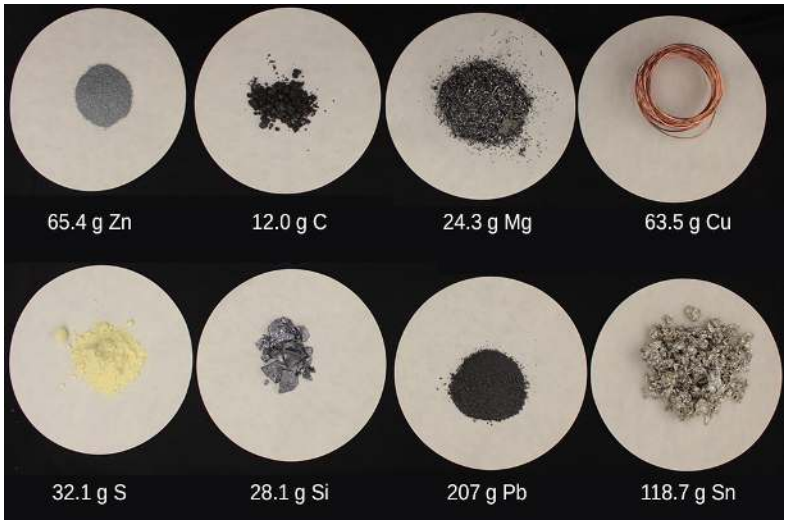
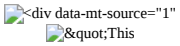


Figure **2.1.4**: Each sample contains $\mathbf{6.022 \times 10^{23}}$ atoms —1.00 mol of atoms. From left to right (top row): 65.4 g zinc, 12.0 g carbon, 24.3 g magnesium, and 63.5 g copper. From left to right (bottom row): 32.1 g sulfur, 28.1 g silicon, 207 g lead, and 118.7 g tin. (credit: modification of work by Mark Ott).

This figure contains eight different substances displayed on white circles. The amount of each substance is visibly different.

Because the definitions of both the mole and the atomic mass unit are based on the same reference substance, ^{12}C, the molar mass of any substance is numerically equivalent to its atomic or formula weight in amu. Per the amu definition, a single ^{12}C atom weighs 12 amu (its atomic mass is 12 amu). According to the definition of the mole, 12 g of ^{12}C contains 1 mole of ^{12}C atoms (its molar mass is 12 g/mol). This relationship holds for all elements, since their atomic masses are measured relative to that of the amu-reference substance, ^{12}C. Extending this principle, the molar mass of a compound in grams is likewise numerically equivalent to its formula mass in amu (Figure **2.1.5**).



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Figure **2.1.5**: Each sample contains $\mathbf{6.022 \times 10^{23}}$ molecules or formula units—1.00 mol of the compound or element. Clock-wise from the upper left: 130.2 g of $C_8H_{17}OH$ (1-octanol, formula mass 130.2 amu), 454.4 g of HgI_2 (mercury(II) iodide, formula mass 454.4 amu), 32.0 g of CH_3OH (methanol, formula mass 32.0 amu) and 256.5 g of S_8 (sulfur, formula mass 256.5 amu). (credit: Sahar Atwa).

Table **2.1.1**: Mass of one mole of elements

Element	Average Atomic Mass (amu)	Molar Mass (g/mol)	Atoms/Mole
C	12.01	12.01	$\mathbf{6.022 \times 10^{23}}$
H	1.008	1.008	$\mathbf{6.022 \times 10^{23}}$
O	16.00	16.00	$\mathbf{6.022 \times 10^{23}}$
Na	22.99	22.99	$\mathbf{6.022 \times 10^{23}}$
Cl	33.45	35.45	$\mathbf{6.022 \times 10^{23}}$

While atomic mass and molar mass are numerically equivalent, keep in mind that they are vastly different in terms of scale, as represented by the vast difference in the magnitudes of their respective units (amu versus g). To appreciate the enormity of the mole, consider a small drop of water after a rainfall. Although this represents just a tiny fraction of 1 mole of water (~18 g), it contains more water molecules than can be clearly imagined. If the molecules were distributed equally among the roughly seven billion people on earth, each person would receive more than 100 billion molecules.



Video **2.1.1**: The mole is used in chemistry to represent $\mathbf{6.022 \times 10^{23}}$ of something, but it can be difficult to conceptualize such a large number. Watch this video and then complete the “Think” questions that follow. Explore more about the mole by reviewing the information under “Dig Deeper.”

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 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.

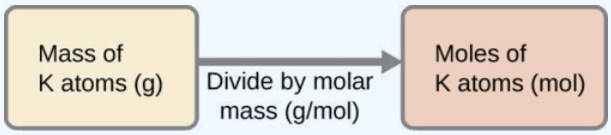
✔ Example **2.1.3**: Deriving Moles from Grams for an Element

According to nutritional guidelines from the US Department of Agriculture, the estimated average requirement for dietary potassium is 4.7 g. What is the estimated average requirement of potassium in moles?

Solution

The mass of K is provided, and the corresponding amount of K in moles is requested. Referring to the periodic table, the atomic mass of K is 39.10 amu, and so its molar mass is 39.10 g/mol. The given mass of K (4.7 g) is a bit more than one-tenth the molar mass (39.10 g), so a reasonable “ballpark” estimate of the number of moles would be slightly greater than 0.1 mol.

The molar amount of a substance may be calculated by dividing its mass (g) by its molar mass (g/mol):



The factor-label method supports this mathematical approach since the unit "g" cancels and the answer has units of "mol:"

$$4.7\ \cancel{g}\,\mathrm{K}\left(\frac{\mathrm{mol\ K}}{39.10\ \cancel{g}}\right) = 0.12\ \mathrm{mol\ K}$$

The calculated magnitude (0.12 mol K) is consistent with our ballpark expectation, since it is a bit greater than 0.1 mol.

? Exercise 2.1.3: Beryllium

Beryllium is a light metal used to fabricate transparent X-ray windows for medical imaging instruments. How many moles of Be are in a thin-foil window weighing 3.24 g?

Answer

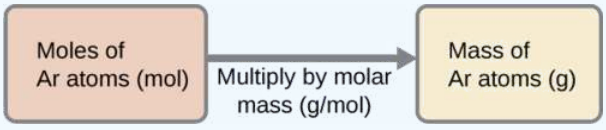
0.360 mol

✓ Example 2.1.4: Deriving Grams from Moles for an Element

A liter of air contains 9.2×10^{-4} mol argon. What is the mass of Ar in a liter of air?

Solution

The molar amount of Ar is provided and must be used to derive the corresponding mass in grams. Since the amount of Ar is less than 1 mole, the mass will be less than the mass of 1 mole of Ar, approximately 40 g. The molar amount in question is approximately one-one thousandth (~10^{-3}) of a mole, and so the corresponding mass should be roughly one-one thousandth of the molar mass (~0.04 g):



In this case, logic dictates (and the factor-label method supports) multiplying the provided amount (mol) by the molar mass (g/mol):

$$9.2 \times 10^{-4}\ \cancel{\mathrm{mol}}\ \mathrm{Ar}\left(\frac{39.95\ \mathrm{g}}{\cancel{\mathrm{mol}}\ \mathrm{Ar}}\right) = 0.037\ \mathrm{g\ Ar}$$

The result is in agreement with our expectations, around 0.04 g Ar.

? Exercise 2.1.4

What is the mass of 2.561 mol of gold?

Answer

504.4 g

Example 2.1.6: Deriving Number of Atoms from Mass for an Element

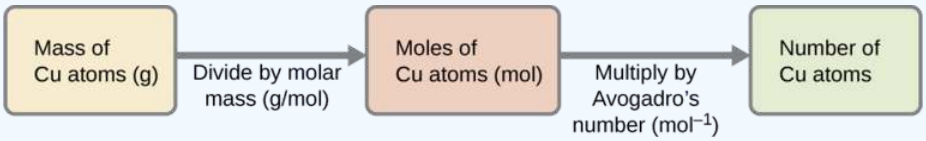
Copper is commonly used to fabricate electrical wire (Figure 2.1.6). How many copper atoms are in 5.00 g of copper wire?



Figure 2.1.6: Copper wire is composed of many, many atoms of Cu. (credit: Emilian Robert Vicol)

Solution

The number of Cu atoms in the wire may be conveniently derived from its mass by a two-step computation: first calculating the molar amount of Cu, and then using Avogadro's number (N_A) to convert this molar amount to number of Cu atoms:



Considering that the provided sample mass (5.00 g) is a little less than one-tenth the mass of 1 mole of Cu (~64 g), a reasonable estimate for the number of atoms in the sample would be on the order of one-tenth N_A, or approximately 10^{22} Cu atoms. Carrying out the two-step computation yields:

$$5.00\ \cancel{g}\ \text{Cu}\left(\frac{\cancel{\text{mol}}\ \text{Cu}}{63.55\ \cancel{g}}\right)\left(\frac{6.022\times10^{23}\ \text{atoms}}{\cancel{\text{mol}}}\right)=4.74\times10^{22}\ \text{atoms of copper}$$

The factor-label method yields the desired cancellation of units, and the computed result is on the order of 10^{22} as expected.

Exercise 2.1.6

A prospector panning for gold in a river collects 15.00 g of pure gold. How many Au atoms are in this quantity of gold?

Answer

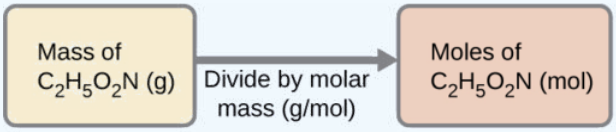
4.586×10^{22} *Au* atoms

Example 2.1.7: Deriving Moles from Grams for a Compound

Our bodies synthesize protein from amino acids. One of these amino acids is glycine, which has the molecular formula $C_2H_5O_2N$. How many moles of glycine molecules are contained in 28.35 g of glycine?

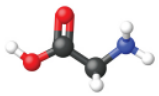
Solution

We can derive the number of moles of a compound from its mass following the same procedure we used for an element in Example 2.1.6:



The molar mass of glycine is required for this calculation, and it is computed in the same fashion as its molecular mass. One mole of glycine, $C_2H_5O_2N$, contains 2 moles of carbon, 5 moles of hydrogen, 2 moles of oxygen, and 1 mole of nitrogen:

Element	Quantity (mol element/ mol compound)		Molar mass (g/mol element)		Subtotal (g/mol compound)
C	2	×	12.01	=	24.02
H	5	×	1.008	=	5.040
O	2	×	16.00	=	32.00
N	1	×	14.007	=	14.007
Molecular mass (g/mol compound)					75.07



A table is shown that is made up of six columns and six rows. The header row reads: “Element,” “Quantity (mol element / mol compound,” a blank space, “Molar mass (g / mol element),” a blank space, and “Subtotal (a m u).” The first column contains the symbols “C,” “H,” “O,” “N,” and a merged cell. The merged cell runs the width of the first five columns. The second column contains the numbers “2,” “5,” “2,” and “1” as well as the merged cell. The third column contains the multiplication symbol in each cell except for the last, merged cell. The fourth column contains the numbers “12.01,” “1.008,” “16.00,” and “14.007” as well as the merged cell. The fifth column contains the symbol “=” in each cell except for the last, merged cell. The sixth column contains the values “24.02,” “5.040,” “32.00,” “14.007,” and “75.07.” There is a thick black line under the number 14.007. The merged cell under the first five columns reads “Molar mass (g / mol compound). There is a ball-and-stick drawing to the right of this table. It shows a black sphere that forms a double bond with a slightly smaller red sphere, a single bond with another red sphere, and a single bond with another black sphere. The red sphere that forms a single bond with the black sphere also forms a single bond with a smaller, white sphere. The second black sphere forms a single bond with a smaller, white sphere and a smaller blue sphere. The blue sphere forms a single bond with two smaller, white spheres each.

The provided mass of glycine (~28 g) is a bit more than one-third the molar mass (~75 g/mol), so we would expect the computed result to be a bit greater than one-third of a mole (~0.33 mol). Dividing the compound’s mass by its molar mass yields:

$$28.35 \cancel{\text{ g}} \text{ glycine} \left(\frac{\text{mol glycine}}{75.07 \cancel{\text{ g}}} \right) = 0.378 \text{ mol glycine}$$

This result is consistent with our rough estimate.

? Exercise 2.1.7

How many moles of sucrose, $C_{12}H_{22}O_{11}$, are in a 25-g sample of sucrose?

Answer

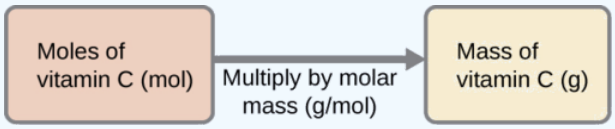
0.073 mol

✔ Example 2.1.8: Deriving Grams from Moles for a Compound

Vitamin C is a covalent compound with the molecular formula $C_6H_8O_6$. The recommended daily dietary allowance of vitamin C for children aged 4–8 years is 1.42×10^{-4} mol. What is the mass of this allowance in grams?

Solution

As for elements, the mass of a compound can be derived from its molar amount as shown:



The molar mass for this compound is computed to be 176.124 g/mol. The given number of moles is a very small fraction of a mole (~10^{-4} or one-ten thousandth); therefore, we would expect the corresponding mass to be about one-ten thousandth of the molar mass (~0.02 g). Performing the calculation, we get:

$$1.42 \times 10^{-4} \cancel{\text{ mol}} \text{ vitamin C} \left(\frac{176.124 \text{ g}}{\cancel{\text{mol}} \text{ vitamin C}} \right) = 0.0250 \text{ g vitamin C}$$

This is consistent with the anticipated result.

Exercise 2.1.8

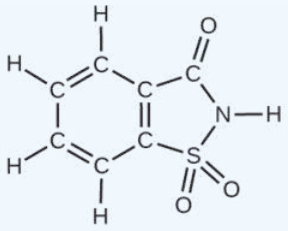
What is the mass of 0.443 mol of hydrazine, N_2H_4?

Answer

14.2 g

Example 2.1.9: Deriving the Number of Molecules from the Compound Mass

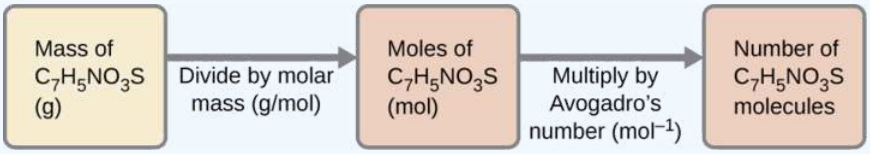
A packet of an artificial sweetener contains 40.0 mg of saccharin ($C_7H_5NO_3S$), which has the structural formula:



Given that saccharin has a molar mass of 183.18 g/mol, how many saccharin molecules are in a 40.0-mg (0.0400-g) sample of saccharin? How many carbon atoms are in the same sample?

Solution

The number of molecules in a given mass of compound is computed by first deriving the number of moles, as demonstrated in Example 2.1.8, and then multiplying by Avogadro's number:



Using the provided mass and molar mass for saccharin yields:

$$0.0400\ \cancel{g}\ C_7H_5NO_3S \left(\frac{\cancel{mol}\ C_7H_5NO_3S}{183.18\ \cancel{g}\ C_7H_5NO_3S}\right)\left(\frac{6.022 \times 10^{23}\ C_7H_5NO_3S\ \text{molecules}}{1\ \cancel{mol}\ C_7H_5NO_3S}\right)$$
$$= 1.31 \times 10^{20}\ C_7H_5NO_3S\ \text{molecules}$$

The compound's formula shows that each molecule contains seven carbon atoms, and so the number of C atoms in the provided sample is:

$$1.31 \times 10^{20}\ C_7H_5NO_3S\ \text{molecules}\left(\frac{7\ \text{C atoms}}{1\ C_7H_5NO_3S\ \text{molecule}}\right) = 9.20 \times 10^{21}\ \text{C atoms}$$

Exercise 2.1.9

How many C_4H_{10} molecules are contained in 9.213 g of this compound? How many hydrogen atoms?

Answer

- 9.545×10^{22} molecules C_4H_{10}
- 9.545×10^{23} atoms H

Summary

The formula mass of a substance is the sum of the average atomic masses of each atom represented in the chemical formula and is expressed in atomic mass units. The formula mass of a covalent compound is also called the molecular mass. A convenient amount unit for expressing very large numbers of atoms or molecules is the mole. Experimental measurements have determined the number of entities composing 1 mole of substance to be 6.022×10^{23}, a quantity called Avogadro's number. The mass in grams of 1 mole of substance is its molar mass. Due to the use of the same reference substance in defining the atomic mass unit and the mole, the formula mass (amu) and molar mass (g/mol) for any substance are numerically equivalent (for example, one H_2O molecule weighs approximately18 amu and 1 mole of H_2O molecules weighs approximately 18 g).

Footnotes

1. 1 Omiatek, Donna M., Amanda J. Bressler, Ann-Sofie Cans, Anne M. Andrews, Michael L. Heien, and Andrew G. Ewing. "The Real Catecholamine Content of Secretory Vesicles in the CNS Revealed by Electrochemical Cytometry." *Scientific Report* 3 (2013): 1447, accessed January 14, 2015, doi:10.1038/srep01447.

Glossary

Avogadro's number (N_A)

experimentally determined value of the number of entities comprising 1 mole of substance, equal to 6.022×10^{23} mol^{-1}

formula mass

sum of the average masses for all atoms represented in a chemical formula; for covalent compounds, this is also the molecular mass

mole

amount of substance containing the same number of atoms, molecules, ions, or other entities as the number of atoms in exactly 12 grams of ^{12}C

molar mass

mass in grams of 1 mole of a substance

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2.2: Determining Empirical and Molecular Formulas

Learning Objectives

- Compute the percent composition of a compound
- Determine the empirical formula of a compound
- Determine the molecular formula of a compound

In the previous section, we discussed the relationship between the bulk mass of a substance and the number of atoms or molecules it contains (moles). Given the chemical formula of the substance, we were able to determine the amount of the substance (moles) from its mass, and vice versa. But what if the chemical formula of a substance is unknown? In this section, we will explore how to apply these very same principles in order to derive the chemical formulas of unknown substances from experimental mass measurements.

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 carbon and hydrogen. The percent composition of this compound could be represented as follows:

$$\%\mathrm{H} = \frac{\text{mass H}}{\text{mass compound}} \times 100\%$$

$$\%\mathrm{C} = \frac{\text{mass C}}{\text{mass compound}} \times 100\%$$

If analysis of a 10.0-g sample of this gas showed it to contain 2.5 g H and 7.5 g C, the percent composition would be calculated to be 25% H and 75% C:

$$\%\mathrm{H} = \frac{2.5\ \text{g H}}{10.0\ \text{g compound}} \times 100\% = 25\%$$

$$\%\mathrm{C} = \frac{7.5\ \text{g C}}{10.0\ \text{g compound}} \times 100\% = 75\%$$

Example 2.2.1: Calculation of Percent Composition

Analysis of a 12.04-g sample of a liquid compound composed of carbon, hydrogen, and nitrogen showed it to contain 7.34 g C, 1.85 g H, and 2.85 g N. What is the percent composition of this compound?

Solution

To calculate percent composition, we divide the experimentally derived mass of each element by the overall mass of the compound, and then convert to a percentage:

$$\%\mathrm{C} = \frac{7.34\ \text{g C}}{12.04\ \text{g compound}} \times 100\% = 61.0\%$$

$$\%\mathrm{H} = \frac{1.85\ \text{g H}}{12.04\ \text{g compound}} \times 100\% = 15.4\%$$

$$\%\mathrm{N} = \frac{2.85\ \text{g N}}{12.04\ \text{g compound}} \times 100\% = 23.7\%$$

The analysis results indicate that the compound is 61.0% C, 15.4% H, and 23.7% N by mass.

? Exercise 2.2.1

A 24.81-g sample of a gaseous compound containing only carbon, oxygen, and chlorine is determined to contain 3.01 g C, 4.00 g O, and 17.81 g Cl. What is this compound's percent composition?

Answer

12.1% C, 16.1% O, 71.8% Cl

Determining Percent Composition from Formula Mass

Percent composition is also useful for evaluating the relative abundance of a given element in different compounds of known formulas. As one example, consider the common nitrogen-containing fertilizers ammonia (NH_3), ammonium nitrate (NH_4NO_3), and urea (CH_4N_2O). The element nitrogen is the active ingredient for agricultural purposes, so the mass percentage of nitrogen in the compound is a practical and economic concern for consumers choosing among these fertilizers. For these sorts of applications, the percent composition of a compound is easily derived from its formula mass and the atomic masses of its constituent elements. A molecule of NH_3 contains one N atom weighing 14.01 amu and three H atoms weighing a total of (3 × 1.008 amu) = 3.024 amu. The formula mass of ammonia is therefore (14.01 amu + 3.024 amu) = 17.03 amu, and its percent composition is:

$$\%\mathrm{N} = \frac{14.01\ \text{amu N}}{17.03\ \text{amu NH}_3} \times 100\% = 82.27\%$$

$$\%\mathrm{H} = \frac{3.024\ \text{amu N}}{17.03\ \text{amu NH}_3} \times 100\% = 17.76\%$$

This same approach may be taken considering a pair of molecules, a dozen molecules, or a mole of molecules, etc. The latter amount is most convenient and would simply involve the use of molar masses instead of atomic and formula masses, as demonstrated Example **2.2.2**. As long as we know the chemical formula of the substance in question, we can easily derive percent composition from the formula mass or molar mass.

✓ Example 2.2.2: Determining Percent Composition from a Molecular Formula

Aspirin is a compound with the molecular formula $C_9H_8O_4$. What is its percent composition?

Solution

To calculate the percent composition, we need to know the masses of C, H, and O in a known mass of $C_9H_8O_4$. It is convenient to consider 1 mol of $C_9H_8O_4$ and use its molar mass (180.159 g/mole, determined from the chemical formula) to calculate the percentages of each of its elements:

$$\%\mathrm{C} = \frac{9\ \text{mol C} \times \text{molar mass C}}{\text{molar mass } C_9H_{18}O_4} \times 100$$
$$= \frac{9 \times 12.01\ \text{g/mol}}{180.159\ \text{g/mol}} \times 100 = \frac{108.09\ \text{g/mol}}{180.159\ \text{g/mol}} \times 100$$
$$\%\mathrm{C} = 60.00\,\%\,\mathrm{C}$$

$$\%\mathrm{H} = \frac{8\ \text{mol H} \times \text{molar mass H}}{\text{molar mass } C_9H_{18}O_4} \times 100$$
$$= \frac{8 \times 1.008\ \text{g/mol}}{180.159\ \text{g/mol}} \times 100 = \frac{8.064\ \text{g/mol}}{180.159\ \text{g/mol}} \times 100$$
$$\%\mathrm{H} = 4.476\,\%\,\mathrm{H}$$

$$\%\mathrm{O} = \frac{4\ \text{mol O} \times \text{molar mass O}}{\text{molar mass } C_9H_{18}O_4} \times 100$$
$$= \frac{4 \times 16.00\ \text{g/mol}}{180.159\ \text{g/mol}} \times 100 = \frac{64.00\ \text{g/mol}}{180.159\ \text{g/mol}} \times 100$$
$$\%\mathrm{O} = 35.52\%$$

Note that these percentages sum to equal 100.00% when appropriately rounded.

? Exercise 2.2.2

To three significant digits, what is the mass percentage of iron in the compound Fe_2O_3?

Answer

69.9% Fe

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 a number of 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. Consider a sample of compound determined to contain 1.71 g C and 0.287 g H. The corresponding numbers of atoms (in moles) are:

$$1.71\ \text{g C} \times \frac{1\ \text{mol C}}{12.01\ \text{g C}} = 0.142\ \text{mol C}$$

$$0.287\ \text{g H} \times \frac{1\ \text{mol H}}{1.008\ \text{g H}} = 0.284\ \text{mol H}$$

Thus, we can accurately represent this compound with the formula $C_{0.142}H_{0.284}$. Of course, per accepted convention, formulas contain whole-number subscripts, which can be achieved by dividing each subscript by the smaller subscript:

$$\text{C}_{\frac{0.142}{0.142}}\ \text{H}_{\frac{0.284}{0.142}}\ \text{or}\ \text{CH}_2$$

(Recall that subscripts of "1" are not written, but rather assumed if no other number is present.)

The empirical formula for this compound is thus CH_2. This may or not be the compound's *molecular formula* as well; however, we would need additional information to make that determination (as discussed later in this section).

Consider as another example a sample of compound determined to contain 5.31 g Cl and 8.40 g O. Following the same approach yields a tentative empirical formula of:

$$\text{Cl}_{0.150}\text{O}_{0.525} = \text{Cl}_{\frac{0.150}{0.150}}\ \text{O}_{\frac{0.525}{0.150}} = \text{ClO}_{3.5}$$

In this case, dividing by the smallest subscript still leaves us with a decimal subscript in the empirical formula. To convert this into a whole number, we must multiply each of the subscripts by two, retaining the same atom ratio and yielding Cl_2O_7 as the final empirical formula.

Procedure

In summary, empirical formulas are derived from experimentally measured element masses by:

1. Deriving the number of moles of each element from its mass
2. Dividing each element's molar amount by the smallest molar amount to yield subscripts for a tentative empirical formula
3. Multiplying all coefficients by an integer, if necessary, to ensure that the smallest whole-number ratio of subscripts is obtained

Figure **2.2.1** outlines this procedure in flow chart fashion for a substance containing elements A and X.

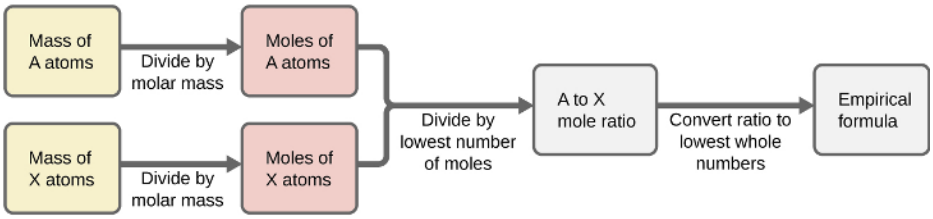


Figure **2.2.1**: The empirical formula of a compound can be derived from the masses of all elements in the sample.

A flow chart is shown that is composed of six boxes, two of which are connected together by a right facing arrow and located above two more that are also connected by a right-facing arrow. These two rows of boxes are connected vertically by a line that leads to a right-facing arrow and the last two boxes, connected by a final right facing arrow. The first two upper boxes have the phrases, “Mass of A atoms” and “Moles of A atoms” respectively, while the arrow that connects them has the phrase, “Divide by molar mass,” written below it. The second two bottom boxes have the phrases, “Mass of X atoms” and “Moles of X atoms” respectively, while the arrow that connects them has the phrase, “Divide by molar mass” written below it. The arrow that connects the upper and lower boxes to the last two boxes has the phrase “Divide by lowest number of moles” written below it. The last two boxes have the phrases, “A to X mole ratio” and “Empirical formula” respectively, while the arrow that connects them has the phrase, “Convert ratio to lowest whole numbers” written below it.

Example **2.2.3**: Determining an Empirical Formula from Masses of Elements

A sample of the black mineral hematite (Figure **2.2.2**), an oxide of iron found in many iron ores, contains 34.97 g of iron and 15.03 g of oxygen. What is the empirical formula of hematite?



Figure **2.2.2**: Hematite is an iron oxide that is used in jewelry. (credit: Mauro Cateb)

Solution

For this problem, we are given the mass in grams of each element. Begin by finding the moles of each:

$$34.97\ \text{g Fe}\left(\frac{\text{mol Fe}}{55.85\ \text{g}}\right) = 0.6261\ \text{mol Fe}$$

$$15.03\ \text{g O}\left(\frac{\text{mol O}}{16.00\ \text{g}}\right) = 0.9394\ \text{mol O}$$

Next, derive the iron-to-oxygen molar ratio by dividing by the lesser number of moles:

$$\frac{0.6261}{0.6261} = 1.000\ \text{mol Fe}$$

$$\frac{0.9394}{0.6261} = 1.500\ \text{mol O}$$

The ratio is 1.000 mol of iron to 1.500 mol of oxygen ($Fe_1O_{1.5}$). Finally, multiply the ratio by two to get the smallest possible whole number subscripts while still maintaining the correct iron-to-oxygen ratio:

$$2(Fe_1O_{1.5}) = Fe_2O_3$$

The empirical formula is Fe_2O_3.

? Exercise 2.2.3

What is the empirical formula of a compound if a sample contains 0.130 g of nitrogen and 0.370 g of oxygen?

Answer

N_2O_5



Video* 2.2.1: Additional worked examples illustrating the derivation of empirical formulas are presented in the brief video clip.*

Deriving Empirical Formulas from Percent Composition

Finally, with regard to deriving empirical formulas, consider instances in which a compound's percent composition is available rather than the absolute masses of the compound's constituent elements. In such cases, the percent composition can be used to calculate the masses of elements present in any convenient mass of compound; these masses can then be used to derive the empirical formula in the usual fashion.

✓ Example 2.2.4: Determining an Empirical Formula from Percent Composition

The bacterial fermentation of grain to produce ethanol forms a gas with a percent composition of 27.29% C and 72.71% O (Figure 2.2.3). What is the empirical formula for this gas?



Figure 2.2.3: An oxide of carbon is removed from these fermentation tanks through the large copper pipes at the top. (credit: "Dual Freq"/Wikimedia Commons)

A picture is shown of four copper-colored industrial containers with a large pipe connecting to the top of each one.

Solution

Since the scale for percentages is 100, it is most convenient to calculate the mass of elements present in a sample weighing 100 g. The calculation is "most convenient" because, per the definition for percent composition, the mass of a given element in grams is numerically equivalent to the element's mass percentage. This numerical equivalence results from the definition of the

"percentage" unit, whose name is derived from the Latin phrase *per centum* meaning "by the hundred." Considering this definition, the mass percentages provided may be more conveniently expressed as fractions:

$$27.29\,\%\,\text{C} = \frac{27.29\ \text{g C}}{100\ \text{g compound}}$$

$$72.71\,\%\,\text{O} = \frac{72.71\ \text{g O}}{100\ \text{g compound}}$$

The molar amounts of carbon and hydrogen in a 100-g sample are calculated by dividing each element's mass by its molar mass:

$$27.29\ \text{g C}\left(\frac{\text{mol C}}{12.01\ \text{g}}\right) = 2.272\ \text{mol C}$$

$$72.71\ \text{g O}\left(\frac{\text{mol O}}{16.00\ \text{g}}\right) = 4.544\ \text{mol O}$$

Coefficients for the tentative empirical formula are derived by dividing each molar amount by the lesser of the two:

$$\frac{2.272\ \text{mol C}}{2.272} = 1$$

$$\frac{4.544\ \text{mol O}}{2.272} = 2$$

Since the resulting ratio is one carbon to two oxygen atoms, the empirical formula is CO_2.

? Exercise 2.2.4

What is the empirical formula of a compound containing 40.0% C, 6.71% H, and 53.28% O?

Answer

CH_2O

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 a number of 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 in order 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:

Double subscripts: use braces to clarify

For example, consider a covalent compound whose empirical formula is determined to be CH_2O. The empirical formula mass for this compound is approximately 30 amu (the sum of 12 amu for one C atom, 2 amu for two H atoms, and 16 amu for one O atom). If the compound's molecular mass is determined to be 180 amu, this indicates that molecules of this compound contain six times the number of atoms represented in the empirical formula:

$$\frac{180\ \text{amu/molecule}}{30\ \frac{\text{amu}}{\text{formula unit}}} = 6\ \text{formula units/molecule}$$

Molecules of this compound are then represented by molecular formulas whose subscripts are six times greater than those in the empirical formula:

$$(CH_2O)_6 = C_6H_{12}O_6$$

Note that this same approach may be used when the molar mass (g/mol) instead of the molecular mass (amu) is used. In this case, we are merely considering one mole of empirical formula units and molecules, as opposed to single units and molecules.

Example 2.2.5: Determination of the Molecular Formula for Nicotine

Nicotine, an alkaloid in the nightshade family of plants that is mainly responsible for the addictive nature of cigarettes, contains 74.02% C, 8.710% H, and 17.27% N. If 40.57 g of nicotine contains 0.2500 mol nicotine, what is the molecular formula?

Solution

Determining the molecular formula from the provided data will require comparison of the compound's empirical formula mass to its molar mass. As the first step, use the percent composition to derive the compound's empirical formula. Assuming a convenient, a 100-g sample of nicotine yields the following molar amounts of its elements:

$$(74.02\ \text{g C})\left(\frac{1\ \text{mol C}}{12.01\ \text{g C}}\right) = 6.163\ \text{mol C} \tag{2.2.1}$$

$$(8.710\ \text{g H})\left(\frac{1\ \text{mol H}}{1.01\ \text{g H}}\right) = 8.624\ \text{mol H} \tag{2.2.2}$$

$$(17.27\ \text{g N})\left(\frac{1\ \text{mol N}}{14.01\ \text{g N}}\right) = 1.233\ \text{mol N} \tag{2.2.3}$$

Next, we calculate the molar ratios of these elements relative to the least abundant element, **N**.

$$6.163\ \text{mol C} / 1.233\ \text{mol N} = 5$$

$$8.264\ \text{mol H} / 1.233\ \text{mol N} = 7$$

$$1.233\ \text{mol N} / 1.233\ \text{mol N} = 1$$

$$1.233/1.233 = 1.000\ \text{mol N}$$

$$6.163/1.233 = 4.998\ \text{mol C}$$

$$8.624/1.233 = 6.994\ \text{mol H}$$

The C-to-N and H-to-N molar ratios are adequately close to whole numbers, and so the empirical formula is C_5H_7N. The empirical formula mass for this compound is therefore 81.13 amu/formula unit, or 81.13 g/mol formula unit.

We calculate the molar mass for nicotine from the given mass and molar amount of compound:

$$\frac{40.57\ \text{g nicotine}}{0.2500\ \text{mol nicotine}} = \frac{162.3\ \text{g}}{\text{mol}}$$

Comparing the molar mass and empirical formula mass indicates that each nicotine molecule contains two formula units:

$$\frac{162.3\ \text{g/mol}}{81.13\ \frac{\text{g}}{\text{formula unit}}} = 2\ \text{formula units/molecule}$$

Thus, we can derive the molecular formula for nicotine from the empirical formula by multiplying each subscript by two:

$$(C_5H_7N)_2 = C_{10}H_{14}N_2$$

Exercise 2.2.5

What is the molecular formula of a compound with a percent composition of 49.47% C, 5.201% H, 28.84% N, and 16.48% O, and a molecular mass of 194.2 amu?

Answer

$C_8H_{10}N_4O_2$

Summary

The chemical identity of a substance is defined by the types and relative numbers of atoms composing its fundamental entities (molecules in the case of covalent compounds, ions in the case of ionic compounds). A compound's percent composition provides the mass percentage of each element in the compound, and it is often experimentally determined and used to derive the compound's empirical formula. The empirical formula mass of a covalent compound may be compared to the compound's molecular or molar mass to derive a molecular formula.

Key Equations

- $\%X = \frac{\text{mass X}}{\text{mass compound}} \times 100\%$
- $\frac{\text{molecular or molar mass}\left(\text{amu or } \frac{\text{g}}{\text{mol}}\right)}{\text{empirical formula mass}\left(\text{amu or } \frac{\text{g}}{\text{mol}}\right)} = n \text{ formula units/molecule}$
- $(A_xB_y)_n = A_{nx}B_{ny}$

Glossary

percent composition

percentage by mass of the various elements in a compound

empirical formula mass

sum of average atomic masses for all atoms represented in an empirical formula

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2.3: Molarity

Learning Objectives

- Describe the fundamental properties of solutions
- Calculate solution concentrations using molarity
- Perform dilution calculations using the dilution equation

In preceding sections, we focused on the composition of substances: samples of matter that contain only one type of element or compound. However, mixtures—samples of matter containing two or more substances physically combined—are more commonly encountered in nature than are pure substances. Similar to a pure substance, the relative composition of a mixture plays an important role in determining its properties. The relative amount of oxygen in a planet's atmosphere determines its ability to sustain aerobic life. The relative amounts of iron, carbon, nickel, and other elements in steel (a mixture known as an "alloy") determine its physical strength and resistance to corrosion. The relative amount of the active ingredient in a medicine determines its effectiveness in achieving the desired pharmacological effect. The relative amount of sugar in a beverage determines its sweetness (Figure **2.3.1**). In this section, we will describe one of the most common ways in which the relative compositions of mixtures may be quantified.



Figure **2.3.1**: Sugar is one of many components in the complex mixture known as coffee. The amount of sugar in a given amount of coffee is an important determinant of the beverage's sweetness. (credit: Jane Whitney)

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:

$$M = \frac{\text{mol solute}}{\text{L solution}} \tag{2.3.1}$$

Example 2.3.1: Calculating Molar Concentrations

A 355-mL soft drink sample contains 0.133 mol of sucrose (table sugar). What is the molar concentration of sucrose in the beverage?

Solution

Since the molar amount of solute and the volume of solution are both given, the molarity can be calculated using the definition of molarity. Per this definition, the solution volume must be converted from mL to L:

$$\begin{aligned} M &= \frac{mol\ solute}{L\ solution} \\ &= \frac{0.133\ mol}{355\ mL \times \frac{1\ L}{1000\ mL}} \\ &= 0.375\ M \end{aligned}$$

Exercise 2.3.1

A teaspoon of table sugar contains about 0.01 mol sucrose. What is the molarity of sucrose if a teaspoon of sugar has been dissolved in a cup of tea with a volume of 200 mL?

Answer

0.05 M

Example 2.3.2: Deriving Moles and Volumes from Molar Concentrations

How much sugar (mol) is contained in a modest sip (~10 mL) of the soft drink from Example **2.3.1**?

Solution

In this case, we can rearrange the definition of molarity to isolate the quantity sought, moles of sugar. We then substitute the value for molarity that we derived in Example 3.4.2, 0.375 *M*:

$$M = \frac{\text{mol solute}}{\text{L solution}} \tag{2.3.2}$$

Multiple \label

Exercise 2.3.2

What volume (mL) of the sweetened tea described in Example **2.3.1** contains the same amount of sugar (mol) as 10 mL of the soft drink in this example?

Answer

80 mL

Example 2.3.3: Calculating Molar Concentrations from the Mass of Solute

Distilled white vinegar (Figure **2.3.2**) is a solution of acetic acid, CH_3CO_2H, in water. A 0.500-L vinegar solution contains 25.2 g of acetic acid. What is the concentration of the acetic acid solution in units of molarity?



Figure **2.3.3**: Distilled white vinegar is a solution of acetic acid in water.

A label on a container is shown. The label has a picture of a salad with the words “Distilled White Vinegar,” and, “Reduced with water to 5% acidity,” written above it.

Solution

As in previous examples, the definition of molarity is the primary equation used to calculate the quantity sought. In this case, the mass of solute is provided instead of its molar amount, so we must use the solute’s molar mass to obtain the amount of solute in moles:

$$M = \frac{\text{mol solute}}{\text{L solution}} = \frac{25.2\ \text{g}\ \ce{CH3CO2H} \times \frac{1\ \text{mol}\ \ce{CH3CO2H}}{60.052\ \text{g}\ \ce{CH3CO2H}}}{0.500\ \text{L solution}} = 0.839\ M \tag{2.3.3}$$

$$M = \frac{0.839\ \text{mol solute}}{1.00\ \text{L solution}}$$

Nov 29, 2019, 5:24 PM

$$M = \frac{\text{mol solute}}{\text{L solution}} = 0.839\ M \tag{2.3.4}$$

? Exercise 2.3.3

Calculate the molarity of 6.52 g of $\ce{CoCl2}$ (128.9 g/mol) dissolved in an aqueous solution with a total volume of 75.0 mL.

Answer

0.674 M

✓ Example 2.3.4: Determining the Mass of Solute in a Given Volume of Solution

How many grams of NaCl are contained in 0.250 L of a 5.30-*M* solution?

Solution

The volume and molarity of the solution are specified, so the amount (mol) of solute is easily computed as demonstrated in Example **2.3.3**:

$$M = \frac{\text{mol solute}}{\text{L solution}} \tag{2.3.5}$$

$$\text{mol solute} = M \times \text{L solution} \tag{2.3.6}$$

$$\text{mol solute} = 5.30\ \frac{\text{mol NaCl}}{\text{L}} \times 0.250\ \text{L} = 1.325\ \text{mol NaCl} \tag{2.3.7}$$

Finally, this molar amount is used to derive the mass of NaCl:

$$1.325\ \text{mol NaCl} \times \frac{58.44\ \text{g NaCl}}{\text{mol NaCl}} = 77.4\ \text{g NaCl} \tag{2.3.8}$$

? Exercise 2.3.4

How many grams of $CaCl_2$ (110.98 g/mol) are contained in 250.0 mL of a 0.200-M solution of calcium chloride?

Answer

5.55 g $CaCl_2$

When performing calculations stepwise, as in Example **2.3.3**, it is important to refrain from rounding any intermediate calculation results, which can lead to rounding errors in the final result. In Example **2.3.4**, the molar amount of NaCl computed in the first step, 1.325 mol, would be properly rounded to 1.32 mol if it were to be reported; however, although the last digit (5) is not significant, it must be retained as a guard digit in the intermediate calculation. If we had not retained this guard digit, the final calculation for the mass of NaCl would have been 77.1 g, a difference of 0.3 g.

In addition to retaining a guard digit for intermediate calculations, we can also avoid rounding errors by performing computations in a single step (Example **2.3.5**). This eliminates intermediate steps so that only the final result is rounded.

✓ Example 2.3.5: Determining the Volume of Solution

In Example **2.3.3**, we found the typical concentration of vinegar to be 0.839 *M*. What volume of vinegar contains 75.6 g of acetic acid?

Solution

First, use the molar mass to calculate moles of acetic acid from the given mass:

$$\text{g solute} \times \frac{\text{mol solute}}{\text{g solute}} = \text{mol solute} \tag{2.3.9}$$

Then, use the molarity of the solution to calculate the volume of solution containing this molar amount of solute:

$$\text{mol solute} \times \frac{\text{L solution}}{\text{mol solute}} = \text{L solution} \tag{2.3.10}$$

Combining these two steps into one yields:

$$\text{g solute} \times \frac{\text{mol solute}}{\text{g solute}} \times \frac{\text{L solution}}{\text{mol solute}} = \text{L solution} \tag{2.3.11}$$

$$75.6\ \text{g } CH_3CO_2H \left(\frac{\text{mol } CH_3CO_2H}{60.05\ \text{g}}\right)\left(\frac{\text{L solution}}{0.839\ \text{mol } CH_3CO_2H}\right) = 1.50\ \text{L solution} \tag{2.3.12}$$

? Exercise 2.3.5:

What volume of a 1.50-M KBr solution contains 66.0 g KBr?

Answer

0.370 L

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 **2.3.2**).

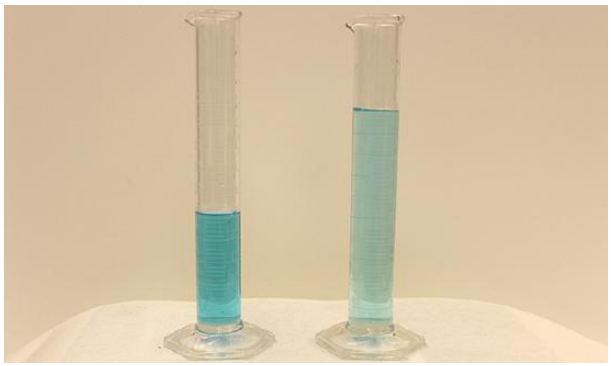


Figure **2.3.2**: Both solutions contain the same mass of copper nitrate. The solution on the right is more dilute because the copper nitrate is dissolved in more solvent. (credit: Mark Ott).

This figure shows two graduated cylinders side-by-side. The first has about half as much blue liquid as the second. The blue liquid is darker in the first cylinder than in the second.

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. For example, commercial pesticides are typically sold as solutions in which the active ingredients are far more concentrated than is appropriate for their application. Before they can be used on crops, the pesticides must be diluted. This is also a very common practice for the preparation of a number of common laboratory reagents (Figure **2.3.3**).



Figure **2.3.3**: A solution of $KMnO_4$ is prepared by mixing water with 4.74 g of KMnO4 in a flask. (credit: modification of work by Mark Ott)

This figure shows two photos. In the first, there is an empty glass container, 4.75 g of K M n O subscript 4 powder on a white circle, and a bottle of distilled water. In the second photo the powder and about half the water have been added to the glass container. The liquid in the glass container is almost black in color.

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*, $n_1 = n_2$. Thus, these two equations may be set equal to one another:

$$M_1L_1 = M_2L_2$$

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.

Example 2.3.6: Determining the Concentration of a Diluted Solution

If 0.850 L of a 5.00-*M* solution of copper nitrate, $Cu(NO_3)_2$, is diluted to a volume of 1.80 L by the addition of water, what is the molarity of the diluted solution?

Solution

We are given the volume and concentration of a stock solution, V_1 and C_1, and the volume of the resultant diluted solution, V_2. We need to find the concentration of the diluted solution, C_2. We thus rearrange the dilution equation in order to isolate C_2:

$$C_1V_1 = C_2V_2$$

$$C_2 = \frac{C_1V_1}{V_2}$$

Since the stock solution is being diluted by more than two-fold (volume is increased from 0.85 L to 1.80 L), we would expect the diluted solution's concentration to be less than one-half 5 *M*. We will compare this ballpark estimate to the calculated result to check for any gross errors in computation (for example, such as an improper substitution of the given quantities). Substituting the given values for the terms on the right side of this equation yields:

$$C_2 = \frac{0.850\ \text{L} \times 5.00\ \frac{\text{mol}}{\text{L}}}{1.80\ \text{L}} = 2.36\ M$$

This result compares well to our ballpark estimate (it's a bit less than one-half the stock concentration, 5 *M*).

Exercise 2.3.6

What is the concentration of the solution that results from diluting 25.0 mL of a 2.04-M solution of CH3OH to 500.0 mL?

Answer

0.102 M CH_3OH

Example 2.3.7: Volume of a Diluted Solution

What volume of 0.12 *M* HBr can be prepared from 11 mL (0.011 L) of 0.45 *M* HBr?

Solution

We are given the volume and concentration of a stock solution, V_1 and C_1, and the concentration of the resultant diluted solution, C_2. We need to find the volume of the diluted solution, V_2. We thus rearrange the dilution equation in order to isolate V_2:

$$C_1V_1 = C_2V_2$$

$$V_2 = \frac{C_1V_1}{C_2}$$

Since the diluted concentration (0.12 *M*) is slightly more than one-fourth the original concentration (0.45 *M*), we would expect the volume of the diluted solution to be roughly four times the original volume, or around 44 mL. Substituting the given values and solving for the unknown volume yields:

$$V_2 = \frac{(0.45\ M)(0.011\ \text{L})}{(0.12\ M)}$$

$$V_2 = 0.041\ \text{L}$$

The volume of the 0.12-*M* solution is 0.041 L (41 mL). The result is reasonable and compares well with our rough estimate.

? Exercise 2.3.7

A laboratory experiment calls for 0.125 M HNO_3. What volume of 0.125 M HNO_3 can be prepared from 0.250 L of 1.88 M HNO_3?

Answer

3.76 L

✓ Example 2.3.8: Volume of a Concentrated Solution Needed for Dilution

What volume of 1.59 *M* KOH is required to prepare 5.00 L of 0.100 *M* KOH?

Solution

We are given the concentration of a stock solution, C_1, and the volume and concentration of the resultant diluted solution, V_2 and C_2. We need to find the volume of the stock solution, V_1. We thus rearrange the dilution equation in order to isolate V_1:

$$C_1V_1 = C_2V_2$$

$$V_1 = \frac{C_2V_2}{C_1}$$

Since the concentration of the diluted solution 0.100 *M* is roughly one-sixteenth that of the stock solution (1.59 *M*), we would expect the volume of the stock solution to be about one-sixteenth that of the diluted solution, or around 0.3 liters. Substituting the given values and solving for the unknown volume yields:

$$V_1 = \frac{(0.100\ M)(5.00\ \text{L})}{1.59\ M}$$

$$V_1 = 0.314\ \text{L}$$

Thus, we would need 0.314 L of the 1.59-*M* solution to prepare the desired solution. This result is consistent with our rough estimate.

? Exercise 2.3.8

What volume of a 0.575-M solution of glucose, $C_6H_{12}O_6$, can be prepared from 50.00 mL of a 3.00-M glucose solution?

Answer

0.261

Summary

Solutions are homogeneous mixtures. Many solutions contain one component, called the solvent, in which other components, called solutes, are dissolved. An aqueous solution is one for which the solvent is water. The concentration of a solution is a measure of the relative amount of solute in a given amount of solution. Concentrations may be measured using various units, with one very useful unit being molarity, defined as the number of moles of solute per liter of solution. The solute concentration of a solution may

be decreased by adding solvent, a process referred to as dilution. The dilution equation is a simple relation between concentrations and volumes of a solution before and after dilution.

Key Equations

- $M = \frac{\text{mol solute}}{\text{L solution}}$
- $C_1V_1 = C_2V_2$

Glossary

aqueous solution
solution for which water is the solvent

concentrated
qualitative term for a solution containing solute at a relatively high concentration

concentration
quantitative measure of the relative amounts of solute and solvent present in a solution

dilute
qualitative term for a solution containing solute at a relatively low concentration

dilution
process of adding solvent to a solution in order to lower the concentration of solutes

dissolved
describes the process by which solute components are dispersed in a solvent

molarity (*M*)
unit of concentration, defined as the number of moles of solute dissolved in 1 liter of solution

solute
solution component present in a concentration less than that of the solvent

solvent
solution component present in a concentration that is higher relative to other components

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2.E: Composition of Substances and Solutions (Exercises)

3.1: Formula Mass and the Mole Concept

What is the total mass (amu) of carbon in each of the following molecules?

1. (a) CH_4
2. (b) $CHCl_3$
3. (c) $C_{12}H_{10}O_6$
4. (d) $CH_3CH_2CH_2CH_2CH_3$

(a) 12.01 amu; (b) 12.01 amu; (c) 144.12 amu; (d) 60.05 amu

What is the total mass of hydrogen in each of the molecules?

1. (a) CH_4
2. (b) $CHCl_3$
3. (c) $C_{12}H_{10}O_6$
4. (d) $CH_3CH_2CH_2CH_2CH_3$

Calculate the molecular or formula mass of each of the following:

(a) P_4

(b) H_2O

(c) $Ca(NO_3)_2$

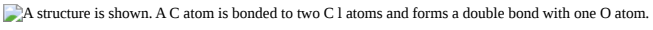
(d) CH_3CO_2H (acetic acid)

(e) $C_{12}H_{22}O_{11}$ (sucrose, cane sugar).

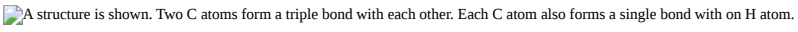
(a) 123.896 amu; (b) 18.015 amu; (c) 164.086 amu; (d) 60.052 amu; (e) 342.297 amu

Determine the molecular mass of the following compounds:

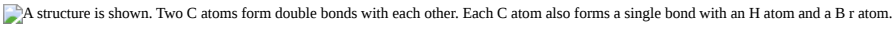
(a)



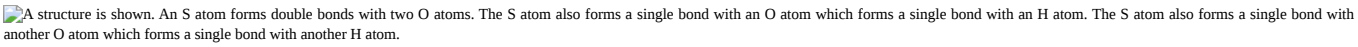
(b)



(c)

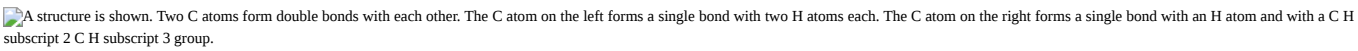


(d)

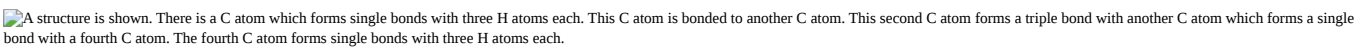


Determine the molecular mass of the following compounds:

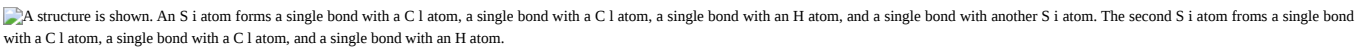
(a)



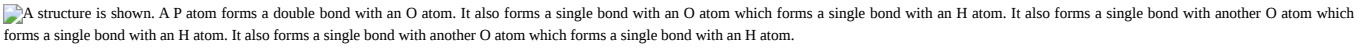
(b)



(c)



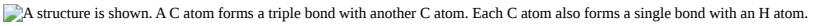
(d)



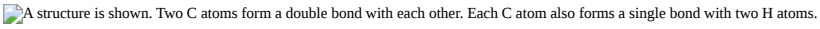
1. (a) 56.107 amu;
2. (b) 54.091 amu;
3. (c) 199.9976 amu;
4. (d) 97.9950 amu

Which molecule has a molecular mass of 28.05 amu?

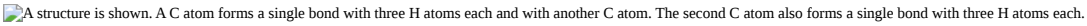
(a)



(b)



(c)



Write a sentence that describes how to determine the number of moles of a compound in a known mass of the compound if we know its molecular formula.

Use the molecular formula to find the molar mass; to obtain the number of moles, divide the mass of compound by the molar mass of the compound expressed in grams.

Compare 1 mole of H_2, 1 mole of O_2, and 1 mole of F_2.

1. (a) Which has the largest number of molecules? Explain why.
2. (b) Which has the greatest mass? Explain why.

Which contains the greatest mass of oxygen: 0.75 mol of ethanol (C_2H_5OH), 0.60 mol of formic acid (HCO_2H), or 1.0 mol of water (H_2O)? Explain why.

Formic acid. Its formula has twice as many oxygen atoms as the other two compounds (one each). Therefore, 0.60 mol of formic acid would be equivalent to 1.20 mol of a compound containing a single oxygen atom.

Which contains the greatest number of moles of oxygen atoms: 1 mol of ethanol (C_2H_5OH), 1 mol of formic acid (HCO_2H), or 1 mol of water (H_2O)? Explain why.

How are the molecular mass and the molar mass of a compound similar and how are they different?

The two masses have the same numerical value, but the units are different: The molecular mass is the mass of 1 molecule while the molar mass is the mass of 6.022×10^{23} molecules.

Calculate the molar mass of each of the following compounds:

1. (a) hydrogen fluoride, HF
2. (b) ammonia, NH_3
3. (c) nitric acid, HNO_3
4. (d) silver sulfate, Ag_2SO_4
5. (e) boric acid, $B(OH)_3$

Calculate the molar mass of each of the following:

1. (a) S_8
2. (b) C_5H_{12}
3. (c) $Sc_2(SO_4)_3$
4. (d) CH_3COCH_3 (acetone)
5. (e) $C_6H_{12}O_6$ (glucose)

(a) 256.528 g/mol; (b) 72.150 g mol^{-1}; (c) 378.103 g mol^{-1}; (d) 58.080 g mol^{-1}; (e) 180.158 g mol^{-1}

Calculate the empirical or molecular formula mass and the molar mass of each of the following minerals:

1. (a) limestone, $CaCO_3$
2. (b) halite, NaCl
3. (c) beryl, $Be_3Al_2Si_6O_{18}$
4. (d) malachite, $Cu_2(OH)_2CO_3$
5. (e) turquoise, $CuAl_6(PO_4)_4(OH)_8(H_2O)_4$

Calculate the molar mass of each of the following:

1. (a) the anesthetic halothane, $C_2HBrClF_3$
2. (b) the herbicide paraquat, $C_{12}H_{14}N_2Cl_2$
3. (c) caffeine, $C_8H_{10}N_4O_2$
4. (d) urea, $CO(NH_2)_2$
5. (e) a typical soap, $C_{17}H_{35}CO_2Na$

(a) 197.382 g mol^{-1}; (b) 257.163 g mol^{-1}; (c) 194.193 g mol^{-1}; (d) 60.056 g mol^{-1}; (e) 306.464 g mol^{-1}

Determine the number of moles of compound and the number of moles of each type of atom in each of the following:

1. (a) 25.0 g of propylene, C_3H_6
2. (b) 3.06×10^{-3} g of the amino acid glycine, $C_2H_5NO_2$
3. (c) 25 lb of the herbicide Treflan, $C_{13}H_{16}N_2O_4F$ (1 lb = 454 g)
4. (d) 0.125 kg of the insecticide Paris Green, $Cu_4(AsO_3)_2(CH_3CO_2)_2$
5. (e) 325 mg of aspirin, $C_6H_4(CO_2H)(CO_2CH_3)$

Determine the mass of each of the following:

1. (a) 0.0146 mol KOH
2. (b) 10.2 mol ethane, C_2H_6
3. (c) 1.6×10^{-3} mol $Na_2 SO_4$
4. (d) 6.854×10^3 mol glucose, $C_6 H_{12} O_6$
5. (e) 2.86 mol $Co(NH_3)_6Cl_3$

1. (a) 0.819 g;
2. (b) 307 g;
3. (c) 0.23 g;
4. (d) 1.235×10^6 g (1235 kg);
5. (e) 765 g

Determine the number of moles of the compound and determine the number of moles of each type of atom in each of the following:

1. (a) 2.12 g of potassium bromide, KBr
2. (b) 0.1488 g of phosphoric acid, H_3PO_4
3. (c) 23 kg of calcium carbonate, $CaCO_3$
4. (d) 78.452 g of aluminum sulfate, $Al_2(SO_4)_3$
5. (e) 0.1250 mg of caffeine, $C_8H_{10}N_4O_2$

Determine the mass of each of the following:

1. (a) 2.345 mol LiCl
2. (b) 0.0872 mol acetylene, C_2H_2
3. (c) 3.3×10^{-2} mol $Na_2 CO_3$
4. (d) 1.23×10^3 mol fructose, $C_6 H_{12} O_6$
5. (e) 0.5758 mol $FeSO_4(H_2O)_7$

1. (a) 99.41 g;
2. (b) 2.27 g;
3. (c) 3.5 g;

4. (d) 222 kg;
5. (e) 160.1 g

The approximate minimum daily dietary requirement of the amino acid leucine, $C_6H_{13}NO_2$, is 1.1 g. What is this requirement in moles?

Determine the mass in grams of each of the following:

1. (a) 0.600 mol of oxygen atoms
2. (b) 0.600 mol of oxygen molecules, O_2
3. (c) 0.600 mol of ozone molecules, O_3

1.

(a) 9.60 g; (b) 19.2 g; (c) 28.8 g

A 55-kg woman has 7.5×10^{-3} mol of hemoglobin (molar mass = 64,456 g/mol) in her blood. How many hemoglobin molecules is this? What is this quantity in grams?

Determine the number of atoms and the mass of zirconium, silicon, and oxygen found in 0.3384 mol of zircon, $ZrSiO_4$, a semiprecious stone.

zirconium: 2.038×10^{23} atoms; 30.87 g; silicon: 2.038×10^{23} atoms; 9.504 g; oxygen: 8.151×10^{23} atoms; 21.66 g

Determine which of the following contains the greatest mass of hydrogen: 1 mol of CH_4, 0.6 mol of C_6H_6, or 0.4 mol of C_3H_8.

Determine which of the following contains the greatest mass of aluminum: 122 g of $AlPO_4$, 266 g of Al_2Cl_6, or 225 g of Al_2S_3.

$AlPO_4$: 1.000 mol

Al_2Cl_6: 1.994 mol

Al_2S_3: 3.00 mol

Diamond is one form of elemental carbon. An engagement ring contains a diamond weighing 1.25 carats (1 carat = 200 mg). How many atoms are present in the diamond?

The Cullinan diamond was the largest natural diamond ever found (January 25, 1905). It weighed 3104 carats (1 carat = 200 mg). How many carbon atoms were present in the stone?

3.113×10^{25} C atoms

One 55-gram serving of a particular cereal supplies 270 mg of sodium, 11% of the recommended daily allowance. How many moles and atoms of sodium are in the recommended daily allowance?

A certain nut crunch cereal contains 11.0 grams of sugar (sucrose, $C_{12}H_{22}O_{11}$) per serving size of 60.0 grams. How many servings of this cereal must be eaten to consume 0.0278 moles of sugar?

0.865 servings, or about 1 serving.

A tube of toothpaste contains 0.76 g of sodium monofluorophosphate (Na_2PO_3F) in 100 mL.

a. What mass of fluorine atoms in mg was present?
b. How many fluorine atoms were present?

Which of the following represents the least number of molecules?

a. 20.0 g of H_2O (18.02 g/mol)
b. 77.0 g of CH_4 (16.06 g/mol)
c. 68.0 g of CaH_2 (42.09 g/mol)
d. 100.0 g of N_2O (44.02 g/mol)
e. 84.0 g of HF (20.01 g/mol)

20.0 g H_2O represents the least number of molecules since it has the least number of moles.

3.2: Determining Empirical and Molecular Formulas

What information do we need to determine the molecular formula of a compound from the empirical formula?

Calculate the following to four significant figures:

a. (a) the percent composition of ammonia, NH_3
b. (b) the percent composition of photographic “hypo,” $Na_2S_2O_3$
c. (c) the percent of calcium ion in $Ca_3(PO_4)_2$

(a) % N = 82.24%

% H = 17.76%;

(b) % Na = 29.08%

% S = 40.56%

% O = 30.36%;

(c) % Ca^{2+} = 38.76%

Determine the following to four significant figures:

a. the percent composition of hydrazoic acid, HN_3
b. the percent composition of TNT, $C_6H_2(CH_3)(NO_2)_3$
c. the percent of SO_4^{2-} in $Al_2(SO_4)_3$

Determine the percent ammonia, NH_3, in $Co(NH_3)_6Cl_3$, to three significant figures.

% NH_3 = 38.2%

Determine the percent water in $CuSO_4 \cdot 5H_2O$ to three significant figures.

Determine the empirical formulas for compounds with the following percent compositions:

(a) 15.8% carbon and 84.2% sulfur

(b) 40.0% carbon, 6.7% hydrogen, and 53.3% oxygen

(a) CS_2

(b) CH_2O

Determine the empirical formulas for compounds with the following percent compositions:

(a) 43.6% phosphorus and 56.4% oxygen

(b) 28.7% K, 1.5% H, 22.8% P, and 47.0% O

A compound of carbon and hydrogen contains 92.3% C and has a molar mass of 78.1 g/mol. What is its molecular formula?

C_6H_6

Dichloroethane, a compound that is often used for dry cleaning, contains carbon, hydrogen, and chlorine. It has a molar mass of 99 g/mol. Analysis of a sample shows that it contains 24.3% carbon and 4.1% hydrogen. What is its molecular formula?

Determine the empirical and molecular formula for chrysotile asbestos. Chrysotile has the following percent composition: 28.03% Mg, 21.60% Si, 1.16% H, and 49.21% O. The molar mass for chrysotile is 520.8 g/mol.

$Mg_3Si_2H_3O_8$ (empirical formula), $Mg_6Si_4H_6O_{16}$ (molecular formula)

Polymers are large molecules composed of simple units repeated many times. Thus, they often have relatively simple empirical formulas. Calculate the empirical formulas of the following polymers:

a. Lucite (Plexiglas); 59.9% C, 8.06% H, 32.0% O
b. Saran; 24.8% C, 2.0% H, 73.1% Cl
c. polyethylene; 86% C, 14% H

d. polystyrene; 92.3% C, 7.7% H
e. Orlon; 67.9% C, 5.70% H, 26.4% N

A major textile dye manufacturer developed a new yellow dye. The dye has a percent composition of 75.95% C, 17.72% N, and 6.33% H by mass with a molar mass of about 240 g/mol. Determine the molecular formula of the dye.

$C_{15}H_{15}N_3$

3.3: Molarity

Questions

Explain what changes and what stays the same when 1.00 L of a solution of NaCl is diluted to 1.80 L.

What information do we need to calculate the molarity of a sulfuric acid solution?

We need to know the number of moles of sulfuric acid dissolved in the solution and the volume of the solution.

What does it mean when we say that a 200-mL sample and a 400-mL sample of a solution of salt have the same molarity? In what ways are the two samples identical? In what ways are these two samples different?

Determine the molarity for each of the following solutions:

a. 0.444 mol of $CoCl_2$ in 0.654 L of solution
b. 98.0 g of phosphoric acid, H_3PO_4, in 1.00 L of solution
c. 0.2074 g of calcium hydroxide, $Ca(OH)_2$, in 40.00 mL of solution
d. 10.5 kg of $Na_2SO_4 \cdot 10H_2O$ in 18.60 L of solution
e. 7.0×10^{-3} mol of I_2 in 100.0 mL of solution
f. 1.8×10^4 mg of HCl in 0.075 L of solution

a. (a) 0.679 *M*;
b. (b) 1.00 *M*;
c. (c) 0.06998 *M*;
d. (d) 1.75 *M*;
e. (e) 0.070 *M*;
f. (f) 6.6 *M*

Determine the molarity of each of the following solutions:

a. 1.457 mol KCl in 1.500 L of solution
b. 0.515 g of H_2SO_4 in 1.00 L of solution
c. 20.54 g of $Al(NO_3)_3$ in 1575 mL of solution
d. 2.76 kg of $CuSO_4 \cdot 5H_2O$ in 1.45 L of solution
e. 0.005653 mol of Br_2 in 10.00 mL of solution
f. 0.000889 g of glycine, $C_2H_5NO_2$, in 1.05 mL of solution

Answers:

a.) 0.9713 M

b.) 5.25×10^{-3} M

c.) 6.122×10^{-2} M

d.) 7.62 M

e.) 0.5653 M

f.) 1.13×10^{-2} M

Consider this question: What is the mass of the solute in 0.500 L of 0.30 *M* glucose, $C_6H_{12}O_6$, used for intravenous injection?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

(a) determine the number of moles of glucose in 0.500 L of solution; determine the molar mass of glucose; determine the mass of glucose from the number of moles and its molar mass; (b) 27 g

Consider this question: What is the mass of solute in 200.0 L of a 1.556-*M* solution of KBr?

1. (a) Outline the steps necessary to answer the question.
2. (b) Answer the question.

Answer:

(a)

1. Calculate to moles of KBr by multiplying the Molarity by the amount of solution (200.0 L)
2. Find the Molar Mass of KBr and convert moles of solute to grams

(b)

$$\frac{1.556\ moles\ \mathrm{KBr}}{1\ \cancel{L}} \times 200.0\ \cancel{L} = 311.2\ moles\ \mathrm{KBr}$$

$$311.2\ \cancel{moles}\ \mathrm{KBr} \times \frac{119.0\ g\ \mathrm{KBr}}{1\ \cancel{mole}\ \mathrm{KBr}} = 37,030\ g$$

37,030g; 37.03 kg

Calculate the number of moles and the mass of the solute in each of the following solutions:

1. (a) 2.00 L of 18.5 *M* H_2SO_4, concentrated sulfuric acid
2. (b) 100.0 mL of 3.8×10^{-5} *M* NaCN, the minimum lethal concentration of sodium cyanide in blood serum
3. (c) 5.50 L of 13.3 *M* H_2CO, the formaldehyde used to “fix” tissue samples
4. (d) 325 mL of 1.8×10^{-6} *M* $FeSO_4$, the minimum concentration of iron sulfate detectable by taste in drinking water

(a) 37.0 mol H_2SO_4;

3.63×10^3 g H_2SO_4;

(b) 3.8×10^{-6} mol NaCN;

1.9×10^{-4} g NaCN;

(c) 73.2 mol H_2CO;

2.20 kg H_2CO;

(d) 5.9×10^{-7} mol $FeSO_4$;

8.9×10^{-5} g $FeSO_4$

Calculate the number of moles and the mass of the solute in each of the following solutions:

a. 325 mL of 8.23×10^{-5} *M* KI, a source of iodine in the diet
b. 75.0 mL of 2.2×10^{-5} *M* H_2SO_4, a sample of acid rain
c. 0.2500 L of 0.1135 *M* K_2CrO_4, an analytical reagent used in iron assays
d. 10.5 L of 3.716 *M* $(NH_4)_2SO_4$, a liquid fertilizer

Answers:

a. 2.67×10^{-5} moles KI; 4.44×10^{-3}g KI

b. 1.7×10^{-6} moles H_2SO_4 ; 1.6×10^{-4} g H_2SO_4

c. 2.838×10^{-2} moles K_2CrO_4 ; 5.510g K_2CrO_4

d. 39.0 moles $(NH_4)_2SO_4$; 5,160 g $(NH_4)_2SO_4$

Consider this question: What is the molarity of $KMnO_4$ in a solution of 0.0908 g of $KMnO_4$ in 0.500 L of solution?

1. (a) Outline the steps necessary to answer the question.
2. (b) Answer the question.

(a) Determine the molar mass of $KMnO_4$; determine the number of moles of $KMnO_4$ in the solution; from the number of moles and the volume of solution, determine the molarity; (b) 1.15×10^{-3} *M*

Consider this question: What is the molarity of HCl if 35.23 mL of a solution of HCl contain 0.3366 g of HCl?

1. (a) Outline the steps necessary to answer the question.
2. (b) Answer the question.

Answer:

(a)

1. Convert g of HCl to moles of HCl and convert mL of solution to L of solution
2. Divide moles of HCl by L of solution

(b)

$$0.3366 \ \cancel{g}\ \text{HCl} \times \frac{1\ mole\ \text{HCl}}{36.46\ \cancel{g}\ \text{HCl}} = 9.232 \times 10^{-3}\ moles\ \text{HCl}$$

$$35.23\ mL = 0.03523\ L$$

$$\frac{9.232 \times 10^{-3}\ moles\ \text{HCl}}{0.03523\ L} = 0.2621\ M\ \text{HCl}$$

0.2621 M ;

Calculate the molarity of each of the following solutions:

(a) 0.195 g of cholesterol, $C_{27}H_{46}O$, in 0.100 L of serum, the average concentration of cholesterol in human serum

(b) 4.25 g of NH_3 in 0.500 L of solution, the concentration of NH_3 in household ammonia

(c) 1.49 kg of isopropyl alcohol, C_3H_7OH, in 2.50 L of solution, the concentration of isopropyl alcohol in rubbing alcohol

(d) 0.029 g of I_2 in 0.100 L of solution, the solubility of I_2 in water at 20 °C

(a) 5.04×10^{-3} *M*;

(b) 0.499 *M*;

(c) 9.92 *M*;

(d) 1.1×10^{-3} *M*

Calculate the molarity of each of the following solutions:

a. 293 g HCl in 666 mL of solution, a concentrated HCl solution
b. 2.026 g $FeCl_3$ in 0.1250 L of a solution used as an unknown in general chemistry laboratories
c. 0.001 mg Cd^{2+} in 0.100 L, the maximum permissible concentration of cadmium in drinking water
d. 0.0079 g $C_7H_5SNO_3$ in one ounce (29.6 mL), the concentration of saccharin in a diet soft drink.

There is about 1.0 g of calcium, as Ca^{2+}, in 1.0 L of milk. What is the molarity of Ca^{2+} in milk?

0.025 *M*

What volume of a 1.00-*M* $Fe(NO_3)_3$ solution can be diluted to prepare 1.00 L of a solution with a concentration of 0.250 *M*?

If 0.1718 L of a 0.3556-*M* C_3H_7OH solution is diluted to a concentration of 0.1222 *M*, what is the volume of the resulting solution?

0.5000 L

If 4.12 L of a 0.850 *M*-H_3PO_4 solution is be diluted to a volume of 10.00 L, what is the concentration the resulting solution?

What volume of a 0.33-*M* $C_{12}H_{22}O_{11}$ solution can be diluted to prepare 25 mL of a solution with a concentration of 0.025 *M*?

1.9 mL

What is the concentration of the NaCl solution that results when 0.150 L of a 0.556-*M* solution is allowed to evaporate until the volume is reduced to 0.105 L?

What is the molarity of the diluted solution when each of the following solutions is diluted to the given final volume?

a. (a) 1.00 L of a 0.250-*M* solution of $Fe(NO_3)_3$ is diluted to a final volume of 2.00 L
b. (b) 0.5000 L of a 0.1222-*M* solution of C_3H_7OH is diluted to a final volume of 1.250 L
c. (c) 2.35 L of a 0.350-*M* solution of H_3PO_4 is diluted to a final volume of 4.00 L
d. (d) 22.50 mL of a 0.025-*M* solution of $C_{12}H_{22}O_{11}$ is diluted to 100.0 mL

1. (a) 0.125 *M*;
2. (b) 0.04888 *M*;
3. (c) 0.206 *M*;
4. (e) 0.0056 *M*

What is the final concentration of the solution produced when 225.5 mL of a 0.09988-*M* solution of Na_2CO_3 is allowed to evaporate until the solution volume is reduced to 45.00 mL?

A 2.00-L bottle of a solution of concentrated HCl was purchased for the general chemistry laboratory. The solution contained 868.8 g of HCl. What is the molarity of the solution?

11.9 *M*

An experiment in a general chemistry laboratory calls for a 2.00-*M* solution of HCl. How many mL of 11.9 *M* HCl would be required to make 250 mL of 2.00 *M* HCl?

What volume of a 0.20-*M* K_2SO_4 solution contains 57 g of K_2SO_4?

1.6 L

The US Environmental Protection Agency (EPA) places limits on the quantities of toxic substances that may be discharged into the sewer system. Limits have been established for a variety of substances, including hexavalent chromium, which is limited to 0.50 mg/L. If an industry is discharging hexavalent chromium as potassium dichromate ($K_2Cr_2O_7$), what is the maximum permissible molarity of that substance?

3.4: Other Units for Solution Concentrations

Questions

1. Consider this question: What mass of a concentrated solution of nitric acid (68.0% HNO3 by mass) is needed to prepare 400.0 g of a 10.0% solution of HNO3 by mass?
   a. Outline the steps necessary to answer the question.
   b. Answer the question.
2. What mass of a 4.00% NaOH solution by mass contains 15.0 g of NaOH?
3. What mass of solid NaOH (97.0% NaOH by mass) is required to prepare 1.00 L of a 10.0% solution of NaOH by mass? The density of the 10.0% solution is 1.109 g/mL.
4. What mass of HCl is contained in 45.0 mL of an aqueous HCl solution that has a density of 1.19 g cm–3 and contains 37.21% HCl by mass?
5. The hardness of water (hardness count) is usually expressed in parts per million (by mass) of $CaCO_3$, which is equivalent to milligrams of $CaCO_3$ per liter of water. What is the molar concentration of Ca^{2+} ions in a water sample with a hardness count of 175 mg $CaCO_3$/L?
6. The level of mercury in a stream was suspected to be above the minimum considered safe (1 part per billion by weight). An analysis indicated that the concentration was 0.68 parts per billion. Assume a density of 1.0 g/mL and calculate the molarity of mercury in the stream.
7. In Canada and the United Kingdom, devices that measure blood glucose levels provide a reading in millimoles per liter. If a measurement of 5.3 mM is observed, what is the concentration of glucose ($C_6H_{12}O_6$) in mg/dL?

8. A throat spray is 1.40% by mass phenol, $\mathbf{C_6H_5OH}$, in water. If the solution has a density of 0.9956 g/mL, calculate the molarity of the solution.
9. Copper(I) iodide (CuI) is often added to table salt as a dietary source of iodine. How many moles of CuI are contained in 1.00 lb (454 g) of table salt containing 0.0100% CuI by mass?
10. A cough syrup contains 5.0% ethyl alcohol, C_2H_5OH, by mass. If the density of the solution is 0.9928 g/mL, determine the molarity of the alcohol in the cough syrup.
11. D5W is a solution used as an intravenous fluid. It is a 5.0% by mass solution of dextrose ($\mathbf{C_6H_{12}O_6}$) in water. If the density of D5W is 1.029 g/mL, calculate the molarity of dextrose in the solution.
12. Find the molarity of a 40.0% by mass aqueous solution of sulfuric acid, $\mathbf{H_2SO_4}$, for which the density is 1.3057 g/mL.

Solutions

1

- (a) The dilution equation can be used, appropriately modified to accommodate mass-based concentration units:

$$\%\,\mathbf{mass_1} \times \mathbf{mass_1} = \%\,\mathbf{mass_2} \times \mathbf{mass_2} \qquad (\mathbf{2.E.1})$$

  This equation can be rearranged to isolate $\mathbf{mass_1}$ and the given quantities substituted into this equation.
- (b) 58.8 g

3. $\mathbf{114\ g}$ 5. $\mathbf{1.75 \times 10^{-3}}\,M$ 7 $\mathbf{95\ mg/dL}$ 9 $\mathbf{2.38 \times 10^{-4}\ mol}$ 11 $\mathbf{0.29 mol}$

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CHAPTER OVERVIEW

3: Stoichiometry of Chemical Reactions

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General Chemistry

This chapter will describe how to symbolize chemical reactions using chemical equations, how to classify some common chemical reactions by identifying patterns of reactivity, and how to determine the quantitative relations between the amounts of substances involved in chemical reactions—that is, the reaction *stoichiometry*.

3.1: Prelude to Stoichiometry

3.2: Writing and Balancing Chemical Equations

3.3: Classifying Chemical Reactions

3.4: Reaction Stoichiometry

3.5: Reaction Yields

3.E: Stoichiometry of Chemical Reactions (Exercises)

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3.1: Prelude to Stoichiometry

Solid-fuel rockets are a central feature in the world's space exploration programs, including the new Space Launch System being developed by the National Aeronautics and Space Administration (NASA) to replace the retired Space Shuttle fleet (Figure **3.1.1**). The engines of these rockets rely on carefully prepared solid mixtures of chemicals combined in precisely measured amounts. Igniting the mixture initiates a vigorous chemical reaction that rapidly generates large amounts of gaseous products. These gases are ejected from the rocket engine through its nozzle, providing the thrust needed to propel heavy payloads into space. Both the nature of this chemical reaction and the relationships between the amounts of the substances being consumed and produced by the reaction are critically important considerations that determine the success of the technology. This chapter will describe how to symbolize chemical reactions using chemical equations, how to classify some common chemical reactions by identifying patterns of reactivity, and how to determine the quantitative relations between the amounts of substances involved in chemical reactions—that is, the reaction *stoichiometry*.



Figure **3.1.1**: Many modern rocket fuels are solid mixtures of substances combined in carefully measured amounts and ignited to yield a thrust-generating chemical reaction. (credit: modification of work by NASA)

An image is shown of a rocket that appears to have just passed through a layer of clouds as it travels skyward. A bright white light is seen in the upper right corner of the image. To the lower left appears the layer of clouds and the bottom of the rocket with fire projecting from the fuel cones at its base.

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3.2: Writing and Balancing Chemical Equations

Learning Objectives

- Derive chemical equations from narrative descriptions of chemical reactions.
- Write and balance chemical equations in molecular, total ionic, and net ionic formats.

The preceding chapter introduced the use of element symbols to represent individual atoms. 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 the upper half of Figure **3.2.1**, with space-filling molecular models shown in the lower half of the figure.

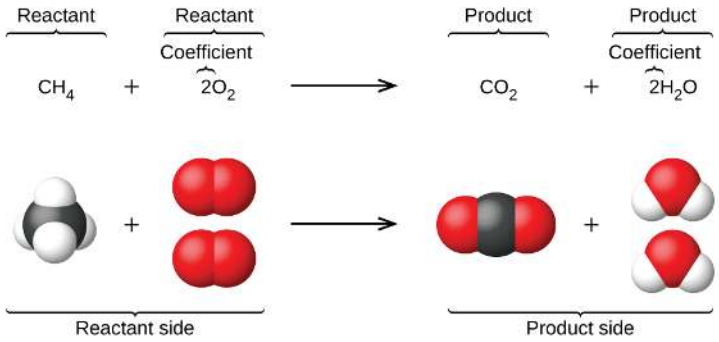


Figure **3.2.1**: The reaction between methane and oxygen to yield carbon dioxide and water (shown at bottom) may be represented by a chemical equation using formulas (top).

This figure shows a balanced chemical equation followed below by a representation of the equation using space-filling models. The equation reads C H subscript 4 plus 2 O subscript 2 arrow C O subscript 2 plus 2 H subscript 2 O. Under the C H subscript 4, the molecule is shown with a central black sphere, representing a C atom, to which 4 smaller white spheres, representing H atoms, are distributed evenly around. All four H atoms are bonded to the central black C atom. This is followed by a plus sign. Under the 2 O subscript 2, two molecules are shown. The molecules are each composed of two red spheres bonded together. The red spheres represent O atoms. To the right of an arrow and under the C O subscript 2, appears a single molecule with a black central sphere with two red spheres bonded to the left and right. Following a plus sign and under the 2 H subscript 2 O, are two molecules, each with a central red sphere and two smaller white spheres attached to the lower right and lower left sides of the central red sphere. Note that in space filling models of molecules, spheres appear slightly compressed in regions where there is a bond between two atoms.

This example illustrates the fundamental aspects of any chemical equation:

1. The substances undergoing reaction are called reactants, and their formulas are placed on the left side of the equation.
2. The substances generated by the reaction are called products, and their formulas are placed on the right sight of the equation.
3. Plus signs (+) separate individual reactant and product formulas, and an arrow (⟶) separates the reactant and product (left and right) sides of the equation.
4. The relative numbers of reactant and product species are represented by coefficients (numbers placed immediately to the left of each formula). A coefficient of 1 is typically omitted.

It is common practice to use the smallest possible whole-number coefficients in a chemical equation, as is done in this example. Realize, however, that these coefficients represent the *relative* numbers of reactants and products, and, therefore, they may be correctly interpreted as ratios. Methane and oxygen react to yield carbon dioxide and water in a 1:2:1:2 ratio. This ratio is satisfied if the numbers of these molecules are, respectively, 1-2-1-2, or 2-4-2-4, or 3-6-3-6, and so on (Figure **3.2.2**). Likewise, these coefficients may be interpreted with regard to 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.

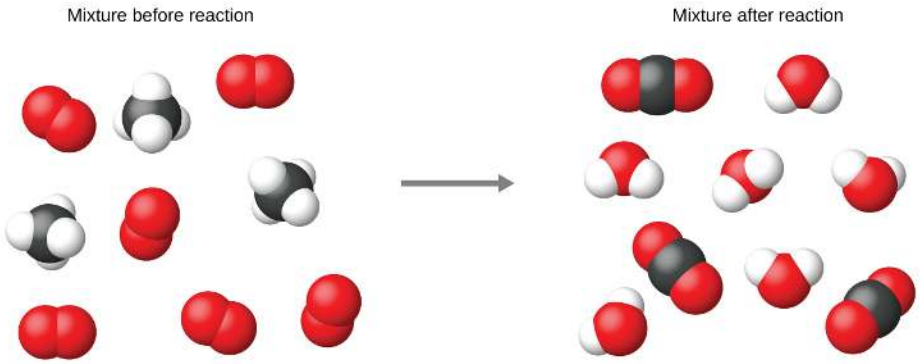


Figure **3.2.2**: Regardless of the absolute number of molecules involved, the ratios between numbers of molecules of each species that react (the reactants) and molecules of each species that form (the products) are the same and are given in the chemical equation.

Balancing Equations

When a chemical equation is balanced it means that equal numbers of atoms for each element involved in the reaction are represented on the reactant and product sides. This is a requirement 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, $\mathbf{CO_2}$ and $\mathbf{H_2O}$, contain the element oxygen, and so the number of oxygen atoms on the product side of the equation is

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

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:

$$\mathbf{CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O}$$

Equation for the reaction

$$\mathbf{CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O}$$

Element	Reactants	Products	Balanced?
C	1 × 1 = 1	1 × 1 = 1	1 = 1, yes
H	4 × 1 = 4	2 × 2 = 4	4 = 4, yes
O	2 × 2 = 4	(1 × 2) + (2 × 1) = 4	4 = 4, yes

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. Consider as an example the decomposition of water to yield molecular hydrogen and oxygen. This process is represented qualitatively by an *unbalanced* chemical equation:

$$\mathbf{H_2O \rightarrow H_2 + O_2} \qquad \textbf{(unbalanced)}$$

Comparing the number of H and O atoms on either side of this equation confirms its imbalance:

Comparisons between H and O atoms

Element	Reactants	Products	Balanced?
H	1 × 2 = 2	1 × 2 = 2	2 = 2, yes
O	1 × 1 = 1	1 × 2 = 2	1 ≠ 2, no

The numbers of H atoms on the reactant and product sides of the equation are equal, but the numbers of O atoms are not. To achieve balance, the *coefficients* of the equation may be changed as needed. Keep in mind, of course, that the *formula subscripts* define, in part, the identity of the substance, and so these cannot be changed without altering the qualitative meaning of the equation. For example, changing the reactant formula from H_2O to H_2O_2 would yield balance in the number of atoms, but doing so also changes the reactant's identity (it's now hydrogen peroxide and not water). The O atom balance may be achieved by changing the coefficient for H_2O to 2.

$$2\,H_2O \rightarrow H_2 + O_2 \qquad \text{(unbalanced)}$$

O atom balance may be achieved by changing the coefficient for H2O to 2

Element	Reactants	Products	Balanced?
H	**2** × 2 = 4	1 × 2 = 2	4 ≠ 2, no
O	2 × 1 = 2	1 × 2 = 2	2 = 2, yes

The H atom balance was upset by this change, but it is easily reestablished by changing the coefficient for the H_2 product to 2.

$$2\,H_2O \rightarrow 2\,H_2 + O_2 \qquad \text{(balanced)}$$

H atom balance upset but easily reestablished by changing the coefficient for the H2 product to 2.

Element	Reactants	Products	Balanced?
H	2 × 2 = 4	**2** × 2 = 2	4 = 4, yes
O	2 × 1 = 2	1 × 2 = 2	2 = 2, yes

These coefficients yield equal numbers of both H and O atoms on the reactant and product sides, and the balanced equation is, therefore:

$$2\,H_2O \rightarrow 2\,H_2 + O_2$$

Example 3.2.1: Balancing Chemical Equations

Write a balanced equation for the reaction of molecular nitrogen (N_2) and oxygen (O_2) to form dinitrogen pentoxide.

Solution

First, write the unbalanced equation.

$$N_2 + O_2 \rightarrow N_2O_5 \qquad \text{(unbalanced)}$$

Next, count the number of each type of atom present in the unbalanced equation.

Unbalanced Equation

Element	Reactants	Products	Balanced?
N	1 × 2 = 2	1 × 2 = 2	2 = 2, yes
O	1 × 2 = 2	1 × 5 = 5	2 ≠ 5, no

Though nitrogen is balanced, changes in coefficients are needed to balance the number of oxygen atoms. To balance the number of oxygen atoms, a reasonable first attempt would be to change the coefficients for the O_2 and N_2O_5 to integers that will yield 10 O atoms (the least common multiple for the O atom subscripts in these two formulas).

$$\mathrm{N_2 + 5\,O_2 \rightarrow 2\,N_2O_5} \qquad \text{(unbalanced)}$$

$$\mathrm{N_2 + 5\,O_2 \rightarrow 2\,N_2O_5} \qquad \text{(unbalanced)}$$

Element	Reactants	Products	Balanced?
N	1 × 2 = 2	**2** × 2 = 4	2 ≠ 4, no
O	**5** × 2 = 10	**2** × 5 = 10	10 = 10, yes

The N atom balance has been upset by this change; it is restored by changing the coefficient for the reactant N_2 to 2.

$$\mathrm{2\,N_2 + 5\,O_2 \rightarrow 2\,N_2O_5}$$

N atom balance upset but restored by changing the coefficient for the reactant N2 to 2.

Element	Reactants	Products	Balanced?
N	**2** × 2 = 4	2 × 2 = 4	4 = 4, yes
O	5 × 2 = 10	2 × 5 = 10	10 = 10, yes

The numbers of N and O atoms on either side of the equation are now equal, and so the equation is balanced.

? Exercise 3.2.1

Write a balanced equation for the decomposition of ammonium nitrate to form molecular nitrogen, molecular oxygen, and water. (Hint: Balance oxygen last, since it is present in more than one molecule on the right side of the equation.)

Answer

$$\mathrm{2\,NH_4NO_3 \rightarrow 2\,N_2 + O_2 + 4\,H_2O}$$

Balancing Reactions Which Contain Polyatomics: Balancing Reactions Which Contain Polyatomics(opens in new window) [youtu.be]

It is sometimes convenient to use fractions instead of integers as intermediate coefficients in the process of balancing a chemical equation. When balance is achieved, all the equation's coefficients may then be multiplied by a whole number to convert the fractional coefficients to integers without upsetting the atom balance. For example, consider the reaction of ethane (C_2H_6) with oxygen to yield H_2O and CO_2, represented by the unbalanced equation:

$$\mathrm{C_2H_6 + O_2 \rightarrow H_2O + CO_2} \qquad \text{(unbalanced)}$$

Following the usual inspection approach, one might first balance C and H atoms by changing the coefficients for the two product species, as shown:

$$C_2H_6 + O_2 \rightarrow 3\,H_2O + 2\,CO_2 \quad \text{(unbalanced)}$$

This results in seven O atoms on the product side of the equation, an odd number—no integer coefficient can be used with the O_2 reactant to yield an odd number, so a fractional coefficient, $\frac{7}{2}$, is used instead to yield a provisional balanced equation:

$$C_2H_6 + \tfrac{7}{2}\,O_2 \rightarrow 3\,H_2O + 2\,CO_2$$

A conventional balanced equation with integer-only coefficients is derived by multiplying each coefficient by 2:

$$2\,C_2H_6 + 7\,O_2 \rightarrow 6\,H_2O + 4\,CO_2$$

Finally with regard to balanced equations, recall that convention dictates use of the *smallest whole-number coefficients*. Although the equation for the reaction between molecular nitrogen and molecular hydrogen to produce ammonia is, indeed, balanced,

$$3\,N_2 + 9\,H_2 \rightarrow 6\,NH_3$$

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:

$$N_2 + 3\,H_2 \rightarrow 2\,NH_3$$

Phet Simulation

Use this interactive tutorial for additional practice balancing equations.

Additional Information in Chemical Equations

The physical states of reactants and products in chemical equations very often are indicated with a parenthetical abbreviation following the formulas. Common abbreviations include *s* for solids, *l* for liquids, *g* for gases, and *aq* for substances dissolved in water (*aqueous solutions*, as introduced in the preceding chapter). These notations are illustrated in the example equation here:

$$2\,Na\,(s) + 2\,H_2O\,(l) \rightarrow 2\,NaOH\,(aq) + H_2\,(g)$$

This equation represents the reaction that takes place when sodium metal is placed in water. The solid sodium reacts with liquid water to produce molecular hydrogen gas and the ionic compound sodium hydroxide (a solid in pure form, but readily dissolved in water).

Special conditions necessary for a reaction are sometimes designated by writing a word or symbol above or below the equation's arrow. For example, a reaction carried out by heating may be indicated by the uppercase Greek letter delta (Δ) over the arrow.

$$CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)$$

Other examples of these special conditions will be encountered in more depth in later chapters.

Equations for Ionic Reactions

Given the abundance of water on earth, it stands to reason that a great many chemical reactions take place in aqueous media. When ions are involved in these reactions, the chemical equations may be written with various levels of detail appropriate to their intended use. To illustrate this, consider a reaction between ionic compounds taking place in an aqueous solution. When aqueous solutions of $CaCl_2$ and $AgNO_3$ are mixed, a reaction takes place producing aqueous $Ca(NO_3)_2$ and solid $AgCl$:

$$CaCl_2(aq) + 2\,AgNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + 2\,AgCl(s)$$

This balanced equation, derived in the usual fashion, is called a molecular equation because it doesn't explicitly represent the ionic species that are present in solution. When ionic compounds dissolve in water, they may *dissociate* into their constituent ions, which are subsequently dispersed homogenously throughout the resulting solution (a thorough discussion of this important process is provided in the chapter on solutions). Ionic compounds dissolved in water are, therefore, more realistically represented as dissociated ions, in this case:

$$CaCl_2(aq) \rightarrow Ca^{2+}(aq) + 2\,Cl^-(aq)$$

$$2\,AgNO_3(aq) \rightarrow 2\,Ag^+(aq) + 2\,NO_3{}^-(aq)$$

$$Ca(NO_3)_2(aq) \rightarrow Ca^{2+}(aq) + 2\,NO_3{}^-(aq)$$

Unlike these three ionic compounds, AgCl does not dissolve in water to a significant extent, as signified by its physical state notation, *(s)*.

Explicitly representing all dissolved ions results in a complete ionic equation. In this particular case, the formulas for the dissolved ionic compounds are replaced by formulas for their dissociated ions:

$$Ca^{2+}(aq) + 2\,Cl^-(aq) + 2\,Ag^+(aq) + 2\,NO_3{}^-(aq) \rightarrow Ca^{2+}(aq) + 2\,NO_3{}^-(aq) + 2\,AgCl(s)$$

Examining this equation shows that two chemical species are present in identical form on both sides of the arrow, $Ca^{2+}(aq)$ and $NO_3{}^-(aq)$. These spectator ions—ions whose presence is required to maintain charge neutrality—are neither chemically nor physically changed by the process, and so they may be eliminated from the equation to yield a more succinct representation called a net ionic equation:

$$\cancel{Ca^{2+}(aq)} + 2\,Cl^-(aq) + 2\,Ag^+(aq) + \cancel{2\,NO_3{}^-(aq)} \rightarrow \cancel{Ca^{2+}(aq)} + \cancel{2\,NO_3{}^-(aq)} + 2\,AgCl(s)$$

$$2\,Cl^-(aq) + 2\,Ag^+(aq) \rightarrow 2\,AgCl(s)$$

Following the convention of using the smallest possible integers as coefficients, this equation is then written:

$$Cl^-(aq) + Ag^+(aq) \rightarrow AgCl(s)$$

This net ionic equation indicates that solid silver chloride may be produced from dissolved chloride and silver(I) ions, regardless of the source of these ions. These molecular and complete ionic equations provide additional information, namely, the ionic compounds used as sources of Cl^- and Ag^+.

✔ Example 3.2.2: 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:

$$CO_2\,(aq) + NaOH\,(aq) \rightarrow Na_2CO_3\,(aq) + H_2O\,(l) \qquad \text{(unbalanced)}$$

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

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

The two dissolved ionic compounds, NaOH and Na_2CO_3, can be represented as dissociated ions to yield the complete ionic equation:

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

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:

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

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

? Exercise 3.2.2

Diatomic chlorine and sodium hydroxide (lye) are commodity chemicals produced in large quantities, along with diatomic hydrogen, via the electrolysis of brine, according to the following unbalanced equation:

$$\mathrm{NaCl(aq) + H_2O(l) \xrightarrow{electricity} NaOH(aq) + H_2(g) + Cl_2(g)}$$

Write balanced molecular, complete ionic, and net ionic equations for this process.

Answer

Balanced molecular equation:

$$\mathrm{2\,NaCl(aq) + 2\,H_2O(l) \longrightarrow 2\,NaOH(aq) + H_2(g) + Cl_2(g)}$$

Balanced ionic equation:

$$\mathrm{2\,Na^+(aq) + 2\,Cl^-(aq) + 2\,H_2O(l) \longrightarrow 2\,Na^+(aq) + 2\,OH^-(aq) + H_2(g) + Cl_2(g)}$$

Balanced net ionic equation:

$$\mathrm{2\,Cl^-(aq) + 2\,H_2O(l) \longrightarrow 2\,OH^-(aq) + H_2(g) + Cl_2(g)}$$

Key Concepts and Summary

Chemical equations are symbolic representations of chemical and physical changes. Formulas for the substances undergoing the change (reactants) and substances generated by the change (products) are separated by an arrow and preceded by integer coefficients indicating their relative numbers. Balanced equations are those whose coefficients result in equal numbers of atoms for each element in the reactants and products. Chemical reactions in aqueous solution that involve ionic reactants or products may be represented more realistically by complete ionic equations and, more succinctly, by net ionic equations.

Glossary

balanced equation
chemical equation with equal numbers of atoms for each element in the reactant and product

chemical equation
symbolic representation of a chemical reaction

coefficient
number placed in front of symbols or formulas in a chemical equation to indicate their relative amount

complete ionic equation
chemical equation in which all dissolved ionic reactants and products, including spectator ions, are explicitly represented by formulas for their dissociated ions

molecular equation
chemical equation in which all reactants and products are represented as neutral substances

net ionic equation
chemical equation in which only those dissolved ionic reactants and products that undergo a chemical or physical change are represented (excludes spectator ions)

product
substance formed by a chemical or physical change; shown on the right side of the arrow in a chemical equation

reactant

substance undergoing a chemical or physical change; shown on the left side of the arrow in a chemical equation

spectator ion

ion that does not undergo a chemical or physical change during a reaction, but its presence is required to maintain charge neutrality

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3.3: Classifying Chemical Reactions

Learning Objectives

- Define three common types of chemical reactions (precipitation, acid-base, and oxidation-reduction)
- Classify chemical reactions as one of these three types given appropriate descriptions or chemical equations
- Identify common acids and bases
- Predict the solubility of common inorganic compounds by using solubility rules
- Compute the oxidation states for elements in compounds

Humans interact with one another in various and complex ways, and we classify these interactions according to common patterns of behavior. When two humans exchange information, we say they are communicating. When they exchange blows with their fists or feet, we say they are fighting. Faced with a wide range of varied interactions between chemical substances, scientists have likewise found it convenient (or even necessary) to classify chemical interactions by identifying common patterns of reactivity. This module will provide an introduction to three of the most prevalent types of chemical reactions: precipitation, acid-base, and oxidation-reduction.

Precipitation Reactions and Solubility Rules

A precipitation reaction is one in which dissolved substances react to form one (or more) solid products. Many reactions of this type involve the exchange of ions between ionic compounds in aqueous solution and are sometimes referred to as *double displacement*, *double replacement*, or *metathesis* reactions. These reactions are common in nature and are responsible for the formation of coral reefs in ocean waters and kidney stones in animals. They are used widely in industry for production of a number of commodity and specialty chemicals. Precipitation reactions also play a central role in many chemical analysis techniques, including spot tests used to identify metal ions and *gravimetric methods* for determining the composition of matter (see the last module of this chapter).

The extent to which a substance may be dissolved in water, or any solvent, is quantitatively expressed as its solubility, defined as the maximum concentration of a substance that can be achieved under specified conditions. Substances with relatively large solubilities are said to be soluble. A substance will precipitate when solution conditions are such that its concentration exceeds its solubility. Substances with relatively low solubilities are said to be insoluble, and these are the substances that readily precipitate from solution. More information on these important concepts is provided in the text chapter on solutions. For purposes of predicting the identities of solids formed by precipitation reactions, one may simply refer to patterns of solubility that have been observed for many ionic compounds (Table **3.3.1**).

Table **3.3.1**: Solubilities of Common Ionic Compounds in Water

Soluble compounds contain	**Exceptions** to these solubility rules include
• group 1 metal cations (Li^+, Na^+, K^+, Rb^+, and Cs^+) and ammonium ion (NH_4^+) • the halide ions (Cl^-, Br^-, and I^-) • the acetate ($C_2H_3O_2^-$), bicarbonate (HCO_3^-), nitrate (NO_3^-), and chlorate (ClO_3^-) ions • the sulfate (SO_4^-) ion	• halides of Ag^+, Hg_2^{2+}, and Pb^{2+} • sulfates of Ag^+, Ba^{2+}, Ca^{2+}, Hg_2^{2+}, Pb^{2+}, and Sr^{2+}
Insoluble compounds contain	**Exceptions** to these insolubility rules include
• carbonate (CO_3^{2-}), chromate (CrO_4^{2-}), phosphate (PO_4^{3-}), and sulfide (S^{2-}) ions • hydroxide ion (OH^-)	• compounds of these anions with group 1 metal cations and ammonium ion • hydroxides of group 1 metal cations and Ba^{2+}

A vivid example of precipitation is observed when solutions of potassium iodide and lead nitrate are mixed, resulting in the formation of solid lead iodide:

$$2\,KI(aq) + Pb(NO_3)_2(aq) \rightarrow PbI_2(s) + 2\,KNO_3(aq)$$

This observation is consistent with the solubility guidelines: The only insoluble compound among all those involved is lead iodide, one of the exceptions to the general solubility of iodide salts.

The net ionic equation representing this reaction is:

$$Pb^{2+}(aq) + 2\,I^-(aq) \rightarrow PbI_2(s)$$

Lead iodide is a bright yellow solid that was formerly used as an artist's pigment known as iodine yellow (Figure **3.3.1**). The properties of pure PbI_2 crystals make them useful for fabrication of X-ray and gamma ray detectors.



Figure **3.3.1**: A precipitate of PbI_2 forms when solutions containing Pb^{2+} and I^- are mixed. (credit: Der Kreole/Wikimedia Commons)

A photograph is shown of a yellow green opaque substance swirled through a clear, colorless liquid in a test tube.

The solubility guidelines in Table **3.3.1** may be used to predict whether a precipitation reaction will occur when solutions of soluble ionic compounds are mixed together. One merely needs to identify all the ions present in the solution and then consider if possible cation/anion pairing could result in an insoluble compound. For example, mixing solutions of silver nitrate and sodium fluoride will yield a solution containing Ag^+, NO_3^-, Na^+, and F^- ions. Aside from the two ionic compounds originally present in the solutions, $AgNO_3$ and NaF, two additional ionic compounds may be derived from this collection of ions: $NaNO_3$ and AgF. The solubility guidelines indicate all nitrate salts are soluble but that AgF is one of the exceptions to the general solubility of fluoride salts. A precipitation reaction, therefore, is predicted to occur, as described by the following equations:

$$NaF(aq) + AgNO_3(aq) \rightarrow AgF(s) + NaNO_3(aq) \quad \text{(molecular)}$$

$$Ag^+(aq) + F^-(aq) \rightarrow AgF(s) \quad \text{(net ionic)}$$

✔ Example 3.3.1: Predicting Precipitation Reactions

Predict the result of mixing reasonably concentrated solutions of the following ionic compounds. If precipitation is expected, write a balanced net ionic equation for the reaction.

a. potassium sulfate and barium nitrate
b. lithium chloride and silver acetate
c. lead nitrate and ammonium carbonate

Solution

(a) The two possible products for this combination are KNO_3 and $BaSO_4$. The solubility guidelines indicate $BaSO_4$ is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is

$$Ba^{2+}(aq) + SO_4{}^{2-}(aq) \rightarrow BaSO_4(s)$$

(b) The two possible products for this combination are $LiC_2H_3O_2$ and AgCl. The solubility guidelines indicate AgCl is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

(c) The two possible products for this combination are $PbCO_3$ and NH_4NO_3. The solubility guidelines indicate $PbCO_3$ is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is

$$Pb^{2+}(aq) + CO_3^{2-}(aq) \rightarrow PbCO_3(s)$$

? Exercise 3.3.1

Which solution could be used to precipitate the barium ion, Ba^{2+}, in a water sample: sodium chloride, sodium hydroxide, or sodium sulfate? What is the formula for the expected precipitate?

Answer

sodium sulfate, $BaSO_4$

Acid-Base Reactions

An acid-base reaction is one in which a hydrogen ion, H^+, is transferred from one chemical species to another. Such reactions are of central importance to numerous natural and technological processes, ranging from the chemical transformations that take place within cells and the lakes and oceans, to the industrial-scale production of fertilizers, pharmaceuticals, and other substances essential to society. The subject of acid-base chemistry, therefore, is worthy of thorough discussion, and a full chapter is devoted to this topic later in the text.

For purposes of this brief introduction, we will consider only the more common types of acid-base reactions that take place in aqueous solutions. In this context, an acid is a substance that will dissolve in water to yield hydronium ions, H_3O^+. As an example, consider the equation shown here:

$$HCl(aq) + H_2O(aq) \rightarrow Cl^-(aq) + H_3O^+(aq)$$

The process represented by this equation confirms that hydrogen chloride is an acid. When dissolved in water, H_3O^+ ions are produced by a chemical reaction in which H^+ ions are transferred from HCl molecules to H_2O molecules (Figure **3.3.2**).

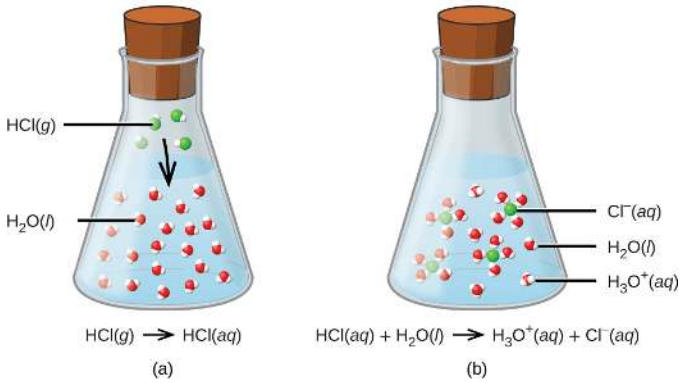


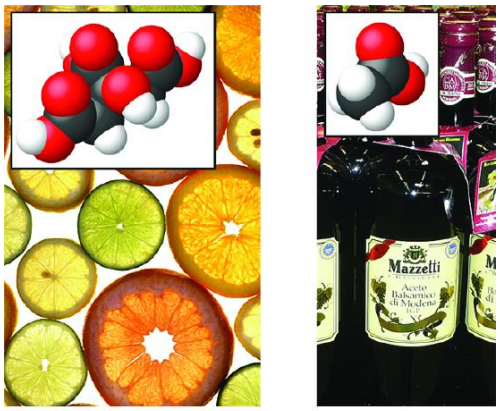
Figure **3.3.2**: When hydrogen chloride gas dissolves in water, (a) it reacts as an acid, transferring protons to water molecules to yield (b) hydronium ions (and solvated chloride ions)

This figure shows two flasks, labeled a and b. The flasks are both sealed with stoppers and are nearly three-quarters full of a liquid. Flask a is labeled H C l followed by g in parentheses. In the liquid there are approximately twenty space-filling molecular models composed of one red sphere and two smaller attached white spheres. The label H subscript 2 O followed by a q in parentheses is connected with a line to one of these models. In the space above the liquid in the flask, four space filling molecular models composed of one larger green sphere to which a smaller white sphere is bonded are shown. To one of these models, the label H C l followed by g in parentheses is attached with a line segment. An arrow is drawn from the space above the liquid pointing down into the liquid below. Flask b is labeled H subscript 3 O superscript positive sign followed by a q in parentheses. This is followed by a plus sign and C l superscript negative sign which is also followed by a q in parentheses. In this flask, no molecules are shown in the open space above the liquid. A label, C l superscript negative sign followed by a q in parentheses, is connected with a line segment to a green sphere. This sphere is surrounded by four molecules composed each of one red sphere and two white smaller spheres. A few of these same molecules appear separate from the green spheres in the liquid. A line segment connects one of them to the label H subscript 2 O which is followed by l in parentheses. There are a few molecules formed from one central larger red sphere to which three smaller white spheres are bonded. A line segment is drawn from one of these to the label H subscript 3 O superscript positive sign, followed by a q in parentheses.

The nature of HCl is such that its reaction with water as just described is essentially 100% efficient: Virtually every HCl molecule that dissolves in water will undergo this reaction. Acids that completely react in this fashion are called strong acids, and HCl is one among just a handful of common acid compounds that are classified as strong (Table **3.3.1**). A far greater number of compounds behave as weak acids and only partially react with water, leaving a large majority of dissolved molecules in their original form and generating a relatively small amount of hydronium ions. Weak acids are commonly encountered in nature, being the substances partly responsible for the tangy taste of citrus fruits, the stinging sensation of insect bites, and the unpleasant smells associated with body odor. A familiar example of a weak acid is acetic acid, the main ingredient in food vinegars:

$$\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{CH_3CO_2^-}(aq) + \mathrm{H_3O^+}(aq)$$

When dissolved in water under typical conditions, only about 1% of acetic acid molecules are present in the ionized form, $\mathrm{CH_3CO_2^-}$ (Figure **3.3.3**). (The use of a double-arrow in the equation above denotes the partial reaction aspect of this process, a concept addressed fully in the chapters on chemical equilibrium.)



(a) (b)

Figure **3.3.3**: (a) Fruits such as oranges, lemons, and grapefruit contain the weak acid citric acid. (b) Vinegars contain the weak acid acetic acid. (credit a: modification of work by Scott Bauer; credit b: modification of work by Brücke-Osteuropa/Wikimedia Commons)

This figure contains two images, each with an associated structural formula provided in the lower left corner of the image. The first image is a photograph of a variety of thinly sliced, circular cross sections of citrus fruits ranging in color for green to yellow, to orange and reddish-orange. The slices are closely packed on a white background. The structural formula with this picture shows a central chain of five C atoms. The leftmost C atom has an O atom double bonded above and to the left and a singly bonded O atom below and to the left. This single bonded O atom has an H atom indicated in red on its left side which is highlighted in pink. The second C atom moving to the right has H atoms bonded above and below. The third C atom has a single bonded O atom above which has an H atom on its right. This third C atom has a C atom bonded below it which has an O atom double bonded below and to the left and a singly bonded O atom below and to the right. An H atom appears in red and is highlighted in pink to the right of the singly bonded O atom. The fourth C atom has H atoms bonded above and below. The fifth C atom is at the right end of the structure. It has an O atom double bonded above and to the right and a singly bonded O atom below and to the right. This single bonded O atom has a red H atom on its right side which is highlighted in pink. The second image is a photograph of bottles of vinegar. The bottles are labeled, “Balsamic Vinegar,” and appear to be clear and colorless. The liquid in this bottle appears to be brown. The structural formula that appears with this image shows a chain of two C atoms. The leftmost C atom has H atoms bonded above, below, and to the left. The C atom on the right has a doubly bonded O atom above and to the right and a singly bonded O atom below and to the right. This O atom has an H atom bonded to its right which is highlighted in pink.

Table **3.3.2**: Common Strong Acids

Compound Formula	Name in Aqueous Solution
HBr	hydrobromic acid
HCl	hydrochloric acid
HI	hydroiodic acid
HNO_3	nitric acid
$HClO_4$	perchloric acid
H_2SO_4	sulfuric acid

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:

$$\mathrm{NaOH}(s) \rightarrow \mathrm{Na}^+(aq) + \mathrm{OH}^-(aq)$$

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. For example, global production of the weak base ammonia is typically well over 100 metric tons annually, being widely used as an agricultural fertilizer, a raw material for chemical synthesis of other compounds, and an active ingredient in household cleaners (Figure **3.3.4**). When dissolved in water, ammonia reacts partially to yield hydroxide ions, as shown here:

$$\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq)$$

This is, by definition, an acid-base reaction, in this case involving the transfer of H^+ ions from water molecules to ammonia molecules. Under typical conditions, only about 1% of the dissolved ammonia is present as $\mathrm{NH_4^+}$ ions.



(a) (b)

Figure **3.3.4**: Ammonia is a weak base used in a variety of applications. (a) Pure ammonia is commonly applied as an agricultural fertilizer. (b) Dilute solutions of ammonia are effective household cleansers. (credit a: modification of work by National Resources Conservation Service; credit b: modification of work by pat00139)

This photograph shows a large agricultural tractor in a field pulling a field sprayer and a large, white cylindrical tank which is labeled “Caution Ammonia.”

The chemical reactions described in which acids and bases dissolved in water produce hydronium and hydroxide ions, respectively, are, by definition, acid-base reactions. In these reactions, water serves as both a solvent *and* a reactant. 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 a salt and water, and neither reactant is the water itself:

$$\mathrm{acid} + \mathrm{base} \rightarrow \mathrm{salt} + \mathrm{water}$$

To illustrate a neutralization reaction, consider what happens when a typical antacid such as milk of magnesia (an aqueous suspension of solid $Mg(OH)_2$) is ingested to ease symptoms associated with excess stomach acid (HCl):

$$\mathrm{Mg(OH)_2}(s) + 2\,\mathrm{HCl}(aq) \rightarrow \mathrm{MgCl_2}(aq) + 2\,\mathrm{H_2O}(l).$$

Note that in addition to water, this reaction produces a salt, magnesium chloride.

✔ Example **3.3.2**: Writing Equations for Acid-Base Reactions

Write balanced chemical equations for the acid-base reactions described here:

a. the weak acid hydrogen hypochlorite reacts with water
b. a solution of barium hydroxide is neutralized with a solution of nitric acid

Solution

(a) The two reactants are provided, HOCl and H_2O. Since the substance is reported to be an acid, its reaction with water will involve the transfer of H^+ from HOCl to H_2O to generate hydronium ions, H_3O^+ and hypochlorite ions, OCl^-.

$$\mathrm{HOCl}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{OCl^-}(aq) + \mathrm{H_3O^+}(aq)$$

A double-arrow is appropriate in this equation because it indicates the HOCl is a weak acid that has not reacted completely.

(b) The two reactants are provided, $Ba(OH)_2$ and HNO_3. Since this is a neutralization reaction, the two products will be water and a salt composed of the cation of the ionic hydroxide (Ba^{2+}) and the anion generated when the acid transfers its hydrogen ion (NO_3^-).

$$Ba(OH)_2(aq) + 2\,HNO_3(aq) \rightarrow Ba(NO_3)_2(aq) + 2\,H_2O(l)$$

? Exercise 3.3.21

Write the net ionic equation representing the neutralization of any strong acid with an ionic hydroxide. (Hint: Consider the ions produced when a strong acid is dissolved in water.)

Answer

$$H_3O^+(aq) + OH^-(aq) \rightarrow 2\,H_2O(l)$$

Explore the microscopic view of strong and weak acids and bases.

Oxidation-Reduction Reactions

Earth's atmosphere contains about 20% molecular oxygen, O_2, a chemically reactive gas that plays an essential role in the metabolism of aerobic organisms and in many environmental processes that shape the world. The term oxidation was originally used to describe chemical reactions involving O_2, but its meaning has evolved to refer to a broad and important reaction class known as *oxidation-reduction (redox) reactions*. A few examples of such reactions will be used to develop a clear picture of this classification.

Some redox reactions involve the transfer of electrons between reactant species to yield ionic products, such as the reaction between sodium and chlorine to yield sodium chloride:

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

It is helpful to view the process with regard to each individual reactant, that is, to represent the fate of each reactant in the form of an equation called a half-reaction:

$$2\,Na(s) \rightarrow 2\,Na^+(s) + 2\,e^-$$
$$Cl_2(g) + 2\,e^- \rightarrow 2\,Cl^-(s)$$

These equations show that Na atoms *lose electrons* while Cl atoms (in the Cl_2 molecule) *gain electrons*, the "s" subscripts for the resulting ions signifying they are present in the form of a solid ionic compound. For redox reactions of this sort, the loss and gain of electrons define the complementary processes that occur:

oxidation = loss of electrons (3.3.1)
reduction = gain of electrons (3.3.2)

In this reaction, then, sodium is *oxidized* and chlorine undergoes reduction. Viewed from a more active perspective, sodium functions as a reducing agent (reductant), since it provides electrons to (or reduces) chlorine. Likewise, chlorine functions as an oxidizing agent (oxidant), as it effectively removes electrons from (oxidizes) sodium.

reducing agent = species that is oxidized (3.3.3)
oxidizing agent = species that is reduced (3.3.4)

Some redox processes, however, do not involve the transfer of electrons. Consider, for example, a reaction similar to the one yielding NaCl:

$$H_2(g) + Cl_2(g) \rightarrow 2\,HCl(g)$$

The product of this reaction is a covalent compound, so transfer of electrons in the explicit sense is not involved. To clarify the similarity of this reaction to the previous one and permit an unambiguous definition of redox reactions, a property called *oxidation number* has been defined. The oxidation number (or oxidation state) of an element in a compound is the charge its atoms would possess *if the compound was ionic*. The following guidelines are used to assign oxidation numbers to each element in a molecule or ion.

1. The oxidation number of an atom in an elemental substance is zero.
2. The oxidation number of a monatomic ion is equal to the ion's charge.
3. Oxidation numbers for common nonmetals are usually assigned as follows:
   - Hydrogen: +1 when combined with nonmetals, −1 when combined with metals
   - Oxygen: −2 in most compounds, sometimes −1 (so-called peroxides, O_2^{2-}), very rarely $-\frac{1}{2}$ (so-called superoxides, O_2^-), positive values when combined with F (values vary)
   - Halogens: −1 for F always, −1 for other halogens except when combined with oxygen or other halogens (positive oxidation numbers in these cases, varying values)
4. The sum of oxidation numbers for all atoms in a molecule or polyatomic ion equals the charge on the molecule or ion.

Note: The proper convention for reporting charge is to write the number first, followed by the sign (e.g., 2+), while oxidation number is written with the reversed sequence, sign followed by number (e.g., +2). This convention aims to emphasize the distinction between these two related properties.

Example 3.3.3: Assigning Oxidation Numbers

Follow the guidelines in this section of the text to assign oxidation numbers to all the elements in the following species:

a. H_2S
b. SO_3^{2-}
c. Na_2SO_4

Solution

(a) According to guideline 1, the oxidation number for H is +1.

Using this oxidation number and the compound's formula, guideline 4 may then be used to calculate the oxidation number for sulfur:

$$\text{charge on } H_2S = 0 = (2 \times +1) + (1 \times x)$$

$$x = 0 - (2 \times +1) = -2$$

(b) Guideline 3 suggests the oxidation number for oxygen is −2.

Using this oxidation number and the ion's formula, guideline 4 may then be used to calculate the oxidation number for sulfur:

$$\text{charge on } SO_3^{2-} = -2 = (3 \times -2) + (1 \times x)$$

$$x = -2 - (3 \times -2) = +4$$

(c) For ionic compounds, it's convenient to assign oxidation numbers for the cation and anion separately.

According to guideline 2, the oxidation number for sodium is +1.

Assuming the usual oxidation number for oxygen (−2 per guideline 3), the oxidation number for sulfur is calculated as directed by guideline 4:

$$\text{charge on } SO_4^{2-} = -2 = (4 \times -2) + (1 \times x)$$

$$x = -2 - (4 \times -2) = +6$$

Exercise 3.3.3

Assign oxidation states to the elements whose atoms are underlined in each of the following compounds or ions:

a. $K\underline{N}O_3$
b. $\underline{Al}H_3$
c. $\underline{N}H_4^+$
d. msubsup

Answer a

N, +5

Answer b

Al, +3

Answer c

N, −3

Answer d

P, +5

Using the oxidation number concept, an all-inclusive definition of redox reaction has been established. Oxidation-reduction (redox) reactions are those in which one or more elements involved undergo a change in oxidation number. While the vast majority of redox reactions involve changes in oxidation number for two or more elements, a few interesting exceptions to this rule do exist as shown below\). Definitions for the complementary processes of this reaction class are correspondingly revised as shown here:

$$\textbf{oxidation} = \textbf{increase in oxidation number} \tag{3.3.5}$$

$$\textbf{reduction} = \textbf{decrease in oxidation number} \tag{3.3.6}$$

Returning to the reactions used to introduce this topic, they may now both be identified as redox processes. In the reaction between sodium and chlorine to yield sodium chloride, sodium is oxidized (its oxidation number increases from 0 in Na to +1 in NaCl) and chlorine is reduced (its oxidation number decreases from 0 in Cl_2 to −1 in NaCl). In the reaction between molecular hydrogen and chlorine, hydrogen is oxidized (its oxidation number increases from 0 in H_2 to +1 in HCl) and chlorine is reduced (its oxidation number decreases from 0 in Cl_2 to −1 in HCl).

Several subclasses of redox reactions are recognized, including combustion reactions in which the reductant (also called a *fuel*) and oxidant (often, but not necessarily, molecular oxygen) react vigorously and produce significant amounts of heat, and often light, in the form of a flame. Solid rocket-fuel reactions such as the one depicted below are combustion processes. A typical propellant reaction in which solid aluminum is oxidized by ammonium perchlorate is represented by this equation:

$$10\,Al(s) + 6\,NH_4ClO_4(s) \rightarrow 4\,Al_2O_3(s) + 2\,AlCl_3(s) + 12\,H_2O(g) + 3\,N_2(g)$$

Watch a brief video showing the test firing of a small-scale, prototype, hybrid rocket engine planned for use in the new Space Launch System being developed by NASA. The first engines firing at 3 s (green flame) use a liquid fuel/oxidant mixture, and the second, more powerful engines firing at 4 s (yellow flame) use a solid mixture.



Single-displacement (replacement) reactions are redox reactions in which an ion in solution is displaced (or replaced) via the oxidation of a metallic element. One common example of this type of reaction is the acid oxidation of certain metals:

$$Zn(s) + 2\,HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

Metallic elements may also be oxidized by solutions of other metal salts; for example:

$$Cu(s) + 2\,AgNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2\,Ag(s)$$

This reaction may be observed by placing copper wire in a solution containing a dissolved silver salt. Silver ions in solution are reduced to elemental silver at the surface of the copper wire, and the resulting Cu^{2+} ions dissolve in the solution to yield a characteristic blue color (Figure **3.3.4**).

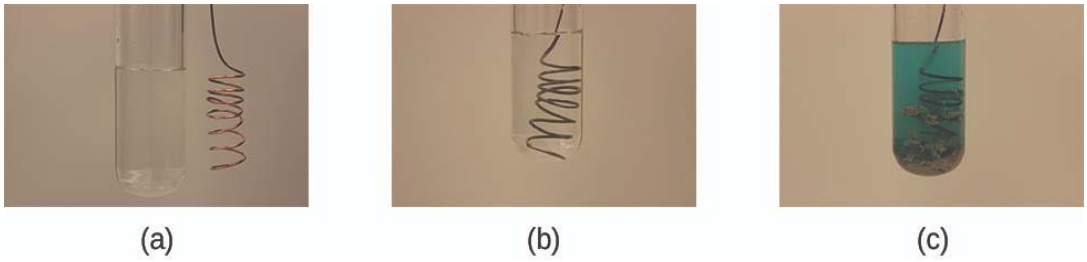


Figure **3.3.4**: (a) A copper wire is shown next to a solution containing silver(I) ions. (b) Displacement of dissolved silver ions by copper ions results in (c) accumulation of gray-colored silver metal on the wire and development of a blue color in the solution, due to dissolved copper ions. (credit: modification of work by Mark Ott)

This figure contains three photographs. In a, a coiled copper wire is shown beside a test tube filled with a clear, colorless liquid. In b, the wire has been inserted into the test tube with the clear, colorless liquid. In c, the test tube contains a light blue liquid and the coiled wire appears to have a fuzzy silver gray coating.

✔ Example 3.3.4: Describing Redox Reactions

Identify which equations represent redox reactions, providing a name for the reaction if appropriate. For those reactions identified as redox, name the oxidant and reductant.

a. $ZnCO_3(s) \rightarrow ZnO(s) + CO_2(g)$
b. $2\,Ga(l) + 3\,Br_2(l) \rightarrow 2\,GaBr_3(s)$
c. $2\,H_2O_2(aq) \rightarrow 2\,H_2O(l) + O_2(g)$
d. $BaCl_2(aq) + K_2SO_4(aq) \rightarrow BaSO_4(s) + 2\,KCl(aq)$
e. $C_2H_4(g) + 3\,O_2(g) \rightarrow 2\,CO_2(g) + 2\,H_2O(l)$

Solution

Redox reactions are identified per definition if one or more elements undergo a change in oxidation number.

a. This is not a redox reaction, since oxidation numbers remain unchanged for all elements.
b. This is a redox reaction. Gallium is oxidized, its oxidation number increasing from 0 in Ga(l) to +3 in $GaBr_3$(s). The reducing agent is Ga(l). Bromine is reduced, its oxidation number decreasing from 0 in Br_2(l) to −1 in $GaBr_3$(s). The oxidizing agent is Br_2(l).
c. This is a redox reaction. It is a particularly interesting process, as it involves the same element, oxygen, undergoing both oxidation and reduction (a so-called *disproportionation reaction)*. Oxygen is oxidized, its oxidation number increasing from −1 in H_2O_2(aq) to 0 in O_2(g). Oxygen is also reduced, its oxidation number decreasing from −1 in H_2O_2(aq) to −2 in H_2O(l). For disproportionation reactions, the same substance functions as an oxidant and a reductant.
d. This is not a redox reaction, since oxidation numbers remain unchanged for all elements.
e. This is a redox reaction (combustion). Carbon is oxidized, its oxidation number increasing from −2 in C_2H_4(g) to +4 in CO_2(g). The reducing agent (fuel) is C_2H_4(g). Oxygen is reduced, its oxidation number decreasing from 0 in O_2(g) to −2 in H_2O(l). The oxidizing agent is O_2(g).

? Exercise 3.3.4

This equation describes the production of tin(II) chloride:

$$Sn(s) + 2\,HCl(g) \rightarrow SnCl_2(s) + H_2(g)$$

Is this a redox reaction? If so, provide a more specific name for the reaction if appropriate, and identify the oxidant and reductant.

Answer

Yes, a single-replacement reaction. Sn(*s*) is the reductant, HCl(*g*) is the oxidant.

Balancing Redox Reactions via the Half-Reaction Method

Redox reactions that take place in aqueous media often involve water, hydronium ions, and hydroxide ions as reactants or products. Although these species are not oxidized or reduced, they do participate in chemical change in other ways (e.g., by providing the elements required to form oxyanions). Equations representing these reactions are sometimes very difficult to balance by inspection, so systematic approaches have been developed to assist in the process. One very useful approach is to use the method of half-reactions, which involves the following steps:

1. Write the two half-reactions representing the redox process.
2. Balance all elements except oxygen and hydrogen.
3. Balance oxygen atoms by adding H_2O molecules.
4. Balance hydrogen atoms by adding H^+ ions.
5. Balance charge[1] by adding electrons.
6. If necessary, multiply each half-reaction's coefficients by the smallest possible integers to yield equal numbers of electrons in each.
7. Add the balanced half-reactions together and simplify by removing species that appear on both sides of the equation.
8. For reactions occurring in basic media (excess hydroxide ions), carry out these additional steps:
   - Add OH^- ions to both sides of the equation in numbers equal to the number of H^+ ions.
   - On the side of the equation containing both H^+ and OH^- ions, combine these ions to yield water molecules.
   - Simplify the equation by removing any redundant water molecules.
9. Finally, check to see that both the number of atoms and the total charges[2] are balanced.

Example 3.3.5: Balancing Redox Reactions in Acidic Solution

Write a balanced equation for the reaction between dichromate ion and iron(II) to yield iron(III) and chromium(III) in acidic solution.

$$Cr_2O_7^{2-} + Fe^{2+} \rightarrow Cr^{3+} + Fe^{3+}$$

Solution

Write the two half-reactions.

Each half-reaction will contain one reactant and one product with one element in common.

$$Fe^{2+} \rightarrow Fe^{3+}$$
$$Cr_2O_7^{2-} \rightarrow Cr^{3+}$$

Balance all elements except oxygen and hydrogen. The iron half-reaction is already balanced, but the chromium half-reaction shows two Cr atoms on the left and one Cr atom on the right. Changing the coefficient on the right side of the equation to 2 achieves balance with regard to Cr atoms.

$$Fe^{2+} \rightarrow Fe^{3+}$$
$$Cr_2O_7^{2-} \rightarrow 2\,Cr^{3+}$$

Balance oxygen atoms by adding H_2O *molecules*. The iron half-reaction does not contain O atoms. The chromium half-reaction shows seven O atoms on the left and none on the right, so seven water molecules are added to the right side.

$$Fe^{2+} \rightarrow Fe^{3+}$$
$$Cr_2O_7^{2-} \rightarrow 2\,Cr^{3+} + 7\,H_2O$$

Balance hydrogen atoms by adding H^+*ions*. The iron half-reaction does not contain H atoms. The chromium half-reaction shows 14 H atoms on the right and none on the left, so 14 hydrogen ions are added to the left side.

$$\mathrm{Fe^{2+} \rightarrow Fe^{3+}}$$
$$\mathrm{Cr_2O_7^{2-} + 14\,H^+ \rightarrow 2\,Cr^{3+} + 7\,H_2O}$$

Balance charge by adding electrons. The iron half-reaction shows a total charge of 2+ on the left side (1 Fe^{2+} ion) and 3+ on the right side (1 Fe^{3+} ion). Adding one electron to the right side bring that side's total charge to (3+) + (1−) = 2+, and charge balance is achieved.

The chromium half-reaction shows a total charge of (1 × 2−) + (14 × 1+) = 12+ on the left side (1 $Cr_2O_7^{2-}$ ion and 14 H^+ ions). The total charge on the right side is (2 × 3+) = 6 + (2 Cr^{3+} ions). Adding six electrons to the left side will bring that side's total charge to (12+ + 6−) = 6+, and charge balance is achieved.

$$\mathrm{Fe^{2+} \rightarrow Fe^{3+} + e^-}$$
$$\mathrm{Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \rightarrow 2\,Cr^{3+} + 7\,H_2O}$$

Multiply the two half-reactions so the number of electrons in one reaction equals the number of electrons in the other reaction. To be consistent with mass conservation, and the idea that redox reactions involve the transfer (not creation or destruction) of electrons, the iron half-reaction's coefficient must be multiplied by 6.

$$\mathrm{6\,Fe^{2+} \rightarrow 6\,Fe^{3+} + 6\,e^-}$$
$$\mathrm{Cr_2O_7^{2-} + 6\,e^- + 14\,H^+ \rightarrow 2\,Cr^{3+} + 7\,H_2O}$$

Add the balanced half-reactions and cancel species that appear on both sides of the equation.

$$\mathrm{6\,Fe^{2+} + Cr_2O_7^{2-} + 6\,e^- + 14\,H^+ \rightarrow 6\,Fe^{3+} + 6\,e^- + 2\,Cr^{3+} + 7\,H_2O}$$

Only the six electrons are redundant species. Removing them from each side of the equation yields the simplified, balanced equation here:

$$\mathrm{6\,Fe^{2+} + Cr_2O_7^{2-} + 14\,H^+ \rightarrow 6\,Fe^{3+} + 2\,Cr^{3+} + 7\,H_2O}$$

A final check of atom and charge balance confirms the equation is balanced.

Final check of atom and charge balance confirms the equation is balanced.

	Reactants	Products
Fe	6	6
Cr	2	2
O	7	7
H	14	14
charge	24+	24+

? Exercise 3.3.5

In acidic solution, hydrogen peroxide reacts with Fe^{2+} to produce Fe^{3+} and H_2O. Write a balanced equation for this reaction.

Answer

$$\mathrm{H_2O_2}(aq) + 2\,\mathrm{H^+}(aq) + 2\,\mathrm{Fe^{2+}} \rightarrow 2\,\mathrm{H_2O}(l) + 2\,\mathrm{Fe^{3+}}$$

Summary

Chemical reactions are classified according to similar patterns of behavior. A large number of important reactions are included in three categories: precipitation, acid-base, and oxidation-reduction (redox). Precipitation reactions involve the formation of one or more insoluble products. Acid-base reactions involve the transfer of hydrogen ions between reactants. Redox reactions involve a change in oxidation number for one or more reactant elements. Writing balanced equations for some redox reactions that occur in aqueous solutions is simplified by using a systematic approach called the half-reaction method.

Footnotes

1. 1 The requirement of “charge balance” is just a specific type of “mass balance” in which the species in question are electrons. An equation must represent equal numbers of electrons on the reactant and product sides, and so both atoms and charges must be balanced.
2. 2 The requirement of “charge balance” is just a specific type of “mass balance” in which the species in question are electrons. An equation must represent equal numbers of electrons on the reactant and product sides, and so both atoms and charges must be balanced.

Glossary

acid
substance that produces H_3O^+ when dissolved in water

acid-base reaction
reaction involving the transfer of a hydrogen ion between reactant species

base
substance that produces OH^- when dissolved in water

combustion reaction
vigorous redox reaction producing significant amounts of energy in the form of heat and, sometimes, light

half-reaction
an equation that shows whether each reactant loses or gains electrons in a reaction.

insoluble
of relatively low solubility; dissolving only to a slight extent

neutralization reaction
reaction between an acid and a base to produce salt and water

oxidation
process in which an element’s oxidation number is increased by loss of electrons

oxidation-reduction reaction
(also, redox reaction) reaction involving a change in oxidation number for one or more reactant elements

oxidation number
(also, oxidation state) the charge each atom of an element would have in a compound if the compound were ionic

oxidizing agent
(also, oxidant) substance that brings about the oxidation of another substance, and in the process becomes reduced

precipitate
insoluble product that forms from reaction of soluble reactants

precipitation reaction

reaction that produces one or more insoluble products; when reactants are ionic compounds, sometimes called double-displacement or metathesis

reduction
process in which an element's oxidation number is decreased by gain of electrons

reducing agent
(also, reductant) substance that brings about the reduction of another substance, and in the process becomes oxidized

salt
ionic compound that can be formed by the reaction of an acid with a base that contains a cation and an anion other than hydroxide or oxide

single-displacement reaction
(also, replacement) redox reaction involving the oxidation of an elemental substance by an ionic species

soluble
of relatively high solubility; dissolving to a relatively large extent

solubility
the extent to which a substance may be dissolved in water, or any solvent

strong acid
acid that reacts completely when dissolved in water to yield hydronium ions

strong base
base that reacts completely when dissolved in water to yield hydroxide ions

weak acid
acid that reacts only to a slight extent when dissolved in water to yield hydronium ions

weak base
base that reacts only to a slight extent when dissolved in water to yield hydroxide ions

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3.4: Reaction Stoichiometry

Learning Objectives

- Explain the concept of stoichiometry as it pertains to chemical reactions
- Use balanced chemical equations to derive stoichiometric factors relating amounts of reactants and products
- Perform stoichiometric calculations involving mass, moles, and solution molarity

A balanced chemical equation provides a great deal of information in a very succinct format. Chemical formulas provide the identities of the reactants and products involved in the chemical change, allowing 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, a term derived from the Greek words *stoicheion* (meaning "element") and *metron* (meaning "measure"). In this module, the use of balanced chemical equations for various stoichiometric applications is explored.

The general approach to using stoichiometric relationships is similar in concept to the way people go about many common activities. Cooking, for example, offers an appropriate comparison. Suppose a recipe for making eight pancakes calls for 1 cup pancake mix, $\frac{3}{4}$ cup milk, and one egg. The "equation" representing the preparation of pancakes per this recipe is

$$\mathrm{1\ cup\ mix} + \frac{3}{4}\ \mathrm{cup\ milk} + \mathrm{1\ egg} \rightarrow \mathrm{8\ pancakes} \tag{3.4.1}$$

If two dozen pancakes are needed for a big family breakfast, the ingredient amounts must be increased proportionally according to the amounts given in the recipe. For example, the number of eggs required to make 24 pancakes is

$$24\ \cancel{\mathrm{pancakes}} \times \frac{1\ \mathrm{egg}}{8\ \cancel{\mathrm{pancakes}}} = 3\ \mathrm{eggs} \tag{3.4.2}$$

Balanced chemical equations are used in much the same fashion to determine the amount of one reactant required to react with a given amount of another reactant, or to yield a given amount of product, and so forth. The coefficients in the balanced equation are used to derive stoichiometric factors that permit computation of the desired quantity. To illustrate this idea, consider the production of ammonia by reaction of hydrogen and nitrogen:

$$\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \rightarrow 2\,\mathrm{NH_3}(g) \tag{3.4.3}$$

This equation shows that ammonia molecules are produced from hydrogen molecules in a 2:3 ratio, and stoichiometric factors may be derived using any amount (number) unit:

$$\frac{2\,NH3\ molecules}{3H2\ molecules} \text{ or } \frac{2\ doz\ NH3\ molecules}{3\ doz\ H2\ molecules} \text{ or } \frac{2\ mol\ NH3\ molecules}{3\ mol\ H2\ molecules} \tag{3.4.4}$$

These stoichiometric factors can be used to compute the number of ammonia molecules produced from a given number of hydrogen molecules, or the number of hydrogen molecules required to produce a given number of ammonia molecules. Similar factors may be derived for any pair of substances in any chemical equation.

Example 3.4.1: Moles of Reactant Required in a Reaction

How many moles of I_2 are required to react with 0.429 mol of Al according to the following equation (see Figure 3.4.2)?

$$2\,\mathrm{Al} + 3\,\mathrm{I_2} \rightarrow 2\,\mathrm{AlI_3} \tag{3.4.5}$$

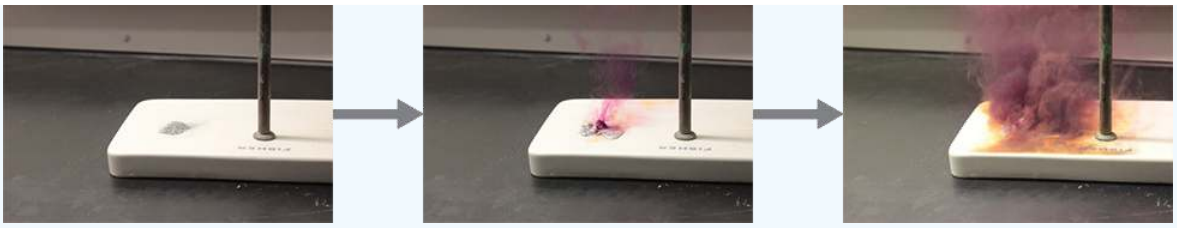
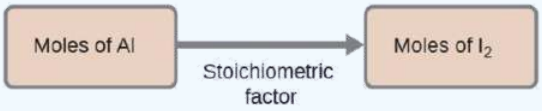


Figure 3.4.1: Aluminum and iodine react to produce aluminum iodide. The heat of the reaction vaporizes some of the solid iodine as a purple vapor. (credit: modification of work by Mark Ott)

Three pictures showing the progression of the reaction between iodine and aluminum. The first diagram shows only a pile of silver powder while the second diagram shows small amount of vapor forming. The final picture shows a large release of purple vapor.

Solution

Referring to the balanced chemical equation, the stoichiometric factor relating the two substances of interest is $\frac{3\ mol\ I2}{2\ mol\ Al}$. The molar amount of iodine is derived by multiplying the provided molar amount of aluminum by this factor:



$$\text{mol I}_2 = 0.429\ \cancel{\text{mol Al}} \times \frac{3\ \text{mol I}_2}{2\ \cancel{\text{mol Al}}}$$

$$= 0.644\ \text{mol I}_2$$

Exercise 3.4.1

How many moles of $Ca(OH)_2$ are required to react with 1.36 mol of H_3PO_4 to produce $Ca_3(PO_4)_2$ according to the equation $3\,Ca(OH)_2 + 2\,H_3PO_4 \rightarrow Ca_3(PO_4)_2 + 6\,H_2O$?

Answer

2.04 mol

Example 3.4.2: Number of Product Molecules Generated by a Reaction

How many carbon dioxide molecules are produced when 0.75 mol of propane is combusted according to this equation?

$$C_3H_8 + 5\,O_2 \rightarrow 3\,CO_2 + 4\,H_2O \tag{3.4.6}$$

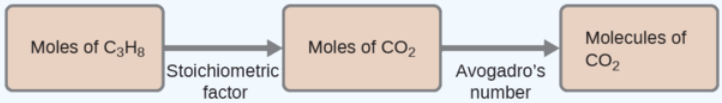
Solution

The approach here is the same as for Example 3.4.1, though the absolute number of molecules is requested, not the number of moles of molecules. This will simply require use of the moles-to-numbers conversion factor, Avogadro's number.

The balanced equation shows that carbon dioxide is produced from propane in a 3:1 ratio:

\[\ce{\dfrac{3\: mol\: CO2}{1\: mol\: C3H8}} \label{4.4.7} \]

Using this stoichiometric factor, the provided molar amount of propane, and Avogadro's number,



$$0.75\ \cancel{\text{mol C}_3\text{H}_8} \times \frac{3\ \cancel{\text{mol CO}_2}}{1\ \cancel{\text{mol C}_3\text{H}_8}} \times \frac{6.022 \times 10^{23}\ \text{CO}_2\ \text{molecules}}{\cancel{\text{mol CO}_2}} \tag{3.4.7}$$

$$= 1.4 \times 10^{24}\ \text{CO}_2\ \text{molecules}$$

? Exercise 3.4.1

How many NH_3 molecules are produced by the reaction of 4.0 mol of $Ca(OH)_2$ according to the following equation:

$$(NH_4)_2SO_4 + Ca(OH)_2 \rightarrow 2\,NH_3 + CaSO_4 + 2\,H_2O \tag{3.4.8}$$

Answer

4.8×10^{24} NH_3 molecules

These examples illustrate the ease with which the amounts of substances involved in a chemical reaction of known stoichiometry may be related. Directly measuring numbers of atoms and molecules is, however, not an easy task, and the practical application of stoichiometry requires that we use the more readily measured property of mass.

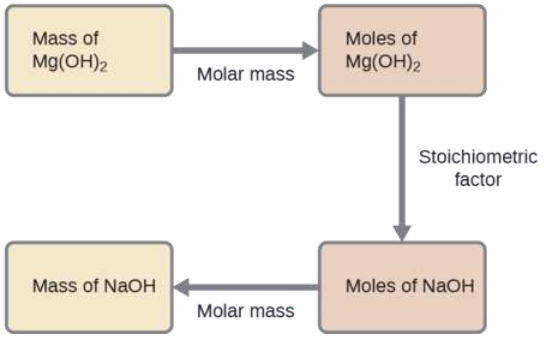
✓ Example 3.4.3: Relating Masses of Reactants and Products

What mass of sodium hydroxide, NaOH, would be required to produce 16 g of the antacid milk of magnesia [magnesium hydroxide, $Mg(OH)_2$] by the following reaction?

$$MgCl_2(aq) + 2\,NaOH(aq) \rightarrow Mg(OH)_2(s) + 2\,NaCl(aq)$$

Solution

The approach used previously in Examples **3.4.1** and **3.4.2** is likewise used here; that is, we must derive an appropriate stoichiometric factor from the balanced chemical equation and use it to relate the amounts of the two substances of interest. In this case, however, masses (not molar amounts) are provided and requested, so additional steps of the sort learned in the previous chapter are required. The calculations required are outlined in this flowchart:



$$16\ \cancel{g\ Mg(OH)_2} \times \frac{1\ \cancel{mol\ Mg(OH)_2}}{58.3\ \cancel{g\ Mg(OH)_2}} \times \frac{2\ \cancel{mol\ NaOH}}{1\ \cancel{mol\ Mg(OH)_2}} \times \frac{40.0\ g\ NaOH}{\cancel{mol\ NaOH}} = 22\ g\ NaOH$$

? Exercise 3.4.3

What mass of gallium oxide, Ga_2O_3, can be prepared from 29.0 g of gallium metal? The equation for the reaction is $4\,Ga + 3\,O_2 \rightarrow 2\,Ga_2O_3$.

Answer

39.0 g

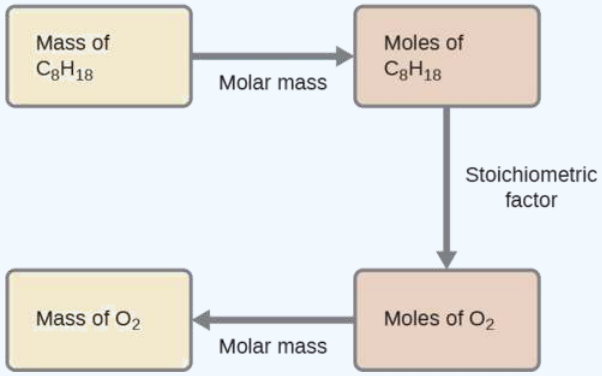
✓ Example 3.4.4: Relating Masses of Reactants

What mass of oxygen gas, O_2, from the air is consumed in the combustion of 702 g of octane, C_8H_{18}, one of the principal components of gasoline?

$$2\,C_8H_{18} + 25\,O_2 \rightarrow 16\,CO_2 + 18\,H_2O$$

Solution

The approach required here is the same as for the Example **3.4.3**, differing only in that the provided and requested masses are both for reactant species.



$$702\ \cancel{\text{g C}_8\text{H}_{18}} \times \frac{1\ \cancel{\text{mol C}_8\text{H}_{18}}}{114.23\ \cancel{\text{g C}_8\text{H}_{18}}} \times \frac{25\ \cancel{\text{mol O}_2}}{2\ \cancel{\text{mol C}_8\text{H}_{18}}} \times \frac{32.00\ \text{g O}_2}{\cancel{\text{mol O}_2}} = 2.46 \times 10^3\ \text{g O}_2$$

? Exercise 3.4.4

What mass of CO is required to react with 25.13 g of Fe_2O_3 according to the equation $\mathbf{Fe_2O_3 + 3\,CO \rightarrow 2\,Fe + 3\,CO_2}$?

Answer

13.22 g

These examples illustrate just a few instances of reaction stoichiometry calculations. Numerous variations on the beginning and ending computational steps are possible depending upon what particular quantities are provided and sought (volumes, solution concentrations, and so forth). Regardless of the details, all these calculations share a common essential component: the use of stoichiometric factors derived from balanced chemical equations. Figure **3.4.2** provides a general outline of the various computational steps associated with many reaction stoichiometry calculations.

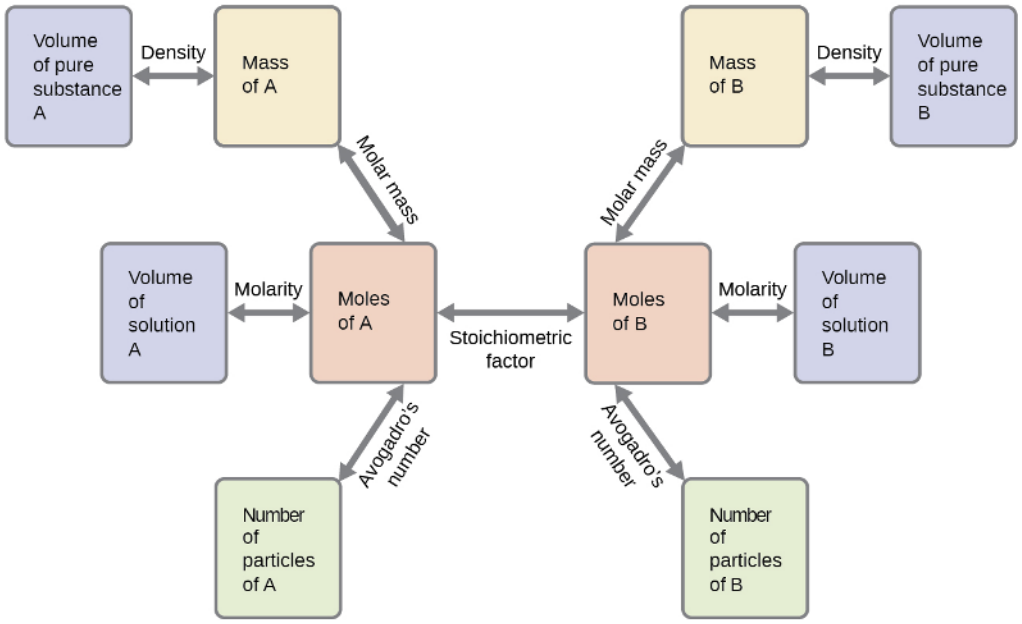


Figure **3.4.2**: The flowchart depicts the various computational steps involved in most reaction stoichiometry calculations.

Schematic flowchart showing how density is used for converting volume of pure substance to mass, molar mass for mass and moles, molarity for moles and volume of solution, Avogadro's number for moles and number of particles, and stoichiometric factor for relating moles of one substance to another.

Airbags

Airbags (Figure **3.4.3**) are a safety feature provided in most automobiles since the 1990s. The effective operation of an airbag requires that it be rapidly inflated with an appropriate amount (volume) of gas when the vehicle is involved in a collision. This requirement is satisfied in many automotive airbag systems through use of explosive chemical reactions, one common choice being the decomposition of sodium azide, NaN_3. When sensors in the vehicle detect a collision, an electrical current is passed through a carefully measured amount of NaN_3 to initiate its decomposition:

$$\mathbf{2\,NaN_3}(s) \rightarrow \mathbf{3\,N_2}(g) + \mathbf{2\,Na}(s)$$

This reaction is very rapid, generating gaseous nitrogen that can deploy and fully inflate a typical airbag in a fraction of a second (~0.03–0.1 s). Among many engineering considerations, the amount of sodium azide used must be appropriate for generating enough nitrogen gas to fully inflate the air bag and ensure its proper function. For example, a small mass (~100 g) of NaN_3 will generate approximately 50 L of N_2.



Figure **3.4.3**: Airbags deploy upon impact to minimize serious injuries to passengers. (credit: Jon Seidman)

Summary

A balanced chemical equation may be used to describe a reaction's stoichiometry (the relationships between amounts of reactants and products). Coefficients from the equation are used to derive stoichiometric factors that subsequently may be used for computations relating reactant and product masses, molar amounts, and other quantitative properties.

Glossary

stoichiometric factor

ratio of coefficients in a balanced chemical equation, used in computations relating amounts of reactants and products

stoichiometry

relationships between the amounts of reactants and products of a chemical reaction

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3.5: Reaction Yields

Learning Objectives

- Explain the concepts of theoretical yield and limiting reactants/reagents.
- Derive the theoretical yield for a reaction under specified conditions.
- Calculate the percent yield for a reaction.

The relative amounts of reactants and products represented in a balanced chemical equation are often referred to as *stoichiometric amounts*. All the exercises of the preceding module involved stoichiometric amounts of reactants. For example, when calculating the amount of product generated from a given amount of reactant, it was assumed that any other reactants required were available in stoichiometric amounts (or greater). In this module, more realistic situations are considered, in which reactants are not present in stoichiometric amounts.

Limiting Reactant

Consider another food analogy, making grilled cheese sandwiches (Figure **3.5.1**):

$$\textbf{1 slice of cheese} + \textbf{2 slices of bread} \rightarrow \textbf{1 sandwich} \tag{3.5.1}$$

Stoichiometric amounts of sandwich ingredients for this recipe are bread and cheese slices in a 2:1 ratio. Provided with 28 slices of bread and 11 slices of cheese, one may prepare 11 sandwiches per the provided recipe, using all the provided cheese and having six slices of bread left over. In this scenario, the number of sandwiches prepared has been *limited* by the number of cheese slices, and the bread slices have been provided in *excess*.

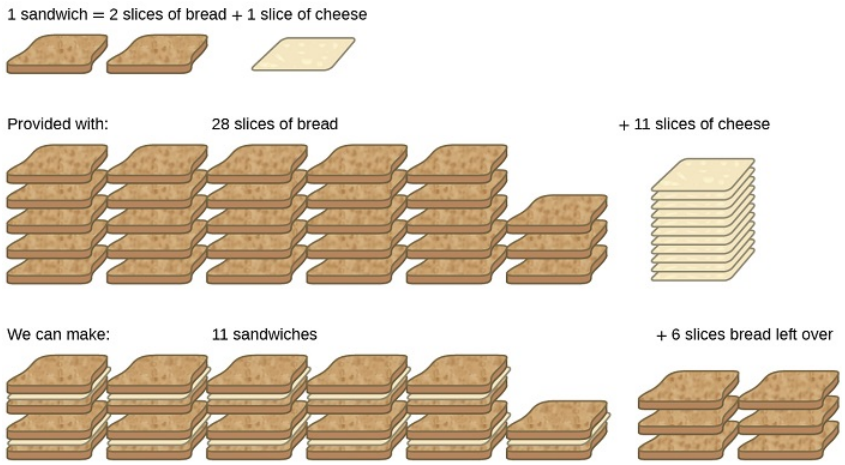


Figure **3.5.1**: Sandwich making can illustrate the concepts of limiting and excess reactants.

This figure has three rows showing the ingredients needed to make a sandwich. The first row reads, “1 sandwich = 2 slices of bread + 1 slice of cheese.” Two slices of bread and one slice of cheese are shown. The second row reads, “Provided with: 28 slices of bread + 11 slices of cheese.” There are 28 slices of bread and 11 slices of cheese shown. The third row reads, “We can make: 11 sandwiches + 6 slices of bread left over.” 11 sandwiches are shown with six extra slices of bread.

Consider this concept now with regard to a chemical process, the reaction of hydrogen with chlorine to yield hydrogen chloride:

$$\mathrm{H_2}(g) + \mathrm{Cl_2}(g) \rightarrow 2\,\mathrm{HCl}(g)$$

The balanced equation shows the hydrogen and chlorine react in a 1:1 stoichiometric ratio. If these reactants are provided in any other amounts, one of the reactants will nearly always be entirely consumed, thus limiting the amount of product that may be generated. This substance is the limiting reactant, and the other substance is the excess reactant. Identifying the limiting and excess reactants for a given situation requires computing the molar amounts of each reactant provided and comparing them to the stoichiometric amounts represented in the balanced chemical equation.

For example, imagine combining 6 moles of H_2 and 4 moles of Cl_2. Identifying the limiting reactant involves comparing the amount of product expected for the complete reaction of each reactant. Each reactant amount is used to separately calculate the

amount of product that would be formed per the reaction's stoichiometry. The reactant yielding the lesser amount of product is the limiting reactant.

For the example in the previous paragraph, the complete reaction of the hydrogen would yield

$$\text{mol HCl produced} = 6\ \text{mol } H_2 \times \frac{2\ \text{mol HCl}}{1\ \text{mol } H_2} = 12\ \text{mol HCl}$$

The complete reaction of the provided chlorine would produce

$$\text{mol HCl produced} = 4\ \text{mol } Cl_2 \times \frac{2\ \text{mol HCl}}{1\ \text{mol } Cl_2} = 8\ \text{mol HCl}$$

The chlorine will be completely consumed once 8 moles of HCl have been produced. Since enough hydrogen was provided to yield 12 moles of HCl, there will be non-reacted hydrogen remaining once this reaction is complete. Chlorine, therefore, is the limiting reactant and hydrogen is the excess reactant (Figure 3.5.2). To determine the amount of excess reactant that remains, the amount of hydrogen consumed in the reaction can be subtracted from the starting quantity of hydrogen.

The amount of hydrogen consumed is

$$\text{mol } H_2 \text{ produced} = 8\ \text{mol HCl} \times \frac{1\ \text{mol } H_2}{2\ \text{mol HCl}} = 4\ \text{mol } H_2$$

Subtract the hydrogen consumed from the starting quantity

$$\text{mole of excess } H_2 = 6\ \text{mol } H_2 \text{ starting} - 4\ \text{mol } H_2 \text{ consumed} = 2\ \text{mol } H_2 \text{ excess}$$

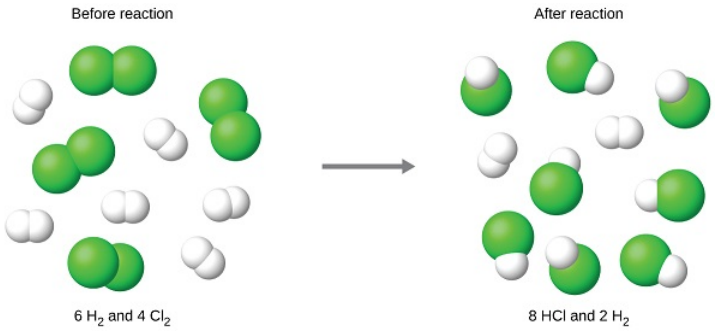


Figure 3.5.2: When H_2 and Cl_2 are combined in nonstoichiometric amounts, one of these reactants will limit the amount of HCl that can be produced. This illustration shows a reaction in which hydrogen is present in excess and chlorine is the limiting reactant.

The figure shows a space-filling molecular models reacting. There is a reaction arrow pointing to the right in the middle. To the left of the reaction arrow there are three molecules each consisting of two green spheres bonded together. There are also five molecules each consisting of two smaller, white spheres bonded together. Above these molecules is the label, "Before reaction," and below these molecules is the label, "6 H subscript 2 and 4 C l subscript 2." To the right of the reaction arrow, there are eight molecules each consisting of one green sphere bonded to a smaller white sphere. There are also two molecules each consisting of two white spheres bonded together. Above these molecules is the label, "After reaction," and below these molecules is the label, "8 H C l and 2 H subscript 2."

Example 3.5.1: Identifying the Limiting Reactant

Silicon nitride is a very hard, high-temperature-resistant ceramic used as a component of turbine blades in jet engines. It is prepared according to the following equation:

$$3\,Si(s) + 2\,N_2(g) \rightarrow Si_3N_4(s)$$

Which is the limiting reactant when 2.00 g of Si and 1.50 g of N_2 react?

Solution

Compute the provided molar amounts of reactants, and then compare these amounts to the balanced equation to identify the limiting reactant.

$$\text{mol Si} = 2.00\ \cancel{\text{g Si}} \times \frac{1\ \text{mol Si}}{28.09\ \cancel{\text{g Si}}} = 0.0712\ \text{mol Si}$$

$$\text{mol N}_2 = 1.50\ \cancel{\text{g N}_2} \times \frac{1\ \text{mol N}_2}{28.02\ \cancel{\text{g N}_2}} = 0.0535\ \text{mol N}_2$$

The provided Si:N_2 molar ratio is:

$$\frac{0.0712\ \text{mol Si}}{0.0535\ \text{mol N}_2} = \frac{1.33\ \text{mol Si}}{1\ \text{mol N}_2}$$

The stoichiometric Si:N_2 ratio is:

$$\frac{3\ \text{mol Si}}{2\ \text{mol N}_2} = \frac{1.5\ \text{mol Si}}{1\ \text{mol N}_2}$$

Comparing these ratios shows that Si is provided in a less-than-stoichiometric amount, and so is the limiting reactant.

Alternatively, compute the amount of product expected for complete reaction of each of the provided reactants. The 0.0712 moles of silicon would yield

$$\text{mol Si}_3\text{N}_4\ \text{produced} = 0.0712\ \text{mol Si} \times \frac{1\ \text{mol Si}_3\text{N}_4}{3\ \text{mol Si}} = 0.0237\ \text{mol Si}_3\text{N}_4$$

while the 0.0535 moles of nitrogen would produce

$$\text{mol Si}_3\text{N}_4\ \text{produced} = 0.0535\ \text{mol N}_2 \times \frac{1\ \text{mol Si}_3\text{N}_4}{2\ \text{mol N}_2} = 0.0268\ \text{mol Si}_3\text{N}_4$$

Since silicon yields the lesser amount of product, it is the limiting reactant.

? Exercise 3.5.1

Which is the limiting reactant when 5.00 g of H_2 and 10.0 g of O_2 react and form water?

Answer

O_2

Percent Yield

The amount of product that *may be* produced by a reaction under specified conditions, as calculated per the stoichiometry of an appropriate balanced chemical equation, is called the theoretical yield of the reaction. In practice, the amount of product obtained is called the actual yield, and it is often less than the theoretical yield for a number of reasons. Some reactions are inherently inefficient, being accompanied by *side reactions* that generate other products. Others are, by nature, incomplete (consider the partial reactions of weak acids and bases discussed earlier in this text). Some products are difficult to collect without some loss, and so less than perfect recovery will reduce the actual yield. The extent to which a reaction's theoretical yield is achieved is commonly expressed as its percent yield:

$$\text{percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$$

Actual and theoretical yields may be expressed as masses or molar amounts (or any other appropriate property; e.g., volume, if the product is a gas). As long as both yields are expressed using the same units, these units will cancel when percent yield is calculated.

Example 3.5.2: Calculation of Percent Yield

Upon reaction of 1.274 g of copper sulfate with excess zinc metal, 0.392 g copper metal was obtained according to the equation:

$$\mathrm{CuSO_4}(aq) + \mathrm{Zn}(s) \rightarrow \mathrm{Cu}(s) + \mathrm{ZnSO_4}(aq)$$

What is the percent yield?

Solution

The provided information identifies copper sulfate as the limiting reactant, and so the theoretical yield is found by the approach illustrated in the previous module, as shown here:

Double subscripts: use braces to clarify

Using this theoretical yield and the provided value for actual yield, the percent yield is calculated to be

$$\text{percent yield} = \left(\frac{\text{actual yield}}{\text{theoretical yield}}\right) \times 100$$

$$\begin{aligned}\text{percent yield} &= \left(\frac{0.392\ \text{g Cu}}{0.5072\ \text{g Cu}}\right) \times 100 \\ &= 77.3\%\end{aligned}$$

Exercise 3.5.2

What is the percent yield of a reaction that produces 12.5 g of the gas Freon CF_2Cl_2 from 32.9 g of CCl_4 and excess HF?

$$\mathrm{CCl_4} + 2\,\mathrm{HF} \rightarrow \mathrm{CF_2Cl_2} + 2\,\mathrm{HCl}$$

Answer

48.3%

Green Chemistry and Atom Economy

The purposeful design of chemical products and processes that minimize the use of environmentally hazardous substances and the generation of waste is known as *green chemistry*. Green chemistry is a philosophical approach that is being applied to many areas of science and technology, and its practice is summarized by guidelines known as the "Twelve Principles of Green Chemistry". One of the 12 principles is aimed specifically at maximizing the efficiency of processes for synthesizing chemical products. The *atom economy* of a process is a measure of this efficiency, defined as the percentage by mass of the final product of a synthesis relative to the masses of *all* the reactants used:

$$\text{atom economy} = \frac{\text{mass of product}}{\text{mass of reactants}} \times 100\%$$

Though the definition of atom economy at first glance appears very similar to that for percent yield, be aware that this property represents a difference in the *theoretical* efficiencies of *different* chemical processes. The percent yield of a given chemical process, on the other hand, evaluates the efficiency of a process by comparing the yield of product actually obtained to the maximum yield predicted by stoichiometry.

The synthesis of the common nonprescription pain medication, ibuprofen, nicely illustrates the success of a green chemistry approach (Figure **3.5.3**). First marketed in the early 1960s, ibuprofen was produced using a six-step synthesis that required 514 g of reactants to generate each mole (206 g) of ibuprofen, an atom economy of 40%. In the 1990s, an alternative process was developed by the BHC Company (now BASF Corporation) that requires only three steps and has an atom economy of ~80%, nearly twice that of the original process. The BHC process generates significantly less chemical waste; uses less-hazardous and recyclable materials; and provides significant cost-savings to the manufacturer (and, subsequently, the consumer). In

recognition of the positive environmental impact of the BHC process, the company received the Environmental Protection Agency's Greener Synthetic Pathways Award in 1997.

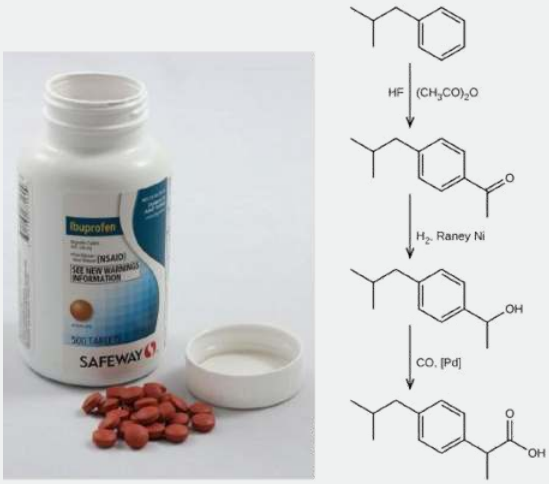


Figure **3.5.3**: (a) Ibuprofen is a popular nonprescription pain medication commonly sold as 200 mg tablets. (b) The BHC process for synthesizing ibuprofen requires only three steps and exhibits an impressive atom economy. (credit a: modification of work by Derrick Coetzee)

Summary

When reactions are carried out using less-than-stoichiometric quantities of reactants, the amount of product generated will be determined by the limiting reactant. The amount of product generated by a chemical reaction is its actual yield. This yield is often less than the amount of product predicted by the stoichiometry of the balanced chemical equation representing the reaction (its theoretical yield). The extent to which a reaction generates the theoretical amount of product is expressed as its percent yield.

Key Equations

- $\text{percent yield} = \left(\frac{\text{actual yield}}{\text{theoretical yield}}\right) \times 100$

Glossary

actual yield
amount of product formed in a reaction

excess reactant
reactant present in an amount greater than required by the reaction stoichiometry

limiting reactant
reactant present in an amount lower than required by the reaction stoichiometry, thus limiting the amount of product generated

percent yield
measure of the efficiency of a reaction, expressed as a percentage of the theoretical yield

theoretical yield
amount of product that may be produced from a given amount of reactant(s) according to the reaction stoichiometry

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3.E: Stoichiometry of Chemical Reactions (Exercises)

4.1: Writing and Balancing Chemical Equations

Q4.1.1

What does it mean to say an equation is balanced? Why is it important for an equation to be balanced?

S4.1.1

An equation is balanced when the same number of each element is represented on the reactant and product sides. Equations must be balanced to accurately reflect the law of conservation of matter.

Q4.1.2

Consider molecular, complete ionic, and net ionic equations.

a. What is the difference between these types of equations?
b. In what circumstance would the complete and net ionic equations for a reaction be identical?

Q4.1.3

Balance the following equations:

a. $\mathrm{PCl_5}(s) + \mathrm{H_2O}(l) \rightarrow \mathrm{POCl_3}(l) + \mathrm{HCl}(aq)$
b. $\mathrm{Cu}(s) + \mathrm{HNO_3}(aq) \rightarrow \mathrm{Cu(NO_3)_2}(aq) + \mathrm{H_2O}(l) + \mathrm{NO}(g)$
c. $\mathrm{H_2}(g) + \mathrm{I_2}(s) \rightarrow \mathrm{HI}(s)$
d. $\mathrm{Fe}(s) + \mathrm{O_2}(g) \rightarrow \mathrm{Fe_2O_3}(s)$
e. $\mathrm{Na}(s) + \mathrm{H_2O}(l) \rightarrow \mathrm{NaOH}(aq) + \mathrm{H_2}(g)$
f. $\mathrm{(NH_4)_2Cr_2O_7}(s) \rightarrow \mathrm{Cr_2O_3}(s) + \mathrm{N_2}(g) + \mathrm{H_2O}(g)$
g. $\mathrm{P_4}(s) + \mathrm{Cl_2}(g) \rightarrow \mathrm{PCl_3}(l)$
h. $\mathrm{PtCl_4}(s) \rightarrow \mathrm{Pt}(s) + \mathrm{Cl_2}(g)$

S4.1.3

a. $\mathrm{PCl_5}(s) + \mathrm{H_2O}(l) \rightarrow \mathrm{POCl_3}(l) + 2\,\mathrm{HCl}(aq)$;
b. $3\,\mathrm{Cu}(s) + 8\,\mathrm{HNO_3}(aq) \rightarrow 3\,\mathrm{Cu(NO_3)_2}(aq) + 4\,\mathrm{H_2O}(l) + 2\,\mathrm{NO}(g)$;
c. $\mathrm{H_2}(g) + \mathrm{I_2}(s) \rightarrow 2\,\mathrm{HI}(s)$;
d. $4\,\mathrm{Fe}(s) + 3\,\mathrm{O_2}(g) \rightarrow 2\,\mathrm{Fe_2O_3}(s)$;
e. $2\,\mathrm{Na}(s) + 2\,\mathrm{H_2O}(l) \rightarrow 2\,\mathrm{NaOH}(aq) + \mathrm{H_2}(g)$;
f. $\mathrm{(NH_4)_2Cr_{52}O_7}(s) \rightarrow \mathrm{Cr_2O_3}(s) + \mathrm{N_2}(g) + 4\,\mathrm{H_2O}(g)$;
g. $\mathrm{P_4}(s) + 6\,\mathrm{Cl_2}(g) \rightarrow 4\,\mathrm{PCl_3}(l)$;
h. $\mathrm{PtCl_4}(s) \rightarrow \mathrm{Pt}(s) + 2\,\mathrm{Cl_2}(g)$

Q4.1.4

Balance the following equations:

a. $\mathrm{Ag}(s) + \mathrm{H_2S}(g) + \mathrm{O_2}(g) \rightarrow \mathrm{Ag_2S}(s) + \mathrm{H_2O}(l)$
b. $\mathrm{P_4}(s) + \mathrm{O_2}(g) \rightarrow \mathrm{P_4O_{10}}(s)$
c. $\mathrm{Pb}(s) + \mathrm{H_2O}(l) + \mathrm{O_2}(g) \rightarrow \mathrm{Pb(OH)_2}(s)$
d. $\mathrm{Fe}(s) + \mathrm{H_2O}(l) \rightarrow \mathrm{Fe_3O_4}(s) + \mathrm{H_2}(g)$
e. $\mathrm{Sc_2O_3}(s) + \mathrm{SO_3}(l) \rightarrow \mathrm{Sc_2(SO_4)_3}(s)$
f. $\mathrm{Ca_3(PO_4)_2}(aq) + \mathrm{H_3PO_4}(aq) \rightarrow \mathrm{Ca(H_2PO_4)_2}(aq)$
g. $\mathrm{Al}(s) + \mathrm{H_2SO_4}(aq) \rightarrow \mathrm{Al_2(SO_4)_3}(s) + \mathrm{H_2}(g)$
h. $\mathrm{TiCl_4}(s) + \mathrm{H_2O}(g) \rightarrow \mathrm{TiO_2}(s) + \mathrm{HCl}(g)$

S4.1.4

a. $4\,Ag(s) + 2\,H_2S(g) + O_2(g) \rightarrow 2\,Ag_2S(s) + 2\,H_2O(l)$
b. $P_4(s) + 5\,O_2(g) \rightarrow P_4O_{10}(s)$
c. $2\,Pb(s) + 2\,H_2O(l) + O_2(g) \rightarrow 2\,Pb(OH)_2(s)$
d. $3\,Fe(s) + 4\,H_2O(l) \rightarrow Fe_3O_4(s) + 4\,H_2(g)$
e. $Sc_2O_3(s) + 3\,SO_3(l) \rightarrow Sc_2(SO_4)_3(s)$
f. $Ca_3(PO_4)_2(aq) + 4\,H_3PO_4(aq) \rightarrow 3\,Ca(H_2PO_4)_2(aq)$
g. $2\,Al(s) + 3\,H_2SO_4(aq) \rightarrow Al_2(SO_4)_3(s) + 3\,H_2(g)$
h. $TiCl_4(s) + 2\,H_2O(g) \rightarrow TiO_2(s) + 4\,HCl(g)$

Q4.1.5

Write a balanced molecular equation describing each of the following chemical reactions.

a. Solid calcium carbonate is heated and decomposes to solid calcium oxide and carbon dioxide gas.
b. Gaseous butane, C_4H_{10}, reacts with diatomic oxygen gas to yield gaseous carbon dioxide and water vapor.
c. Aqueous solutions of magnesium chloride and sodium hydroxide react to produce solid magnesium hydroxide and aqueous sodium chloride.
d. Water vapor reacts with sodium metal to produce solid sodium hydroxide and hydrogen gas.

S4.1.5

a. $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$;
b. $2\,C_4H_{10}(g) + 13\,O_2(g) \rightarrow 8\,CO_2(g) + 10\,H_2O(g)$;
c. $MgCl_2(aq) + 2\,NaOH(aq) \rightarrow Mg(OH)_2(s) + 2\,NaCl(aq)$;
d. $2\,H_2O(g) + 2\,Na(s) \rightarrow 2\,NaOH(s) + H_2(g)$

Q4.1.6

Write a balanced equation describing each of the following chemical reactions.

a. Solid potassium chlorate, $KClO_3$, decomposes to form solid potassium chloride and diatomic oxygen gas.
b. Solid aluminum metal reacts with solid diatomic iodine to form solid Al_2I_6.
c. When solid sodium chloride is added to aqueous sulfuric acid, hydrogen chloride gas and aqueous sodium sulfate are produced.
d. Aqueous solutions of phosphoric acid and potassium hydroxide react to produce aqueous potassium dihydrogen phosphate and liquid water.

Q4.1.7

Colorful fireworks often involve the decomposition of barium nitrate and potassium chlorate and the reaction of the metals magnesium, aluminum, and iron with oxygen.

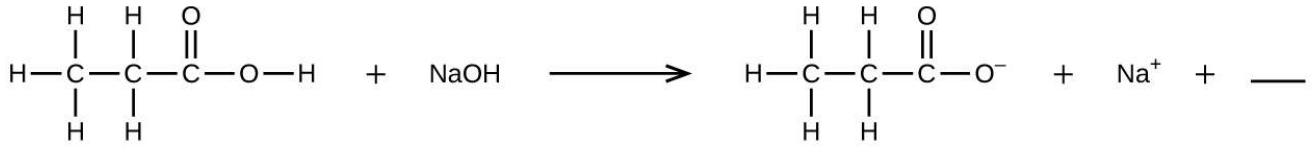
a. Write the formulas of barium nitrate and potassium chlorate.
b. The decomposition of solid potassium chlorate leads to the formation of solid potassium chloride and diatomic oxygen gas. Write an equation for the reaction.
c. The decomposition of solid barium nitrate leads to the formation of solid barium oxide, diatomic nitrogen gas, and diatomic oxygen gas. Write an equation for the reaction.
d. Write separate equations for the reactions of the solid metals magnesium, aluminum, and iron with diatomic oxygen gas to yield the corresponding metal oxides. (Assume the iron oxide contains Fe^{3+} ions.)

Q4.1.7

a. $Ba(NO_3)_2$, $KClO_3$;
b. $2\,KClO_3(s) \rightarrow 2\,KCl(s) + 3\,O_2(g)$;
c. $2\,Ba(NO_3)_2(s) \rightarrow 2\,BaO(s) + 2\,N_2(g) + 5\,O_2(g)$;
d. $2\,Mg(s) + O_2(g) \rightarrow 2\,MgO(s)$; $4\,Al(s) + 3\,O_2(g) \rightarrow 2\,Al_2O_3(g)$; $4\,Fe(s) + 3\,O_2(g) \rightarrow 2\,Fe_2O_3(s)$

Q4.1.8

Fill in the blank with a single chemical formula for a covalent compound that will balance the equation:



Q4.1.9

Aqueous hydrogen fluoride (hydrofluoric acid) is used to etch glass and to analyze minerals for their silicon content. Hydrogen fluoride will also react with sand (silicon dioxide).

a. Write an equation for the reaction of solid silicon dioxide with hydrofluoric acid to yield gaseous silicon tetrafluoride and liquid water.
b. The mineral fluorite (calcium fluoride) occurs extensively in Illinois. Solid calcium fluoride can also be prepared by the reaction of aqueous solutions of calcium chloride and sodium fluoride, yielding aqueous sodium chloride as the other product. Write complete and net ionic equations for this reaction.

S4.1.9

a. $4\,HF(aq) + SiO_2(s) \rightarrow SiF_4(g) + 2\,H_2O(l)$;
b. complete ionic equation: $2\,Na^+(aq) + 2\,F^-(aq) + Ca^{2+}(aq) + 2\,Cl^-(aq) \rightarrow CaF_2(s) + 2\,Na^+(aq) + 2\,Cl^-(aq)$, net ionic equation: $2\,F^-(aq) + Ca^{2+}(aq) \rightarrow CaF_2(s)$

Q4.1.10

A novel process for obtaining magnesium from sea water involves several reactions. Write a balanced chemical equation for each step of the process.

a. The first step is the decomposition of solid calcium carbonate from seashells to form solid calcium oxide and gaseous carbon dioxide.
b. The second step is the formation of solid calcium hydroxide as the only product from the reaction of the solid calcium oxide with liquid water.
c. Solid calcium hydroxide is then added to the seawater, reacting with dissolved magnesium chloride to yield solid magnesium hydroxide and aqueous calcium chloride.
d. The solid magnesium hydroxide is added to a hydrochloric acid solution, producing dissolved magnesium chloride and liquid water.
e. Finally, the magnesium chloride is melted and electrolyzed to yield liquid magnesium metal and diatomic chlorine gas.

Q4.1.11

From the balanced molecular equations, write the complete ionic and net ionic equations for the following:

a. $K_2C_2O_4(aq) + Ba(OH)_2(aq) \rightarrow 2\,KOH(aq) + BaC_2O_2(s)$
b. $Pb(NO_3)_2(aq) + H_2SO_4(aq) \rightarrow PbSO_4(s) + 2\,HNO_3(aq)$
c. $CaCO_3(s) + H_2SO_4(aq) \rightarrow CaSO_4(s) + CO_2(g) + H_2O(l)$

S4.1.11

a.

$$2\,K^+(aq) + {C_2O_4}^{2-}(aq) + Ba^{2+}(aq) + 2\,OH^-(aq) \rightarrow 2\,K^+(aq) + 2\,OH^-(aq) + BaC_2O_4(s) \quad \text{(complete)} \tag{3.E.1}$$

$$Ba^{2+}(aq) + {C_2O_4}^{2-}(aq) \rightarrow BaC_2O_4(s) \quad \text{(net)} \tag{3.E.2}$$

b.

$$Pb^{2+}(aq) + 2\,{NO_3}^-(aq) + 2\,H^+(aq) + {SO_4}^{2-}(aq) \rightarrow PbSO_4(s) + 2\,H^+(aq) + 2\,{NO_3}^-(aq) \quad \text{(complete)} \tag{3.E.3}$$

$$Pb^{2+}(aq) + {SO_4}^{2-}(aq) \rightarrow PbSO_4(s) \quad \text{(net)} \tag{3.E.4}$$

c. $$\mathrm{CaCO_3}(s) + 2\,\mathrm{H^+}(aq) + \mathrm{SO_4^{2-}}(aq) \rightarrow \mathrm{CaSO_4}(s) + \mathrm{CO_2}(g) + \mathrm{H_2O}(l) \quad \text{(complete)} \tag{3.E.5}$$

$$\mathrm{CaCO_3}(s) + 2\,\mathrm{H^+}(aq) + \mathrm{SO_4^{2-}}(aq) \rightarrow \mathrm{CaSO_4}(s) + \mathrm{CO_2}(g) + \mathrm{H_2O}(l) \quad \text{(net)} \tag{3.E.6}$$

4.2: Classifying Chemical Reactions

Q4.2.1

Use the following equations to answer the next five questions:

i. $\mathrm{H_2O}(s) \rightarrow \mathrm{H_2O}(l)$
ii. $\mathrm{Na^+}(aq) + \mathrm{Cl^-}(aq)\mathrm{Ag^+}(aq) + \mathrm{NO_3^-}(aq) \rightarrow \mathrm{AgCl}(s) + \mathrm{Na^+}(aq) + \mathrm{NO_3^-}(aq)$
iii. $\mathrm{CH_3OH}(g) + \mathrm{O_2}(g) \rightarrow \mathrm{CO_2}(g) + \mathrm{H_2O}(g)$
iv. $2\,\mathrm{H_2O}(l) \rightarrow 2\,\mathrm{H_2}(g) + \mathrm{O_2}(g)$
v. $\mathrm{H^+}(aq) + \mathrm{OH^-}(aq) \rightarrow \mathrm{H_2O}(l)$

a. Which equation describes a physical change?
b. Which equation identifies the reactants and products of a combustion reaction?
c. Which equation is not balanced?
d. Which is a net ionic equation?

S4.2.1

a.) **i.** $H_2O(solid) \rightarrow H_2O(liquid)$

b.) **iii.**

c.) **iii.** $2\,\mathrm{CH_3OH}(g) + 3\,\mathrm{O_2}(g) \rightarrow 2\,\mathrm{CO_2}(g) + 4\,\mathrm{H_2O}(g)$

d.) **v.**

Q4.2.2

Indicate what type, or types, of reaction each of the following represents:

a. $\mathrm{Ca}(s) + \mathrm{Br_2}(l) \rightarrow \mathrm{CaBr_2}(s)$
b. $\mathrm{Ca(OH)_2}(aq) + 2\,\mathrm{HBr}(aq) \rightarrow \mathrm{CaBr_2}(aq) + 2\,\mathrm{H_2O}(l)$
c. $\mathrm{C_6H_{12}}(l) + 9\,\mathrm{O_2}(g) \rightarrow 6\,\mathrm{CO_2}(g) + 6\,\mathrm{H_2O}(g)$

S4.2.2

oxidation-reduction (addition); acid-base (neutralization); oxidation-reduction (combustion)

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Q4.2.3

Indicate what type, or types, of reaction each of the following represents:

a. $\mathrm{H_2O}(g) + \mathrm{C}(s) \rightarrow \mathrm{CO}(g) + \mathrm{H_2}(g)$
b. $2\,\mathrm{KClO_3}(s) \rightarrow 2\,\mathrm{KCl}(s) + 3\,\mathrm{O_2}(g)$
c. $\mathrm{Al(OH)_3}(aq) + 3\,\mathrm{HCl}(aq) \rightarrow \mathrm{AlBr_3}(aq) + 3\,\mathrm{H_2O}(l)$
d. $\mathrm{Pb(NO_3)_2}(aq) + \mathrm{H_2SO_4}(aq) \rightarrow \mathrm{PbSO_4}(s) + 2\,\mathrm{HNO_3}(aq)$

Q4.2.4

Silver can be separated from gold because silver dissolves in nitric acid while gold does not. Is the dissolution of silver in nitric acid an acid-base reaction or an oxidation-reduction reaction? Explain your answer.

S4.2.4

It is an oxidation-reduction reaction because the oxidation state of the silver changes during the reaction.

Q4.2.5

Determine the oxidation states of the elements in the following compounds:

a. NaI
b. $GdCl_3$
c. $LiNO_3$
d. H_2Se
e. Mg_2Si
f. RbO_2, rubidium superoxide
g. HF

Q4.2.6

Determine the oxidation states of the elements in the compounds listed. None of the oxygen-containing compounds are peroxides or superoxides.

a. H_3PO_4
b. $Al(OH)_3$
c. SeO_2
d. KNO_2
e. In_2S_3
f. P_4O_6

S4.2.6

H +1, P +5, O −2; Al +3, H +1, O −2; Se +4, O −2; K +1, N +3, O −2; In +3, S −2; P +3, O −2

Q4.2.7

Determine the oxidation states of the elements in the compounds listed. None of the oxygen-containing compounds are peroxides or superoxides.

a. H_2SO_4
b. $Ca(OH)_2$
c. BrOH
d. $ClNO_2$
e. $TiCl_4$
f. NaH

S4.2.7

a. H^{1+}, O^{2-}, S^{6+}
b. H^{1+}, O^{2-}, Ca^{+2}
c. H^{1+}, O^{2-}, Br^{1+}
d. O^{2-}, Cl^{1-}, N^{5+}
e. Cl^{1-}, Ti^{4+}
f. H^{1+}, Na^{1-}

Q4.2.8

Classify the following as acid-base reactions or oxidation-reduction reactions:

a. $\mathbf{Na_2S(aq) + 2\,HCl(aq) \rightarrow 2\,NaCl(aq) + H_2S(g)}$
b. $\mathbf{2\,Na(s) + 2\,HCl(aq) \rightarrow 2\,NaCl(aq) + H_2(g)}$
c. $\mathbf{Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)}$
d. $\mathbf{MgO(s) + 2\,HCl(aq) \rightarrow MgCl_2(aq) + H_2O(l)}$
e. $\mathbf{K_3P(s) + 2\,O_2(g) \rightarrow K_3PO_4(s)}$
f. $\mathbf{3\,KOH(aq) + H_3PO_4(aq) \rightarrow K_3PO_4(aq) + 3\,H_2O(l)}$

S4.2.9

acid-base; oxidation-reduction: Na is oxidized, H^+ is reduced; oxidation-reduction: Mg is oxidized, Cl_2 is reduced; acid-base; oxidation-reduction: P^{3-} is oxidized, O_2 is reduced; acid-base

Q4.2.10

Identify the atoms that are oxidized and reduced, the change in oxidation state for each, and the oxidizing and reducing agents in each of the following equations:

a. $\mathrm{Mg}(s) + \mathrm{NiCl_2}(aq) \rightarrow \mathrm{MgCl_2}(aq) + \mathrm{Ni}(s)$
b. $\mathrm{PCl_3}(l) + \mathrm{Cl_2}(g) \rightarrow \mathrm{PCl_5}(s)$
c. $\mathrm{C_2H_4}(g) + 3\,\mathrm{O_2}(g) \rightarrow 2\,\mathrm{CO_2}(g) + 2\,\mathrm{H_2O}(g)$
d. $\mathrm{Zn}(s) + \mathrm{H_2SO_4}(aq) \rightarrow \mathrm{ZnSO_4}(aq) + \mathrm{H_2}(g)$
e. $2\,\mathrm{K_2S_2O_3}(s) + \mathrm{I_2}(s) \rightarrow \mathrm{K_2S_4O_6}(s) + 2\,\mathrm{KI}(s)$
f. $3\,\mathrm{Cu}(s) + 8\,\mathrm{HNO_3}(aq) \rightarrow 3\,\mathrm{Cu(NO_3)_2}(aq) + 2\,\mathrm{NO}(g) + 4\,\mathrm{H_2O}(l)$

Q4.2.11

Complete and balance the following acid-base equations:

a. HCl gas reacts with solid $Ca(OH)_2(s)$.
b. A solution of $Sr(OH)_2$ is added to a solution of HNO_3.

S4.2.11

a. $2\,\mathrm{HCl}(g) + \mathrm{Ca(OH)_2}(s) \rightarrow \mathrm{CaCl_2}(s) + 2\,\mathrm{H_2O}(l)$;
b. $\mathrm{Sr(OH)_2}(aq) + 2\,\mathrm{HNO_3}(aq) \rightarrow \mathrm{Sr(NO_3)_2}(aq) + 2\,\mathrm{H_2O}(l)$

Q4.2.12

Complete and balance the following acid-base equations:

a. A solution of $HClO_4$ is added to a solution of LiOH.
b. Aqueous H_2SO_4 reacts with NaOH.
c. $Ba(OH)_2$ reacts with HF gas.

Q4.2.13

Complete and balance the following oxidation-reduction reactions, which give the highest possible oxidation state for the oxidized atoms.

a. $\mathrm{Al}(s) + \mathrm{F_2}(g) \rightarrow$
b. $\mathrm{Al}(s) + \mathrm{CuBr_2}(aq) \rightarrow$ (single displacement)
c. $\mathrm{P_4}(s) + \mathrm{O_2}(g) \rightarrow$
d. $\mathrm{Ca}(s) + \mathrm{H_2O}(l) \rightarrow$ (products are a strong base and a diatomic gas)

S4.2.13

a. $2\,\mathrm{Al}(s) + 3\,\mathrm{F_2}(g) \rightarrow 2\,\mathrm{AlF_3}(s)$;
b. $2\,\mathrm{Al}(s) + 3\,\mathrm{CuBr_2}(aq) \rightarrow 3\,\mathrm{Cu}(s) + 2\,\mathrm{AlBr_3}(aq)$;
c. $\mathrm{P_4}(s) + 5\,\mathrm{O_2}(g) \rightarrow \mathrm{P_4O_{10}}(s)$; $\mathrm{Ca}(s) + 2\,\mathrm{H_2O}(l) \rightarrow \mathrm{Ca(OH)_2}(aq) + \mathrm{H_2}(g)$

Q4.2.14

Complete and balance the following oxidation-reduction reactions, which give the highest possible oxidation state for the oxidized atoms.

a. $\mathrm{K}(s) + \mathrm{H_2O}(l) \rightarrow$
b. $\mathrm{Ba}(s) + \mathrm{HBr}(aq) \rightarrow$
c. $\mathrm{Sn}(s) + \mathrm{I_2}(s) \rightarrow$

Q4.2.15

Complete and balance the equations for the following acid-base neutralization reactions. If water is used as a solvent, write the reactants and products as aqueous ions. In some cases, there may be more than one correct answer, depending on the amounts of reactants used.

a. $\mathrm{Mg(OH)_2}(s) + \mathrm{HClO_4}(aq) \rightarrow$
b. $\mathrm{SO_3}(g) + \mathrm{H_2O}(l) \rightarrow$ (assume an excess of water and that the product dissolves)
c. $\mathrm{SrO}(s) + \mathrm{H_2SO_4}(l) \rightarrow$

S4.2.15

a. $\mathrm{Mg(OH)_2}(s) + 2\,\mathrm{HClO_4}(aq) \rightarrow \mathrm{Mg^{2+}}(aq) + 2\,\mathrm{ClO_4^-}(aq) + 2\,\mathrm{H_2O}(l)$;
b. $\mathrm{SO_3}(g) + 2\,\mathrm{H_2O}(l) \rightarrow \mathrm{H_3O^+}(aq) + \mathrm{HSO_4^-}(aq)$, (a solution of H_2SO_4);
c. $\mathrm{SrO}(s) + \mathrm{H_2SO_4}(l) \rightarrow \mathrm{SrSO_4}(s) + \mathrm{H_2O}$

Q4.2.16

When heated to 700–800 °C, diamonds, which are pure carbon, are oxidized by atmospheric oxygen. (They burn!) Write the balanced equation for this reaction.

Q4.2.17

The military has experimented with lasers that produce very intense light when fluorine combines explosively with hydrogen. What is the balanced equation for this reaction?

S4.2.17

$\mathrm{H_2}(g) + \mathrm{F_2}(g) \rightarrow 2\,\mathrm{HF}(g)$

Q4.2.18

Write the molecular, total ionic, and net ionic equations for the following reactions:

a. $\mathrm{Ca(OH)_2}(aq) + \mathrm{HC_2H_3O_2}(aq) \rightarrow$
b. $\mathrm{H_3PO_4}(aq) + \mathrm{CaCl_2}(aq) \rightarrow$

Q4.2.19

Great Lakes Chemical Company produces bromine, Br_2, from bromide salts such as NaBr, in Arkansas brine by treating the brine with chlorine gas. Write a balanced equation for the reaction of NaBr with Cl_2.

S4.2.19

$2\,\mathrm{NaBr}(aq) + \mathrm{Cl_2}(g) \rightarrow 2\,\mathrm{NaCl}(aq) + \mathrm{Br_2}(l)$

Q4.2.20

In a common experiment in the general chemistry laboratory, magnesium metal is heated in air to produce MgO. MgO is a white solid, but in these experiments it often looks gray, due to small amounts of Mg_3N_2, a compound formed as some of the magnesium reacts with nitrogen. Write a balanced equation for each reaction.

Q4.2.21

Lithium hydroxide may be used to absorb carbon dioxide in enclosed environments, such as manned spacecraft and submarines. Write an equation for the reaction that involves 2 mol of LiOH per 1 mol of CO_2. (Hint: Water is one of the products.)

S4.2.21

$2\,\mathrm{LiOH}(aq) + \mathrm{CO_2}(g) \rightarrow \mathrm{Li_2CO_3}(aq) + \mathrm{H_2O}(l)$

Q4.2.22

Calcium propionate is sometimes added to bread to retard spoilage. This compound can be prepared by the reaction of calcium carbonate, $CaCO_3$, with propionic acid, $C_2H_5CO_2H$, which has properties similar to those of acetic acid. Write the balanced

equation for the formation of calcium propionate.

Q4.2.23

Complete and balance the equations of the following reactions, each of which could be used to remove hydrogen sulfide from natural gas:

a. $\mathrm{Ca(OH)_2}(s) + \mathrm{H_2S}(g) \rightarrow$
b. $\mathrm{Na_2CO_3}(aq) + \mathrm{H_2S}(g) \rightarrow$

S4.2.23

a. $\mathrm{Ca(OH)_2}(s) + \mathrm{H_2S}(g) \rightarrow \mathrm{CaS}(s) + 2\,\mathrm{H_2O}(l)$;
b. $\mathrm{Na_2CO_3}(aq) + \mathrm{H_2S}(g) \rightarrow \mathrm{Na_2S}(aq) + \mathrm{CO_2}(g) + \mathrm{H_2O}(l)$

Q4.2.24

Copper(II) sulfide is oxidized by molecular oxygen to produce gaseous sulfur trioxide and solid copper(II) oxide. The gaseous product then reacts with liquid water to produce liquid hydrogen sulfate as the only product. Write the two equations which represent these reactions.

Q4.2.25

Write balanced chemical equations for the reactions used to prepare each of the following compounds from the given starting material(s). In some cases, additional reactants may be required.

a. solid ammonium nitrate from gaseous molecular nitrogen via a two-step process (first reduce the nitrogen to ammonia, then neutralize the ammonia with an appropriate acid)
b. gaseous hydrogen bromide from liquid molecular bromine via a one-step redox reaction
c. gaseous H_2S from solid Zn and S via a two-step process (first a redox reaction between the starting materials, then reaction of the product with a strong acid)

S4.2.25

a. step 1: $\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \rightarrow 2\,\mathrm{NH_3}(g)$, step 2: $\mathrm{NH_3}(g) + \mathrm{HNO_3}(aq) \rightarrow \mathrm{NH_4NO_3}(aq) \rightarrow \mathrm{NH_4NO_3}(s)(\text{after drying})$;
b. $\mathrm{H_2}(g) + \mathrm{Br_2}(l) \rightarrow 2\,\mathrm{HBr}(g)$;
c. $\mathrm{Zn}(s) + \mathrm{S}(s) \rightarrow \mathrm{ZnS}(s)$ and $\mathrm{ZnS}(s) + 2\,\mathrm{HCl}(aq) \rightarrow \mathrm{ZnCl_2}(aq) + \mathrm{H_2S}(g)$

Q4.2.26

Calcium cyclamate $Ca(C_6H_{11}NHSO_3)_2$ is an artificial sweetener used in many countries around the world but is banned in the United States. It can be purified industrially by converting it to the barium salt through reaction of the acid $C_6H_{11}NHSO_3H$ with barium carbonate, treatment with sulfuric acid (barium sulfate is very insoluble), and then neutralization with calcium hydroxide. Write the balanced equations for these reactions.

Q4.2.27

Complete and balance each of the following half-reactions (steps 2–5 in half-reaction method):

a. $\mathrm{Sn^{4+}}(aq) \rightarrow \mathrm{Sn^{2+}}(aq)$
b. $[\mathrm{Ag(NH_3)_2}]^+(aq) \rightarrow \mathrm{Ag}(s) + \mathrm{NH_3}(aq)$
c. $\mathrm{Hg_2Cl_2}(s) \rightarrow \mathrm{Hg}(l) + \mathrm{Cl^-}(aq)$
d. $\mathrm{H_2O}(l) \rightarrow \mathrm{O_2}(g)\ (\text{in acidic solution})$
e. $\mathrm{IO_3^-}(aq) \rightarrow \mathrm{I_2}(s)$
f. $\mathrm{SO_3^{2-}}(aq) \rightarrow \mathrm{SO_4^{2-}}(aq)\ (\text{in acidic solution})$
g. $\mathrm{MnO_4^-}(aq) \rightarrow \mathrm{Mn^{2+}}(aq)\ (\text{in acidic solution})$
h. $\mathrm{Cl^-}(aq) \rightarrow \mathrm{ClO_3^-}(aq)\ (\text{in basic solution})$

S4.2.27

a. $\mathrm{Sn^{4+}}(aq) + 2\,\mathrm{e^-} \rightarrow \mathrm{Sn^{2+}}(aq)$,
b. $[\mathrm{Ag(NH_3)_2}]^+(aq) + \mathrm{e^-} \rightarrow \mathrm{Ag}(s) + 2\,\mathrm{NH_3}(aq)$;

c. $Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(l) + 2Cl^-(aq)$;
d. $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$;
e. $6H_2O(l) + 2IO_3^-(aq) + 10e^- \rightarrow I_2(s) + 12OH^-(aq)$;
f. $H_2O(l) + SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e^-$;
g. (g) $8H^+(aq) + MnO_4^-(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$;
h. (h) $Cl^-(aq) + 6OH^-(aq) \rightarrow ClO_3^-(aq) + 3H_2O(l) + 6e^-$

Q4.2.28

Complete and balance each of the following half-reactions (steps 2–5 in half-reaction method):

a. $Cr^{2+}(aq) \rightarrow Cr^{3+}(aq)$
b. $Hg(l) + Br^-(aq) \rightarrow HgBr_4^{2-}(aq)$
c. $ZnS(s) \rightarrow Zn(s) + S^{2-}(aq)$
d. $H_2(g) \rightarrow H_2O(l)$ (in basic solution)
e. $H_2(g) \rightarrow H_3O^+(aq)$ (in acidic solution)
f. $NO_3^-(aq) \rightarrow HNO_2(aq)$ (in acidic solution)
g. $MnO_2(s) \rightarrow MnO_4^-(aq)$ (in basic solution)
h. $Cl^-(aq) \rightarrow ClO_3^-(aq)$ (in acidic solution)

Q4.2.29

Balance each of the following equations according to the half-reaction method:

a. $Sn^{2+}(aq) + Cu^{2+}(aq) \rightarrow Sn^{4+}(aq) + Cu^+(aq)$
b. $H_2S(g) + Hg_2^{2+}(aq) \rightarrow Hg(l) + S(s)$ (in acid)
c. $CN^-(aq) + ClO_2(aq) \rightarrow CNO^-(aq) + Cl^-(aq)$ (in acid)
d. $Fe^{2+}(aq) + Ce^{4+}(aq) \rightarrow Fe^{3+}(aq) + Ce^{3+}(aq)$
e. $HBrO(aq) \rightarrow Br^-(aq) + O_2(g)$ (in acid)

S4.2.29

a. $Sn^{2+}(aq) + 2Cu^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2Cu^+(aq)$;
b. $H_2S(g) + Hg_2^{2+}(aq) + 2H_2O(l) \rightarrow 2Hg(l) + S(s) + 2H_3O^+(aq)$;
c. $5CN^-(aq) + 2ClO_2(aq) + 3H_2O(l) \rightarrow 5CNO^-(aq) + 2Cl^-(aq) + 2H_3O^+(aq)$;
d. $Fe^{2+}(aq) + Ce^{4+}(aq) \rightarrow Fe^{3+}(aq) + Ce^{3+}(aq)$;
e. $2HBrO(aq) + 2H_2O(l) \rightarrow 2H_3O^+(aq) + 2Br^-(aq) + O_2(g)$

Q4.2.30

Balance each of the following equations according to the half-reaction method:

a. $Zn(s) + NO_3^-(aq) \rightarrow Zn^{2+}(aq) + N_2(g)$ (in acid)
b. $Zn(s) + NO_3^-(aq) \rightarrow Zn^{2+}(aq) + NH_3(aq)$ (in base)
c. $CuS(s) + NO_3^-(aq) \rightarrow Cu^{2+}(aq) + S(s) + NO(g)$ (in acid)
d. $NH_3(aq) + O_2(g) \rightarrow NO_2(g)$ (gas phase)
e. $Cl_2(g) + OH^-(aq) \rightarrow Cl^-(aq) + ClO_3^-(aq)$ (in base)
f. $H_2O_2(aq) + MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + O_2(g)$ (in acid)
g. $NO_2(g) \rightarrow NO_3^-(aq) + NO_2^-(aq)$ (in base)
h. $Fe^{3+}(aq) + I^-(aq) \rightarrow Fe^{2+}(aq) + I_2(aq)$

Q4.2.31

Balance each of the following equations according to the half-reaction method:

a. $MnO_4^-(aq) + NO_2^-(aq) \rightarrow MnO_2(s) + NO_3^-(aq)$ (in base)
b. $MnO_4^{2-}(aq) \rightarrow MnO_4^-(aq) + MnO_2(s)$ (in base)
c. $Br_2(l) + SO_2(g) \rightarrow Br^-(aq) + SO_4^{2-}(aq)$ (in acid)

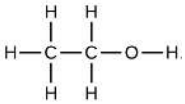
S4.2.31

a. $2\,MnO_4^-(aq) + 3\,NO_2^-(aq) + H_2O(l) \rightarrow 2\,MnO_2(s) + 3\,NO_3^-(aq) + 2\,OH^-(aq)$;
b. $3\,MnO_4^{2-}(aq) + 2\,H_2O(l) \rightarrow 2\,MnO_4^-(aq) + 4\,OH^-(aq) + MnO_2(s)$ (in base);
c. $Br_2(l) + SO_2(g) + 2\,H_2O(l) \rightarrow 4\,H^+(aq) + 2\,Br^-(aq) + SO_4^{2-}(aq)$

4.3: Reaction Stoichiometry

Q4.3.1

Write the balanced equation, then outline the steps necessary to determine the information requested in each of the following:

a. The number of moles and the mass of chlorine, Cl_2, required to react with 10.0 g of sodium metal, Na, to produce sodium chloride, NaCl.
b. The number of moles and the mass of oxygen formed by the decomposition of 1.252 g of mercury(II) oxide.
c. The number of moles and the mass of sodium nitrate, $NaNO_3$, required to produce 128 g of oxygen. ($NaNO_2$ is the other product.)
d. The number of moles and the mass of carbon dioxide formed by the combustion of 20.0 kg of carbon in an excess of oxygen.
e. The number of moles and the mass of copper(II) carbonate needed to produce 1.500 kg of copper(II) oxide. (CO_2 is the other product.)
f. The number of moles and the mass of  required to react with H_2O to produce 9.55 g of .

Q4.3.2

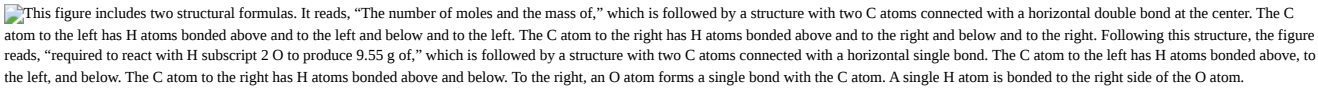
Determine the number of moles and the mass requested for each reaction in Exercise.

S4.3.2

0.435 mol Na, 0.217 mol Cl_2, 15.4 g Cl_2; 0.005780 mol HgO, 2.890×10^{-3} mol O_2, 9.248×10^{-2} g O_2; 8.00 mol $NaNO_3$, 6.8×10^2 g $NaNO_3$; 1665 mol CO_2, 73.3 kg CO_2; 18.86 mol CuO, 2.330 kg $CuCO_3$; 0.4580 mol $C_2H_4Br_2$, 86.05 g $C_2H_4Br_2$

Q4.3.3

Write the balanced equation, then outline the steps necessary to determine the information requested in each of the following:

a. The number of moles and the mass of Mg required to react with 5.00 g of HCl and produce $MgCl_2$ and H_2.
b. The number of moles and the mass of oxygen formed by the decomposition of 1.252 g of silver(I) oxide.
c. The number of moles and the mass of magnesium carbonate, $MgCO_3$, required to produce 283 g of carbon dioxide. (MgO is the other product.)
d. The number of moles and the mass of water formed by the combustion of 20.0 kg of acetylene, C_2H_2, in an excess of oxygen.
e. The number of moles and the mass of barium peroxide, BaO_2, needed to produce 2.500 kg of barium oxide, BaO (O_2 is the other product.)
f. 

Q4.3.4

Determine the number of moles and the mass requested for each reaction in Exercise.

S4.3.4

0.0686 mol Mg, 1.67 g Mg; 2.701×10^{-3} mol O_2, 0.08644 g O_2; 6.43 mol $MgCO_3$, 542 g $MgCO_3$ 713 mol H_2O, 12.8 kg H_2O; 16.31 mol BaO_2, 2762 g BaO_2; 0.207 mol C_2H_4, 5.81 g C_2H_4

Q4.3.5

H_2 is produced by the reaction of 118.5 mL of a 0.8775-M solution of H_3PO_4 according to the following equation: $2\,Cr + 2\,H_3PO_4 \rightarrow 3\,H_2 + 2\,CrPO_4$.

a. Outline the steps necessary to determine the number of moles and mass of H_2.
b. Perform the calculations outlined.

S4.3.5

a.)

1. Convert mL to L
2. Multiply L by the molarity to determine moles of H_3PO_4
3. Convert moles of H_3PO_4 to moles of H_2
4. Multiply moles of H_2 by the molar mass of H_2 to get the answer in grams

b.)

1. $118.5\,mL \times \dfrac{1\,L}{1000\,mL} = 0.1185\,L$
2. $0.1185\,L \times \dfrac{0.8775\,moles\,H_3PO_4}{1\,L} = 0.1040\,moles\,H_3PO_4$
3. $0.1040\,moles\,H_3PO_4 \times \dfrac{3\,moles\,H_2}{2\,moles\,H_3PO_4} = 0.1560\,moles\,H_2$
4. $0.1560\,moles\,H_2 \times \dfrac{2.02g}{1\,mole} = 0.3151g\,H_2$

Q4.3.6

Gallium chloride is formed by the reaction of 2.6 L of a 1.44 M solution of HCl according to the following equation: $2\,Ga + 6\,HCl \rightarrow 2\,GaCl_3 + 3\,H_2$.

a. Outline the steps necessary to determine the number of moles and mass of gallium chloride.
b. Perform the calculations outlined.

S4.3.6

$\text{volume HCl solution} \rightarrow \text{mol HCl} \rightarrow \text{mol } GaCl_3$; 1.25 mol $GaCl_3$, 2.2×10^2 g $GaCl_3$

Q4.3.7

I_2 is produced by the reaction of 0.4235 mol of $CuCl_2$ according to the following equation: $2\,CuCl_2 + 4\,KI \rightarrow 2\,CuI + 4\,KCl + I_2$.

a. How many molecules of I_2 are produced?
b. What mass of I_2 is produced?

Q4.3.8

Silver is often extracted from ores as $K[Ag(CN)_2]$ and then recovered by the reaction

$$2\,K[Ag(CN)_2](aq) + Zn(s) \rightarrow 2\,Ag(s) + Zn(CN)_2(aq) + 2\,KCN(aq)$$

a. How many molecules of $Zn(CN)_2$ are produced by the reaction of 35.27 g of $K[Ag(CN)_2]$?
b. What mass of $Zn(CN)_2$ is produced?

S4.3.8

5.337×10^{22} molecules; 10.41 g $Zn(CN)_2$

Q4.3.9

What mass of silver oxide, Ag_2O, is required to produce 25.0 g of silver sulfadiazine, $AgC_{10}H_9N_4SO_2$, from the reaction of silver oxide and sulfadiazine?

$$2\,C_{10}H_{10}N_4SO_2 + Ag_2O \rightarrow 2\,AgC_{10}H_9N_4SO_2 + H_2O$$

Q4.3.10

Carborundum is silicon carbide, SiC, a very hard material used as an abrasive on sandpaper and in other applications. It is prepared by the reaction of pure sand, SiO_2, with carbon at high temperature. Carbon monoxide, CO, is the other product of this reaction.

Write the balanced equation for the reaction, and calculate how much SiO_2 is required to produce 3.00 kg of SiC.

S4.3.10

$\mathbf{SiO_2 + 3\,C \rightarrow SiC + 2\,CO}$, 4.50 kg SiO_2

Q4.3.11

Automotive air bags inflate when a sample of sodium azide, NaN_3, is very rapidly decomposed.

$$\mathbf{2\,NaN_3}(s) \rightarrow \mathbf{2\,Na}(s) + \mathbf{3\,N_2}(g)$$

What mass of sodium azide is required to produce 2.6 ft^3 (73.6 L) of nitrogen gas with a density of 1.25 g/L?

S4.3.11

142g NaN_3

Q4.3.12

Urea, $CO(NH_2)_2$, is manufactured on a large scale for use in producing urea-formaldehyde plastics and as a fertilizer. What is the maximum mass of urea that can be manufactured from the CO_2 produced by combustion of 1.00×10^3 kg of carbon followed by the reaction?

$$\mathbf{CO_2}(g) + \mathbf{2\,NH_3}(g) \rightarrow \mathbf{CO(NH_2)_2}(s) + \mathbf{H_2O}(l) \tag{3.E.7}$$

S4.3.12

5.00×10^3 kg

Q4.3.13

In an accident, a solution containing 2.5 kg of nitric acid was spilled. Two kilograms of Na_2CO_3 was quickly spread on the area and CO_2 was released by the reaction. Was sufficient Na_2CO_3 used to neutralize all of the acid?

Q4.3.14

A compact car gets 37.5 miles per gallon on the highway. If gasoline contains 84.2% carbon by mass and has a density of 0.8205 g/mL, determine the mass of carbon dioxide produced during a 500-mile trip (3.785 liters per gallon).

S4.3.14

1.28×10^5 g CO_2

Q4.3.15

What volume of a 0.750 M solution of hydrochloric acid, a solution of HCl, can be prepared from the HCl produced by the reaction of 25.0 g of NaCl with an excess of sulfuric acid?

$$\mathbf{NaCl}(s) + \mathbf{H_2SO_4}(l) \rightarrow \mathbf{HCl}(g) + \mathbf{NaHSO_4}(s) \tag{3.E.8}$$

Q4.3.16

What volume of a 0.2089 *M* KI solution contains enough KI to react exactly with the $Cu(NO_3)_2$ in 43.88 mL of a 0.3842 *M* solution of $Cu(NO_3)_2$?

$$\mathbf{2\,Cu(NO_3)_2 + 4\,KI \rightarrow 2\,CuI + I_2 + 4\,KNO_3} \tag{3.E.9}$$

S4.3.16

161.40 mL KI solution

Q4.3.17

A mordant is a substance that combines with a dye to produce a stable fixed color in a dyed fabric. Calcium acetate is used as a mordant. It is prepared by the reaction of acetic acid with calcium hydroxide.

$$\mathbf{2\,CH_3CO_2H + Ca(OH)_2 \rightarrow Ca(CH_3CO_2)_2 + 2\,H_2O} \tag{3.E.10}$$

What mass of $Ca(OH)_2$ is required to react with the acetic acid in 25.0 mL of a solution having a density of 1.065 g/mL and containing 58.0% acetic acid by mass?

Q4.3.18

The toxic pigment called white lead, $Pb_3(OH)_2(CO_3)_2$, has been replaced in white paints by rutile, TiO_2. How much rutile (g) can be prepared from 379 g of an ore that contains 88.3% ilmenite ($FeTiO_3$) by mass?

$$2\,FeTiO_3 + 4\,HCl + Cl_2 \rightarrow 2\,FeCl_3 + 2\,TiO_2 + 2\,H_2O \tag{3.E.11}$$

S4.3.18

176 g TiO_2

4.4: Reaction Yields

Q4.4.1

The following quantities are placed in a container: 1.5×10^{24} atoms of hydrogen, 1.0 mol of sulfur, and 88.0 g of diatomic oxygen.

a. What is the total mass in grams for the collection of all three elements?
b. What is the total number of moles of atoms for the three elements?
c. If the mixture of the three elements formed a compound with molecules that contain two hydrogen atoms, one sulfur atom, and four oxygen atoms, which substance is consumed first?
d. How many atoms of each remaining element would remain unreacted in the change described in ?

Q4.4.2

What is the limiting reactant in a reaction that produces sodium chloride from 8 g of sodium and 8 g of diatomic chlorine?

S4.4.2

The limiting reactant is Cl_2.

Q4.4.3

Which of the postulates of Dalton's atomic theory explains why we can calculate a theoretical yield for a chemical reaction?

Q4.4.4

A student isolated 25 g of a compound following a procedure that would theoretically yield 81 g. What was his percent yield?

S4.4.4

$\textbf{Percent yield} = 31\%$

Q4.4.5

A sample of 0.53 g of carbon dioxide was obtained by heating 1.31 g of calcium carbonate. What is the percent yield for this reaction?

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(s) \tag{3.E.12}$$

Q4.4.6

Freon-12, CCl_2F_2, is prepared from CCl_4 by reaction with HF. The other product of this reaction is HCl. Outline the steps needed to determine the percent yield of a reaction that produces 12.5 g of CCl_2F_2 from 32.9 g of CCl_4. Freon-12 has been banned and is no longer used as a refrigerant because it catalyzes the decomposition of ozone and has a very long lifetime in the atmosphere. Determine the percent yield.

S4.4.6

$\text{g } CCl_4 \rightarrow \text{mol } CCl_4 \rightarrow \text{mol } CCl_2F_2 \rightarrow \text{g } CCl_2F_2, \text{ percent yield} = 48.3\%$

Q4.4.7

Citric acid, $C_6H_8O_7$, a component of jams, jellies, and fruity soft drinks, is prepared industrially via fermentation of sucrose by the mold *Aspergillus niger*. The equation representing this reaction is

$$\mathbf{C_{12}H_{22}O_{11} + H_2O + 3\,O_2 \rightarrow 2\,C_6H_8O_7 + 4\,H_2O} \tag{3.E.13}$$

What mass of citric acid is produced from exactly 1 metric ton (1.000×10^3 kg) of sucrose if the yield is 92.30%?

Q4.4.8

Toluene, $C_6H_5CH_3$, is oxidized by air under carefully controlled conditions to benzoic acid, $C_6H_5CO_2H$, which is used to prepare the food preservative sodium benzoate, $C_6H_5CO_2Na$. What is the percent yield of a reaction that converts 1.000 kg of toluene to 1.21 kg of benzoic acid?

$$\mathbf{2\,C_6H_5CH_3 + 3\,O_2 \rightarrow 2\,C_6H_5CO_2H + 2\,H_2O} \tag{3.E.14}$$

S4.4.8

$\mathbf{\text{percent yield} = 91.3\%}$

Q4.4.9

In a laboratory experiment, the reaction of 3.0 mol of H_2 with 2.0 mol of I_2 produced 1.0 mol of HI. Determine the theoretical yield in grams and the percent yield for this reaction.

Q4.4.10

Outline the steps needed to solve the following problem, then do the calculations. Ether, $(C_2H_5)_2O$, which was originally used as an anesthetic but has been replaced by safer and more effective medications, is prepared by the reaction of ethanol with sulfuric acid.

$$2C_2H_5OH + H_2SO_4 \longrightarrow (C_2H_5)_2 + H_2SO_4{\cdot}H_2O$$

Q4.4.11

What is the percent yield of ether if 1.17 L (d = 0.7134 g/mL) is isolated from the reaction of 1.500 L of C_2H_5OH (d = 0.7894 g/mL)?

S4.4.11

Convert mass of ethanol to moles of ethanol; relate the moles of ethanol to the moles of ether produced using the stoichiometry of the balanced equation. Convert moles of ether to grams; divide the actual grams of ether (determined through the density) by the theoretical mass to determine the percent yield; 87.6%

Q4.4.12

Outline the steps needed to determine the limiting reactant when 30.0 g of propane, C_3H_8, is burned with 75.0 g of oxygen.

$$\mathbf{\text{percent yield} = \frac{0.8347\ \cancel{g}}{0.9525\ \cancel{g}} \times 100\% = 87.6\%} \tag{3.E.15}$$

Determine the limiting reactant.

Q4.4.13

Outline the steps needed to determine the limiting reactant when 0.50 g of Cr and 0.75 g of H_3PO_4 react according to the following chemical equation?

$$\mathbf{2\,Cr + 2\,H_3PO_4 \rightarrow 2\,CrPO_4 + 3\,H_2} \tag{3.E.16}$$

Determine the limiting reactant.

S4.4.13

The conversion needed is $\mathbf{\text{mol Cr} \rightarrow \text{mol } H_2PO_4}$. Then compare the amount of Cr to the amount of acid present. Cr is the limiting reactant.

Q4.4.14

What is the limiting reactant when 1.50 g of lithium and 1.50 g of nitrogen combine to form lithium nitride, a component of advanced batteries, according to the following unbalanced equation?

$$\mathrm{Li} + \mathrm{N_2} \rightarrow \mathrm{Li_3N} \tag{3.E.17}$$

S4.4.14

$$6\,\mathrm{Li} + \mathrm{N_2} \rightarrow 2\,\mathrm{Li_3N} \tag{3.E.18}$$

$$1.50g\,\mathrm{Li} \times \frac{1\,mole\,\mathrm{Li}}{6.94g\,\mathrm{Li}} \times \frac{2\,mole\,\mathrm{Li_3N}}{6\,mole\,\mathrm{Li}} = 0.0720\,moles\,\mathrm{Li_3N} \tag{3.E.19}$$

$$1.50g\,\mathrm{N_2} \times \frac{1\,mole\,\mathrm{N_2}}{28.02g\,\mathrm{N_2}} \times \frac{2\,mole\,\mathrm{Li_3N}}{1\,mole\,\mathrm{N_2}} = 0.107\,moles\,\mathrm{Li_3N} \tag{3.E.20}$$

Li is the limiting reactant

Q4.4.15

Uranium can be isolated from its ores by dissolving it as $UO_2(NO_3)_2$, then separating it as solid $UO_2(C_2O_4)\cdot 3H_2O$. Addition of 0.4031 g of sodium oxalate, $Na_2C_2O_4$, to a solution containing 1.481 g of uranyl nitrate, $UO_2(NO_2)_2$, yields 1.073 g of solid $UO_2(C_2O_4)\cdot 3H_2O$.

$$\mathrm{Na_2C_2O_4} + \mathrm{UO_2(NO_3)_2} + 3\,\mathrm{H_2O} \longrightarrow \mathrm{UO_2(C_2O_4)\cdot 3\,H_2O} + 2\,\mathrm{NaNO_3} \tag{3.E.21}$$

Determine the limiting reactant and the percent yield of this reaction.

S4.4.15

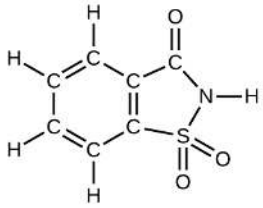
$Na_2C_2O_4$ is the limiting reactant. percent yield = 86.6%

Q4.4.16

How many molecules of $C_2H_4Cl_2$ can be prepared from 15 C_2H_4 molecules and 8 Cl_2 molecules?

Q4.4.17

How many molecules of the sweetener saccharin can be prepared from 30 C atoms, 25 H atoms, 12 O atoms, 8 S atoms, and 14 N atoms?



S4.4.17

Only four molecules can be made.

Q4.4.18

The phosphorus pentoxide used to produce phosphoric acid for cola soft drinks is prepared by burning phosphorus in oxygen.

a. What is the limiting reactant when 0.200 mol of P_4 and 0.200 mol of O_2 react according to

$$\mathrm{P_4} + 5\,\mathrm{O_2} \rightarrow \mathrm{P_4O_{10}} \tag{3.E.22}$$

b. Calculate the percent yield if 10.0 g of P_4O_{10} is isolated from the reaction.

Q4.4.19

Would you agree to buy 1 trillion (1,000,000,000,000) gold atoms for $5? Explain why or why not. Find the current price of gold at http://money.cnn.com/data/commodities/ $(1\ \text{troy ounce} = 31.1\ \text{g})$

S4.4.19

This amount cannot be weighted by ordinary balances and is worthless.

4.5: Quantitative Chemical Analysis

Q4.5.1

What volume of 0.0105-M HBr solution is be required to titrate 125 mL of a 0.0100-*M* $Ca(OH)_2$ solution?

$$\text{Ca(OH)}_2(aq) + 2\,\text{HBr}(aq) \rightarrow \text{CaBr}_2(aq) + 2\,\text{H}_2\text{O}(l) \tag{3.E.23}$$

Q4.5.2

Titration of a 20.0-mL sample of acid rain required 1.7 mL of 0.0811 *M* NaOH to reach the end point. If we assume that the acidity of the rain is due to the presence of sulfuric acid, what was the concentration of sulfuric acid in this sample of rain?

S4.5.2

3.4×10^{-3} *M* H_2SO_4

Q4.5.3

What is the concentration of NaCl in a solution if titration of 15.00 mL of the solution with 0.2503 *M* $AgNO_3$ requires 20.22 mL of the $AgNO_3$ solution to reach the end point?

$$\text{AgNO}_3(aq) + \text{NaCl}(aq) \rightarrow \text{AgCl}(s) + \text{NaNO}_3(aq) \tag{3.E.24}$$

Q4.5.4

In a common medical laboratory determination of the concentration of free chloride ion in blood serum, a serum sample is titrated with a $Hg(NO_3)_2$ solution.

$$2\,\text{Cl}^-(aq) + \text{Hg(NO}_3)_2(aq) \rightarrow 2\,\text{NO}_3{}^-(aq) + \text{HgCl}_2(s) \tag{3.E.25}$$

What is the Cl^- concentration in a 0.25-mL sample of normal serum that requires 1.46 mL of 5.25×10^{-4} *M* $Hg(NO_3)_2(aq)$ to reach the end point?

S4.5.4

9.6×10^{-3} *M* Cl^-

Q4.5.5

Potatoes can be peeled commercially by soaking them in a 3-M to 6-M solution of sodium hydroxide, then removing the loosened skins by spraying them with water. Does a sodium hydroxide solution have a suitable concentration if titration of 12.00 mL of the solution requires 30.6 mL of 1.65 M HCI to reach the end point?

Q4.5.6

A sample of gallium bromide, $GaBr_2$, weighing 0.165 g was dissolved in water and treated with silver nitrate, $AgNO_3$, resulting in the precipitation of 0.299 g AgBr. Use these data to compute the %Ga (by mass) $GaBr_2$.

S4.5.6

22.4%

Q4.5.7

The principal component of mothballs is naphthalene, a compound with a molecular mass of about 130 amu, containing only carbon and hydrogen. A 3.000-mg sample of naphthalene burns to give 10.3 mg of CO_2. Determine its empirical and molecular

formulas.

Q4.5.8

A 0.025-g sample of a compound composed of boron and hydrogen, with a molecular mass of ~28 amu, burns spontaneously when exposed to air, producing 0.063 g of B_2O_3. What are the empirical and molecular formulas of the compound.

S4.5.8

The empirical formula is BH_3. The molecular formula is B_2H_6.

Q4.5.9

Sodium bicarbonate (baking soda), $NaHCO_3$, can be purified by dissolving it in hot water (60 °C), filtering to remove insoluble impurities, cooling to 0 °C to precipitate solid $NaHCO_3$, and then filtering to remove the solid, leaving soluble impurities in solution. Any $NaHCO_3$ that remains in solution is not recovered. The solubility of $NaHCO_3$ in hot water of 60 °C is 164 g L. Its solubility in cold water of 0 °C is 69 g/L. What is the percent yield of $NaHCO_3$ when it is purified by this method?

Q4.5.10

What volume of 0.600 *M* HCl is required to react completely with 2.50 g of sodium hydrogen carbonate?

$$\mathrm{NaHCO_3}(aq) + \mathrm{HCl}(aq) \rightarrow \mathrm{NaCl}(aq) + \mathrm{CO_2}(g) + \mathrm{H_2O}(l) \tag{3.E.26}$$

S4.5.10

49.6 mL

Q4.5.11

What volume of 0.08892 *M* HNO_3 is required to react completely with 0.2352 g of potassium hydrogen phosphate?

$$2\,\mathrm{HNO_3}(aq) + \mathrm{K_2HPO_4}(aq) \rightarrow \mathrm{H_2PO_4}(aq) + 2\,\mathrm{KNO_3}(aq) \tag{3.E.27}$$

Q4.5.12

What volume of a 0.3300-*M* solution of sodium hydroxide would be required to titrate 15.00 mL of 0.1500 *M* oxalic acid?

$$\mathrm{C_2O_4H_2}(aq) + 2\,\mathrm{NaOH}(aq) \rightarrow \mathrm{Na_2C_2O_4}(aq) + 2\,\mathrm{H_2O}(l) \tag{3.E.28}$$

S4.5.12

13.64 mL

Q4.5.13

What volume of a 0.00945-*M* solution of potassium hydroxide would be required to titrate 50.00 mL of a sample of acid rain with a H_2SO_4 concentration of 1.23×10^{-4} *M*.

$$\mathrm{H_2SO_4}(aq) + 2\,\mathrm{KOH}(aq) \rightarrow \mathrm{K_2SO_4}(aq) + 2\,\mathrm{H_2O}(l) \tag{3.E.29}$$

S4.5.13

1.30 mL

Q4.5.14

A sample of solid calcium hydroxide, $Ca(OH)_2$, is allowed to stand in water until a saturated solution is formed. A titration of 75.00 mL of this solution with 5.00×10^{-2} *M* HCl requires 36.6 mL of the acid to reach the end point.

$$\mathrm{Ca(OH)_2}(aq) + 2\,\mathrm{HCl}(aq) \rightarrow \mathrm{CaCl_2}(aq) + 2\,\mathrm{H_2O}(l) \tag{3.E.30}$$

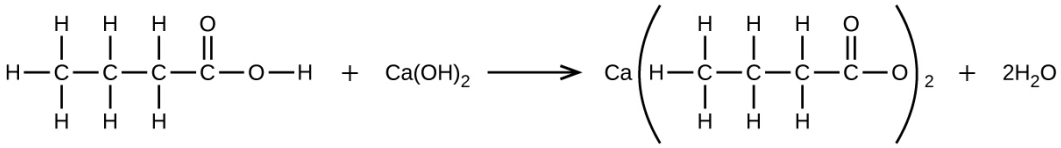
What is the molarity?

S4.5.14

1.22 *M*

Q4.5.15

What mass of $Ca(OH)_2$ will react with 25.0 g of propionic acid to form the preservative calcium propionate according to the equation?



Q4.5.16

How many milliliters of a 0.1500-*M* solution of KOH will be required to titrate 40.00 mL of a 0.0656-*M* solution of H_3PO_4?

$$\mathbf{H_3PO_4}(aq) + \mathbf{2\,KOH}(aq) \rightarrow \mathbf{K_2HPO_4}(aq) + \mathbf{2\,H_2O}(l) \tag{3.E.31}$$

S4.5.16

34.99 mL KOH

Q4.5.17

Potassium acid phthalate, $KHC_6H_4O_4$, or KHP, is used in many laboratories, including general chemistry laboratories, to standardize solutions of base. KHP is one of only a few stable solid acids that can be dried by warming and weighed. A 0.3420-g sample of $KHC_6H_4O_4$ reacts with 35.73 mL of a NaOH solution in a titration. What is the molar concentration of the NaOH?

$$\mathbf{KHC_6H_4O_4}(aq) + \mathbf{NaOH}(aq) \rightarrow \mathbf{KNaC_6H_4O_4}(aq) + \mathbf{H_2O}(aq) \tag{3.E.32}$$

Q4.5.18

The reaction of WCl_6 with Al at ~400 °C gives black crystals of a compound containing only tungsten and chlorine. A sample of this compound, when reduced with hydrogen, gives 0.2232 g of tungsten metal and hydrogen chloride, which is absorbed in water. Titration of the hydrochloric acid thus produced requires 46.2 mL of 0.1051 *M* NaOH to reach the end point. What is the empirical formula of the black tungsten chloride?

S4.5.19

The empirical formula is WCl_4.

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CHAPTER OVERVIEW

4: Thermochemistry

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General Chemistry

Useful forms of energy are also available from a variety of chemical reactions other than combustion. For example, the energy produced by the batteries in a cell phone, car, or flashlight results from chemical reactions. This chapter introduces many of the basic ideas necessary to explore the relationships between chemical changes and energy, with a focus on thermal energy.

4.1: Prelude to Thermochemistry

4.2: Energy Basics

4.3: Enthalpy

4.E: Thermochemistry (Exercises)

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4.1: Prelude to Thermochemistry

Chemical reactions, such as those that occur when you light a match, involve changes in energy as well as matter. Societies at all levels of development could not function without the energy released by chemical reactions. In 2012, about 85% of US energy consumption came from the combustion of petroleum products, coal, wood, and garbage. We use this energy to produce electricity (38%); to transport food, raw materials, manufactured goods, and people (27%); for industrial production (21%); and to heat and power our homes and businesses (10%).[1] While these combustion reactions help us meet our essential energy needs, they are also recognized by the majority of the scientific community as a major contributor to global climate change.



Figure **4.1.1**: Sliding a match head along a rough surface initiates a combustion reaction that produces energy in the form of heat and light. (credit: modification of work by Laszlo Ilyes).

Useful forms of energy are also available from a variety of chemical reactions other than combustion. For example, the energy produced by the batteries in a cell phone, car, or flashlight results from chemical reactions. This chapter introduces many of the basic ideas necessary to explore the relationships between chemical changes and energy, with a focus on thermal energy.

Footnotes

1. US Energy Information Administration, *Primary Energy Consumption by Source and Sector, 2012*, Total Energy [www.eia.gov]. Data derived from US Energy Information Administration, *Monthly Energy Review* (January 2014).

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4.2: Energy Basics

Learning Objectives

- Define energy, distinguish types of energy, and describe the nature of energy changes that accompany chemical and physical changes
- Distinguish the related properties of heat, thermal energy, and temperature
- Define and distinguish specific heat and heat capacity, and describe the physical implications of both
- Perform calculations involving heat, specific heat, and temperature change

Chemical changes and their accompanying changes in energy are important parts of our everyday world (Figure **4.2.1**). The macronutrients in food (proteins, fats, and carbohydrates) undergo metabolic reactions that provide the energy to keep our bodies functioning. We burn a variety of fuels (gasoline, natural gas, coal) to produce energy for transportation, heating, and the generation of electricity. Industrial chemical reactions use enormous amounts of energy to produce raw materials (such as iron and aluminum). Energy is then used to manufacture those raw materials into useful products, such as cars, skyscrapers, and bridges.



(a) (b) (c)

Figure **4.2.1**: The energy involved in chemical changes is important to our daily lives: (a) A cheeseburger for lunch provides the energy you need to get through the rest of the day; (b) the combustion of gasoline provides the energy that moves your car (and you) between home, work, and school; and (c) coke, a processed form of coal, provides the energy needed to convert iron ore into iron, which is essential for making many of the products we use daily. (credit a: modification of work by “Pink Sherbet Photography”/Flickr; credit b: modification of work by Jeffery Turner).

Over 90% of the energy we use comes originally from the sun. Every day, the sun provides the earth with almost 10,000 times the amount of energy necessary to meet all of the world’s energy needs for that day. Our challenge is to find ways to convert and store incoming solar energy so that it can be used in reactions or chemical processes that are both convenient and nonpolluting. Plants and many bacteria capture solar energy through photosynthesis. We release the energy stored in plants when we burn wood or plant products such as ethanol. We also use this energy to fuel our bodies by eating food that comes directly from plants or from animals that got their energy by eating plants. Burning coal and petroleum also releases stored solar energy: These fuels are fossilized plant and animal matter.

This chapter will introduce the basic ideas of an important area of science concerned with the amount of heat absorbed or released during chemical and physical changes—an area called thermochemistry. The concepts introduced in this chapter are widely used in almost all scientific and technical fields. Food scientists use them to determine the energy content of foods. Biologists study the energetics of living organisms, such as the metabolic combustion of sugar into carbon dioxide and water. The oil, gas, and transportation industries, renewable energy providers, and many others endeavor to find better methods to produce energy for our commercial and personal needs. Engineers strive to improve energy efficiency, find better ways to heat and cool our homes, refrigerate our food and drinks, and meet the energy and cooling needs of computers and electronics, among other applications. Understanding thermochemical principles is essential for chemists, physicists, biologists, geologists, every type of engineer, and just about anyone who studies or does any kind of science.

Energy

Energy can be defined as the capacity to supply heat or do work. One type of work (w) is the process of causing matter to move against an opposing force. For example, we do work when we inflate a bicycle tire—we move matter (the air in the pump) against

the opposing force of the air surrounding the tire.

Like matter, energy comes in different types. One scheme classifies energy into two types: potential energy, the energy an object has because of its relative position, composition, or condition, and kinetic energy, the energy that an object possesses because of its motion. Water at the top of a waterfall or dam has potential energy because of its position; when it flows downward through generators, it has kinetic energy that can be used to do work and produce electricity in a hydroelectric plant (Figure **4.2.2**). A battery has potential energy because the chemicals within it can produce electricity that can do work.



(a) (b)

Figure **4.2.2**: (a) Water that is higher in elevation, for example, at the top of Victoria Falls, has a higher potential energy than water at a lower elevation. As the water falls, some of its potential energy is converted into kinetic energy. (b) If the water flows through generators at the bottom of a dam, such as the Hoover Dam shown here, its kinetic energy is converted into electrical energy. (credit a: modification of work by Steve Jurvetson; credit b: modification of work by "curimedia"/Wikimedia commons).

Two pictures are shown and labeled a and b. Picture a shows a large waterfall with water falling from a high elevation at the top of the falls to a lower elevation. The second picture is a view looking down into the Hoover Dam. Water is shown behind the high wall of the dam on one side and at the base of the dam on the other.

Energy can be converted from one form into another, but all of the energy present before a change occurs always exists in some form after the change is completed. This observation is expressed in the law of conservation of energy: during a chemical or physical change, energy can be neither created nor destroyed, although it can be changed in form. (This is also one version of the first law of thermodynamics, as you will learn later.)

When one substance is converted into another, there is always an associated conversion of one form of energy into another. Heat is usually released or absorbed, but sometimes the conversion involves light, electrical energy, or some other form of energy. For example, chemical energy (a type of potential energy) is stored in the molecules that compose gasoline. When gasoline is combusted within the cylinders of a car's engine, the rapidly expanding gaseous products of this chemical reaction generate mechanical energy (a type of kinetic energy) when they move the cylinders' pistons.

According to the law of conservation of matter (seen in an earlier chapter), there is no detectable change in the total amount of matter during a chemical change. When chemical reactions occur, the energy changes are relatively modest and the mass changes are too small to measure, so the laws of conservation of matter and energy hold well. However, in nuclear reactions, the energy changes are much larger (by factors of a million or so), the mass changes are measurable, and matter-energy conversions are significant. This will be examined in more detail in a later chapter on nuclear chemistry. To encompass both chemical and nuclear changes, we combine these laws into one statement: The total quantity of matter and energy in the universe is fixed.

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 **4.2.3**). 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.

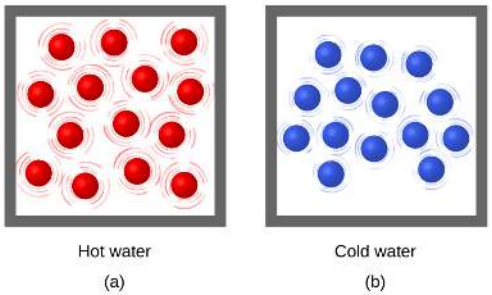
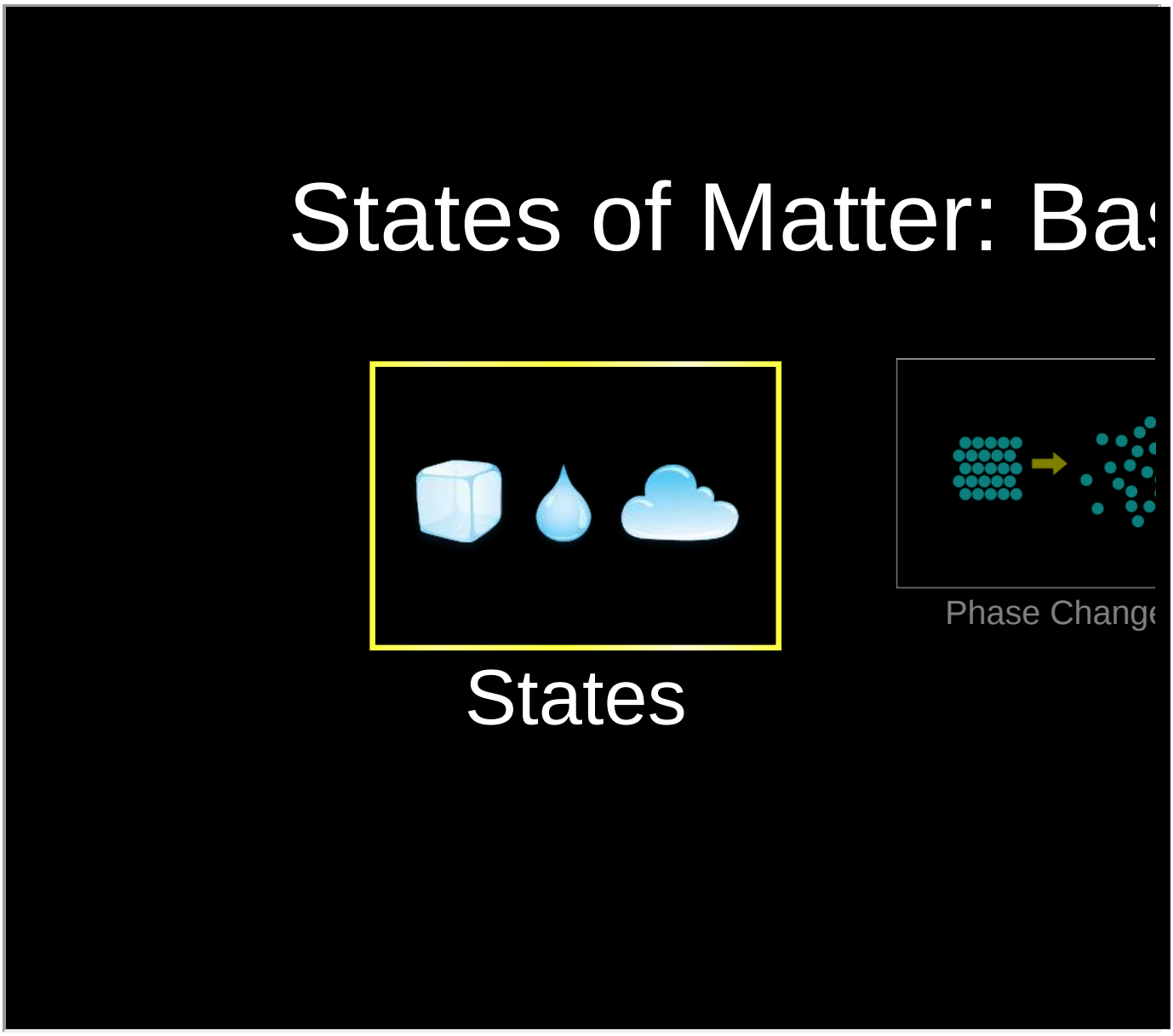


Figure **4.2.3**: (a) The molecules in a sample of hot water move more rapidly than (b) those in a sample of cold water.

Two molecular drawings are shown and labeled a and b. Drawing a is a box containing fourteen red spheres that are surrounded by lines indicating that the particles are moving rapidly. This drawing has a label that reads “Hot water.” Drawing b depicts another box of equal size that also contains fourteen spheres, but these are blue. They are all surrounded by smaller lines that depict some particle motion, but not as much as in drawing a. This drawing has a label that reads “Cold water.”



Measuring Energy and Heat Capacity

Historically, energy was measured in units of calories (cal). A calorie is the amount of energy required to raise one gram of water by 1 degree C (1 kelvin). However, this quantity depends on the atmospheric pressure and the starting temperature of the water. The ease of measurement of energy changes in calories has meant that the calorie is still frequently used. The Calorie (with a capital C), or large calorie, commonly used in quantifying food energy content, is a kilocalorie. The SI unit of heat, work, and energy is the joule. A joule (J) is defined as the amount of energy used when a force of 1 newton moves an object 1 meter. It is named in honor of the English physicist James Prescott Joule. One joule is equivalent to 1 kg m^2/s^2, which is also called 1 newton–meter. A kilojoule (kJ) is 1000 joules. To standardize its definition, 1 calorie has been set to equal 4.184 joules.

We now introduce two concepts useful in describing heat flow and temperature change. The heat capacity (C) of a body of matter is the quantity of heat (q) it absorbs or releases when it experiences a temperature change (ΔT) of 1 degree Celsius (or equivalently, 1 kelvin)

$$C = \frac{q}{\Delta T} \tag{4.2.1}$$

Heat capacity is determined by both the type and amount of substance that absorbs or releases heat. It is therefore an extensive property—its value is proportional to the amount of the substance.

For example, consider the heat capacities of two cast iron frying pans. The heat capacity of the large pan is five times greater than that of the small pan because, although both are made of the same material, the mass of the large pan is five times greater than the mass of the small pan. More mass means more atoms are present in the larger pan, so it takes more energy to make all of those atoms vibrate faster. The heat capacity of the small cast iron frying pan is found by observing that it takes 18,150 J of energy to raise the temperature of the pan by 50.0 °C

$$C_{\text{small pan}} = \frac{18,140 \text{ J}}{50.0 \text{ °C}} = 363 \text{ J/°C} \tag{4.2.2}$$

The larger cast iron frying pan, while made of the same substance, requires 90,700 J of energy to raise its temperature by 50.0 °C. The larger pan has a (proportionally) larger heat capacity because the larger amount of material requires a (proportionally) larger amount of energy to yield the same temperature change:

$$C_{\text{large pan}} = \frac{90,700 \text{ J}}{50.0 \text{ °C}} = 1814 \text{ J/°C} \tag{4.2.3}$$

The specific heat capacity (c) of a substance, commonly called its “specific heat,” is the quantity of heat required to raise the temperature of 1 gram of a substance by 1 degree Celsius (or 1 kelvin):

$$c = \frac{q}{\text{m}\Delta\text{T}} \tag{4.2.4}$$

Specific heat capacity depends only on the kind of substance absorbing or releasing heat. It is an intensive property—the type, but not the amount, of the substance is all that matters. For example, the small cast iron frying pan has a mass of 808 g. The specific heat of iron (the material used to make the pan) is therefore:

$$c_{\text{iron}} = \frac{18,140 \text{ J}}{(808 \text{ g})(50.0 \text{ °C})} = 0.449 \text{ J/g °C} \tag{4.2.5}$$

The large frying pan has a mass of 4040 g. Using the data for this pan, we can also calculate the specific heat of iron:

$$c_{\text{iron}} = \frac{90,700 \text{ J}}{(4,040 \text{ g})(50.0 \text{ °C})} = 0.449 \text{ J/g °C} \tag{4.2.6}$$

Although the large pan is more massive than the small pan, since both are made of the same material, they both yield the same value for specific heat (for the material of construction, iron). Note that specific heat is measured in units of energy per temperature per mass and is an intensive property, being derived from a ratio of two extensive properties (heat and mass). The molar heat capacity, also an intensive property, is the heat capacity per mole of a particular substance and has units of J/mol °C (Figure **4.2.7**).



Figure **4.2.7**: Due to its larger mass, a large frying pan has a larger heat capacity than a small frying pan. Because they are made of the same material, both frying pans have the same specific heat. (credit: Mark Blaser).

The picture shows two black metal frying pans sitting on a flat surface. The left pan is about half the size of the right pan.

Liquid water has a relatively high specific heat (about 4.2 J/g °C); most metals have much lower specific heats (usually less than 1 J/g °C). The specific heat of a substance varies somewhat with temperature. However, this variation is usually small enough that we will treat specific heat as constant over the range of temperatures that will be considered in this chapter. Specific heats of some common substances are listed in Table **4.2.1**.

Table **4.2.1**: Specific Heats of Common Substances at 25 °C and 1 bar

Substance	Symbol (state)	Specific Heat (J/g °C)
helium	$He(g)$	5.193
water	$H_2O(l)$	4.184
ethanol	$C_2H_6O(l)$	2.376
ice	$H_2O(s)$	2.093 (at −10 °C)
water vapor	$H_2O(g)$	1.864
nitrogen	$N_2(g)$	1.040
air		1.007
oxygen	$O_2(g)$	0.918
aluminum	$Al(s)$	0.897
carbon dioxide	$CO_2(g)$	0.853
argon	$Ar(g)$	0.522
iron	$Fe(s)$	0.449
copper	$Cu(s)$	0.385
lead	$Pb(s)$	0.130
gold	$Au(s)$	0.129
silicon	$Si(s)$	0.712

If we know the mass of a substance and its specific heat, we can determine the amount of heat, q, entering or leaving the substance by measuring the temperature change before and after the heat is gained or lost:

$$q = (\text{specific heat}) \times (\text{mass of substance}) \times (\text{temperature change})$$
$$q = c \times m \times \Delta T$$
$$= c \times m \times (T_{\text{final}} - T_{\text{initial}})$$

In this equation, c is the specific heat of the substance, m is its mass, and ΔT (which is read “delta T”) is the temperature change, $T_{\text{final}} - T_{\text{initial}}$. If a substance gains thermal energy, its temperature increases, its final temperature is higher than its initial temperature, $T_{\text{final}} - T_{\text{initial}}$ has a positive value, and the value of q is positive. If a substance loses thermal energy, its temperature decreases, the final temperature is lower than the initial temperature, $T_{\text{final}} - T_{\text{initial}}$ has a negative value, and the value of q is negative.

Example 4.2.1: Measuring Heat

A flask containing 8.0×10^2 g of water is heated, and the temperature of the water increases from 21 °C to 85 °C. How much heat did the water absorb?

Solution

To answer this question, consider these factors:

- the specific heat of the substance being heated (in this case, water)
- the amount of substance being heated (in this case, 800 g)
- the magnitude of the temperature change (in this case, from 21 °C to 85 °C).

The specific heat of water is 4.184 J/g °C, so to heat 1 g of water by 1 °C requires 4.184 J. We note that since 4.184 J is required to heat 1 g of water by 1 °C, we will need 800 times as much to heat 800 g of water by 1 °C. Finally, we observe that since 4.184 J are required to heat 1 g of water by 1 °C, we will need 64 times as much to heat it by 64 °C (that is, from 21 °C to 85 °C).

This can be summarized using the equation:

$$\begin{aligned} q &= c \times m \times \Delta T \\ &= c \times m \times (T_{\text{final}} - T_{\text{initial}}) \\ &= (4.184\ \text{J}/\cancel{\text{g}}^{\circ}\text{C}) \times (800\ \cancel{\text{g}}) \times (85 - 21)^{\circ}\text{C} \\ &= (4.184\ \text{J}/\cancel{\text{g}}^{\circ}\cancel{\text{C}}) \times (800\ \cancel{\text{g}}) \times (64)^{\circ}\cancel{\text{C}} \\ &= 210,000\ \text{J} (= 210\ \text{kJ}) \end{aligned}$$

Because the temperature increased, the water absorbed heat and q is positive.

Exercise 4.2.1

How much heat, in joules, must be added to a 5.00×10^2 g iron skillet to increase its temperature from 25 °C to 250 °C? The specific heat of iron is 0.451 J/g °C.

Answer

5.05×10^4 J

Note that the relationship between heat, specific heat, mass, and temperature change can be used to determine any of these quantities (not just heat) if the other three are known or can be deduced.

Example 4.2.2: Determining Other Quantities

A piece of unknown metal weighs 348 g. When the metal piece absorbs 6.64 kJ of heat, its temperature increases from 22.4 °C to 43.6 °C. Determine the specific heat of this metal (which might provide a clue to its identity).

Solution

Since mass, heat, and temperature change are known for this metal, we can determine its specific heat using the relationship:

$$q = c \times m \times \Delta T$$
$$= c \times m \times (T_{\text{final}} - T_{\text{initial}})$$

Substituting the known values:

$$6,640 \text{ J} = c \times (348 \text{ g}) \times (43.6 - 22.4) \text{ °C}$$

Solving:

$$c = \frac{6,640 \text{ J}}{(348 \text{ g}) \times (21.2 \text{°C})} = 0.900 \text{ J/g °C}$$

Comparing this value with the values in Table 4.2.1, this value matches the specific heat of aluminum, which suggests that the unknown metal may be aluminum.

? Exercise 4.2.2

A piece of unknown metal weighs 217 g. When the metal piece absorbs 1.43 kJ of heat, its temperature increases from 24.5 °C to 39.1 °C. Determine the specific heat of this metal, and predict its identity.

Answer

$c = 0.45 \text{ J/g °C}$; the metal is likely to be iron from checking Table 4.2.1.

Solar Thermal Energy Power Plants

The sunlight that reaches the earth contains thousands of times more energy than we presently capture. Solar thermal systems provide one possible solution to the problem of converting energy from the sun into energy we can use. Large-scale solar thermal plants have different design specifics, but all concentrate sunlight to heat some substance; the heat "stored" in that substance is then converted into electricity.

The Solana Generating Station in Arizona's Sonora Desert produces 280 megawatts of electrical power. It uses parabolic mirrors that focus sunlight on pipes filled with a heat transfer fluid (HTF) (Figure 4.2.8). The HTF then does two things: It turns water into steam, which spins turbines, which in turn produces electricity, and it melts and heats a mixture of salts, which functions as a thermal energy storage system. After the sun goes down, the molten salt mixture can then release enough of its stored heat to produce steam to run the turbines for 6 hours. Molten salts are used because they possess a number of beneficial properties, including high heat capacities and thermal conductivities.

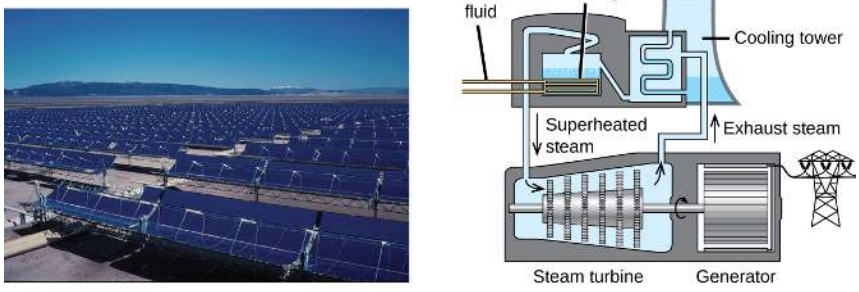


Figure 4.2.8: This solar thermal plant uses parabolic trough mirrors to concentrate sunlight. (credit a: modification of work by Bureau of Land Management)

This figure has two parts labeled a and b. Part a shows rows and rows of trough mirrors. Part b shows how a solar thermal plant works. Heat transfer fluid enters a tank via pipes. The tank contains water which is heated. As the heat is exchanged from the pipes to the water, the water becomes steam. The steam travels to a steam turbine. The steam turbine begins to turn which powers a generator. Exhaust steam exits the steam turbine and enters a cooling tower.

The 377-megawatt Ivanpah Solar Generating System, located in the Mojave Desert in California, is the largest solar thermal power plant in the world (Figure **4.2.9**). Its 170,000 mirrors focus huge amounts of sunlight on three water-filled towers, producing steam at over 538 °C that drives electricity-producing turbines. It produces enough energy to power 140,000 homes. Water is used as the working fluid because of its large heat capacity and heat of vaporization.



(a) (b)

Figure **4.2.9**: (a) The Ivanpah solar thermal plant uses 170,000 mirrors to concentrate sunlight on water-filled towers. (b) It covers 4000 acres of public land near the Mojave Desert and the California-Nevada border. (credit a: modification of work by Craig Dietrich; credit b: modification of work by "USFWS Pacific Southwest Region"/Flickr)

Two pictures are shown and labeled a and b. Picture a shows a thermal plant with three tall metal towers. Picture b is an arial picture of the mirrors used at the plant. They are arranged in rows.

Summary

Energy is the capacity to do work (applying a force to move matter). Kinetic energy (KE) is the energy of motion; potential energy is energy due to relative position, composition, or condition. When energy is converted from one form into another, energy is neither created nor destroyed (law of conservation of energy or first law of thermodynamics). Matter has thermal energy due to the KE of its molecules and temperature that corresponds to the average KE of its molecules. Heat is energy that is transferred between objects at different temperatures; it flows from a high to a low temperature. Chemical and physical processes can absorb heat (endothermic) or release heat (exothermic). The SI unit of energy, heat, and work is the joule (J). Specific heat and heat capacity are measures of the energy needed to change the temperature of a substance or object. The amount of heat absorbed or released by a substance depends directly on the type of substance, its mass, and the temperature change it undergoes.

Key Equations

- $q = c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}})$

Glossary

calorie (cal)

unit of heat or other energy; the amount of energy required to raise 1 gram of water by 1 degree Celsius; 1 cal is defined as 4.184 J

endothermic process

chemical reaction or physical change that absorbs heat

energy

capacity to supply heat or do work

exothermic process

chemical reaction or physical change that releases heat

heat (q)

transfer of thermal energy between two bodies

heat capacity (C)

extensive property of a body of matter that represents the quantity of heat required to increase its temperature by 1 degree Celsius (or 1 kelvin)

joule (J)

SI unit of energy; 1 joule is the kinetic energy of an object with a mass of 2 kilograms moving with a velocity of 1 meter per second, 1 J = 1 kg m^2/s and 4.184 J = 1 cal

kinetic energy

energy of a moving body, in joules, equal to $\frac{1}{2}mv^2$ (where m = mass and v = velocity)

potential energy

energy of a particle or system of particles derived from relative position, composition, or condition

specific heat capacity (*c*)

intensive property of a substance that represents the quantity of heat required to raise the temperature of 1 gram of the substance by 1 degree Celsius (or 1 kelvin)

temperature

intensive property of matter that is a quantitative measure of “hotness” and “coldness”

thermal energy

kinetic energy associated with the random motion of atoms and molecules

thermochemistry

study of measuring the amount of heat absorbed or released during a chemical reaction or a physical change

work (*w*)

energy transfer due to changes in external, macroscopic variables such as pressure and volume; or causing matter to move against an opposing force

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4.3: Enthalpy

Learning Objectives

- State the first law of thermodynamics
- Define enthalpy and explain its classification as a state function
- Write and balance thermochemical equations
- Calculate enthalpy changes for various chemical reactions
- Explain Hess's law and use it to compute reaction enthalpies

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. As we concentrate on thermochemistry in this chapter, we need to consider some widely used concepts of thermodynamics.

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 the internal energy (U), sometimes symbolized as E.

As a system undergoes a change, 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 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.

The relationship between internal energy, heat, and work can be represented by the equation:

$$\Delta U = q + w \tag{4.3.1}$$

as shown in Figure 4.3.1. This is one version of the first law of thermodynamics, and it shows that the internal energy of a system changes through heat flow into or out of the system (positive q is heat flow in; negative q is heat flow out) or work done on or by the system. The work, w, is positive if it is done on the system and negative if it is done by the system.

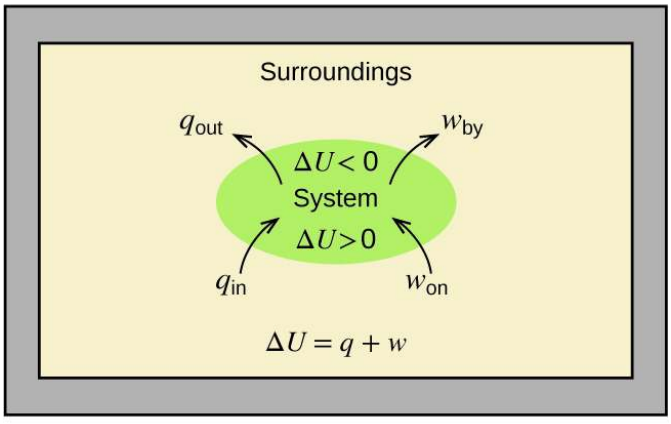


Figure 4.3.1: The internal energy, U, of a system can be changed by heat flow and work. If heat flows into the system, q_{in}, or work is done on the system, w_{on}, its internal energy increases, $\Delta U > 0$. If heat flows out of the system, q_{out}, or work is done by the system, w_{by}, its internal energy decreases, $\Delta U < 0$.

A type of work called expansion work (or pressure-volume work) occurs when a system pushes back the surroundings against a restraining pressure, or when the surroundings compress the system. An example of this occurs during the operation of an internal

combustion engine. The reaction of gasoline and oxygen is exothermic. Some of this energy is given off as heat, and some does work pushing the piston in the cylinder. The substances involved in the reaction are the system, and the engine and the rest of the universe are the surroundings. The system loses energy by both heating and doing work on the surroundings, and its internal energy decreases. (The engine is able to keep the car moving because this process is repeated many times per second while the engine is running.) We will consider how to determine the amount of work involved in a chemical or physical change in the chapter on thermodynamics.

As discussed, the relationship between internal energy, heat, and work can be represented as $\Delta U = q + w$. Internal energy is a type of quantity known as a state function (or state variable), whereas heat and work are not state functions. The value of a state function depends only on the state that a system is in, and not on how that state is reached. If a quantity is not a state function, then its value *does* depend on how the state is reached. An example of a state function is altitude or elevation. If you stand on the summit of Mt. Kilimanjaro, you are at an altitude of 5895 m, and it does not matter whether you hiked there or parachuted there. The distance you traveled to the top of Kilimanjaro, however, is not a state function. You could climb to the summit by a direct route or by a more roundabout, circuitous path (Figure **4.3.2**). The distances traveled would differ (distance is not a state function) but the elevation reached would be the same (altitude is a state function).

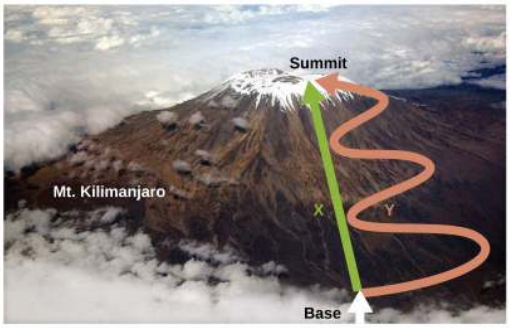


Figure **4.3.2**: Paths X and Y represent two different routes to the summit of Mt. Kilimanjaro. Both have the same change in elevation (altitude or elevation on a mountain is a state function; it does not depend on path), but they have very different distances traveled (distance walked is not a state function; it depends on the path). (credit: modification of work by Paul Shaffner)

An aerial photo depicts a view of Mount Kilimanjaro. A straight, green arrow labeled X is drawn from the term “base,” written at the bottom of the mountain, to the term “Summit,” written at the top of the mountain. Another arrow labeled Y is draw from the base to the summit alongside the green arrow, but this arrow is pink and has three large S-shaped curves along its length.

Chemists ordinarily use a property known as enthalpy (H) to describe the thermodynamics of chemical and physical processes. Enthalpy is defined as the sum of a system’s internal energy (U) and the mathematical product of its pressure (P) and volume (V):

$$H = U + PV \tag{4.3.2}$$

Since it is derived from three state functions (U, P, and V), enthalpy is also a state function. Enthalpy values for specific substances cannot be measured directly; only enthalpy changes for chemical or physical processes can be determined. For processes that take place at constant pressure (a common condition for many chemical and physical changes), the enthalpy change (ΔH) is:

$$\Delta H = \Delta U + P\Delta V \tag{4.3.3}$$

The mathematical product $P\Delta V$ represents work (w), namely, expansion or pressure-volume work as noted. By their definitions, the arithmetic signs of ΔV and w will always be opposite:

$$P\Delta V = -w \tag{4.3.4}$$

Substituting Equation 4.3.4 and the definition of internal energy (Equation 4.3.1) into Equation 4.3.3 yields:

$$\Delta H = \Delta U + P\Delta V \tag{4.3.5}$$
$$= q_p + \cancel{w} - \cancel{w} \tag{4.3.6}$$
$$= q_p \tag{4.3.7}$$

where q_p is the heat of reaction under conditions of constant pressure.

And so, if a chemical or physical process is carried out at constant pressure with the only work done caused by expansion or contraction, then the heat flow (q_p) and enthalpy change (ΔH) for the process are equal.

The heat given off when you operate a Bunsen burner is equal to the enthalpy change of the methane combustion reaction that takes place, since it occurs at the essentially constant pressure of the atmosphere. On the other hand, the heat produced by a reaction measured in a bomb calorimeter is not equal to ΔH because the closed, constant-volume metal container prevents expansion work from occurring. Chemists usually perform experiments under normal atmospheric conditions, at constant external pressure with $q = \Delta H$, which makes enthalpy the most convenient choice for determining heat.

The following conventions apply when we use ΔH:

1. Chemists use a thermochemical equation 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:

$$\mathrm{H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) \longrightarrow H_2O\,(l)} \quad \Delta H = -286\ \mathrm{kJ} \tag{4.3.8}$$

   This equation indicates that when 1 mole of hydrogen gas and 12 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).

Multiple \label

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 12 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 are released.

$$\mathrm{H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) \longrightarrow H_2O\,(g)} \quad \Delta H = -242\ k\,\mathrm{J} \tag{4.3.9}$$

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

Example 4.3.1: Measurement of an Enthalpy Change

When 0.0500 mol of HCl(*aq*) reacts with 0.0500 mol of NaOH(*aq*) to form 0.0500 mol of NaCl(*aq*), 2.9 kJ of heat are produced. What is ΔH, the enthalpy change, per mole of acid reacting, for the acid-base reaction run under the conditions described ?

$$\mathrm{HCl\,(aq) + NaOH\,(aq) \rightarrow NaCl\,(aq) + H_2O\,(l)}$$

Solution

For the reaction of 0.0500 mol acid (HCl), q = −2.9 kJ. This ratio

$$\frac{-2.9\ \mathrm{kJ}}{0.0500\ \mathrm{mol\ HCl}}$$

can be used as a conversion factor to find the heat produced when 1 mole of HCl reacts:

$$\Delta H = 1\ \cancel{\mathrm{mol\ HCl}} \times \frac{-2.9\ \mathrm{kJ}}{0.0500\ \cancel{\mathrm{mol\ HCl}}} = -58\ \mathrm{kJ}$$

The enthalpy change when 1 mole of HCl reacts is −58 kJ. Since that is the number of moles in the chemical equation, we write the thermochemical equation as:

$$HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)} \quad \Delta H = -58\ kJ$$

? Exercise 4.3.1

When 1.34 g Zn(s) reacts with 60.0 mL of 0.750 M HCl(aq), 3.14 kJ of heat are produced. Determine the enthalpy change per mole of zinc reacting for the reaction:

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

Answer

ΔH = −153 kJ

Be sure to take both stoichiometry and limiting reactants into account when determining the Δ*H* for a chemical reaction.

✓ Example 4.3.2: Another Example of the Measurement of an Enthalpy Change

A gummy bear contains 2.67 g sucrose, $C_{12}H_{22}O_{11}$. When it reacts with 7.19 g potassium chlorate, $KClO_3$, 43.7 kJ of heat are produced. Determine the enthalpy change for the reaction

$$C_{12}H_{22}O_{11}(aq) + 8\,KClO_3(aq) \longrightarrow 12\,CO_2(g) + 11\,H_2O(l) + 8\,KCl(aq)$$

Solution

We have $2.67\ \cancel{g} \times \dfrac{1\ mol}{342.3\ \cancel{g}} = 0.00780\ mol\ C_{12}H_{22}O_{11}$ available, and

$7.19\ \cancel{g} \times \dfrac{1\ mol}{122.5\ \cancel{g}} = 0.0587\ mol\ KClO_3$ available.

Since

$$0.0587\ mol\ KClO_3 \times \frac{1\ mol\ C_{12}H_{22}O_{11}}{8\ mol\ KClO_3} = 0.00734\ mol\ C_{12}H_{22}O_{11}$$

is needed, $C_{12}H_{22}O_{11}$ is the excess reactant and $KClO_3$ is the limiting reactant.

The reaction uses 8 mol $KClO_3$, and the conversion factor is $\dfrac{-43.7\ kJ}{0.0587\ mol\ KClO_3}$, so we have $\Delta H = 8\ mol \times \dfrac{-43.7\ kJ}{0.0587\ mol\ KClO_3} = -5960\ kJ$. The enthalpy change for this reaction is −5960 kJ, and the thermochemical equation is:

$$C_{12}H_{22}O_{11} + 8\,KClO_3 \longrightarrow 12\,CO_2 + 11\,H_2O + 8\,KCl \quad \Delta H = -5960\ kJ$$

? Exercise 4.3.2

When 1.42 g of iron reacts with 1.80 g of chlorine, 3.22 g of $FeCl_{2(s)}$ and 8.60 kJ of heat is produced. What is the enthalpy change for the reaction when 1 mole of $FeCl_2\,(s)$ is produced?

Answer

ΔH = −338 kJ

Enthalpy changes are typically tabulated for reactions in which both the reactants and products are at 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 different conditions. For chemists, the IUPAC standard state refers to materials under a pressure of 1 bar and solutions at 1 M, and **does not specify a temperature** (it used too). Many thermochemical tables list values with a standard state of 1 atm. Because the Δ*H* of a reaction changes very little with such small changes in pressure (1 bar = 0.987 atm), Δ*H* 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 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°_{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.)

The enthalpy changes for many types of chemical and physical processes are available in the reference literature, including those for combustion reactions, phase transitions, and formation reactions. As we discuss these quantities, it is important to pay attention to the *extensive* nature of enthalpy and enthalpy changes. Since the enthalpy change for a given reaction is proportional to the amounts of substances involved, it may be reported on that basis (i.e., as the ΔH for specific amounts of reactants). However, we often find it more useful to divide one extensive property (ΔH) by another (amount of substance), and report a per-amount *intensive* value of ΔH, often "normalized" to a per-mole basis. (Note that this is similar to determining the intensive property specific heat from the extensive property heat capacity, as seen previously.)

Enthalpy of Combustion

Standard enthalpy of combustion (ΔH°_C) 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.

$$\mathrm{C_2H_5OH}(l) + 3\,\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{CO_2} + 3\,\mathrm{H_2O}(l) \quad \Delta H^\circ_{298} = -1366.8\ \mathrm{kJ} \tag{4.3.10}$$

Enthalpies of combustion for many substances have been measured; a few of these are listed in Table **4.3.1**. 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.

Table **4.3.1**: Standard Molar Enthalpies of Combustion

Substance	Combustion Reaction	Enthalpy of Combustion $\Delta H^\circ_c \left(\frac{\mathrm{kJ}}{\mathrm{mol}}\ \text{at}\ 25°\mathrm{C}\right)$
carbon	$\mathrm{C}(s) + \mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g)$	−393.5
hydrogen	$\mathrm{H_2}(g) + \frac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{H_2O}(l)$	−285.8
magnesium	$\mathrm{Mg}(s) + \frac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{MgO}(s)$	−601.6
sulfur	$\mathrm{S}(s) + \mathrm{O_2}(g) \longrightarrow \mathrm{SO_2}(g)$	−296.8
carbon monoxide	$\mathrm{CO}(g) + \frac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g)$	−283.0
methane	$\mathrm{CH_4}(g) + 2\,\mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) + 2\,\mathrm{H_2O}(l)$	−890.8
acetylene	$\mathrm{C_2H_2}(g) + \frac{5}{2}\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{CO_2}(g) + \mathrm{H_2O}(l)$	−1301.1
ethanol	$\mathrm{C_2H_5OH}(l) + 3\,\mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) + 3\,\mathrm{H_2O}(l)$	−1366.8
methanol	$\mathrm{CH_3OH}(l) + \frac{3}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) + 2\,\mathrm{H_2O}(l)$	−726.1
isooctane	$\mathrm{C_8H_{18}}(l) + \frac{25}{2}\mathrm{O_2}(g) \longrightarrow 8\,\mathrm{CO_2}(g) + 9\,\mathrm{H_2O}(l)$	−5461

Example 4.3.3: Using Enthalpy of Combustion

As Figure **4.3.3** suggests, the combustion of gasoline is a highly exothermic process. Let us determine the approximate amount of heat produced by burning 1.00 L of gasoline, assuming the enthalpy of combustion of gasoline is the same as that of isooctane, a common component of gasoline. The density of isooctane is 0.692 g/mL.



Figure 4.3.3: The combustion of gasoline is very exothermic. (credit: modification of work by “AlexEagle”/Flickr)

Solution

Starting with a known amount (1.00 L of isooctane), we can perform conversions between units until we arrive at the desired amount of heat or energy. The enthalpy of combustion of isooctane provides one of the necessary conversions. Table 4.3.1 gives this value as −5460 kJ per 1 mole of isooctane (C_8H_{18}).

Using these data,

$$1.00\ \cancel{\text{L } C_8H_{18}} \times \frac{1000\ \cancel{\text{mL } C_8H_{18}}}{1\ \cancel{\text{L } C_8H_{18}}} \times \frac{0.692\ \cancel{\text{g } C_8H_{18}}}{1\ \cancel{\text{mL } C_8H_{18}}} \times \frac{1\ \cancel{\text{mol } C_8H_{18}}}{114\ \cancel{\text{g } C_8H_{18}}} \times \frac{-5460\ \text{kJ}}{1\ \cancel{\text{mol } C_8H_{18}}}$$
$$= -3.31 \times 10^4\ \text{kJ}$$

The combustion of 1.00 L of isooctane produces 33,100 kJ of heat. (This amount of energy is enough to melt 99.2 kg, or about 218 lbs, of ice.)

Note: If you do this calculation one step at a time, you would find:

$$1.00\ \text{L } C_8H_{18} \longrightarrow 1.00 \times 10^3\ \text{mL } C_8H_{18}$$
$$1.00 \times 10^3\ \text{mL } C_8H_{18} \longrightarrow 692\ \text{g } C_8H_{18}$$
$$692\ \text{g } C_8H_{18} \longrightarrow 6.07\ \text{mol } C_8H_{18}$$
$$692\ \text{g } C_8H_{18} \longrightarrow -3.31 \times 10^4\ \text{kJ}$$

? Exercise 4.3.3

How much heat is produced by the combustion of 125 g of acetylene?

Answer

6.25×10^3 kJ

Emerging Algae-Based Energy Technologies (Biofuels)

As reserves of fossil fuels diminish and become more costly to extract, the search is ongoing for replacement fuel sources for the future. Among the most promising biofuels are those derived from algae (Figure 4.3.4). The species of algae used are nontoxic, biodegradable, and among the world’s fastest growing organisms. About 50% of algal weight is oil, which can be readily converted into fuel such as biodiesel. Algae can yield 26,000 gallons of biofuel per hectare—much more energy per acre than other crops. Some strains of algae can flourish in brackish water that is not usable for growing other crops. Algae can produce biodiesel, biogasoline, ethanol, butanol, methane, and even jet fuel.



Figure **4.3.4**: (a) Tiny algal organisms can be (b) grown in large quantities and eventually (c) turned into a useful fuel such as biodiesel. (credit a: modification of work by Micah Sittig; credit b: modification of work by Robert Kerton; credit c: modification of work by John F. Williams)

According to the US Department of Energy, only 39,000 square kilometers (about 0.4% of the land mass of the US or less than $\frac{1}{7}$ of the area used to grow corn) can produce enough algal fuel to replace all the petroleum-based fuel used in the US. The cost of algal fuels is becoming more competitive—for instance, the US Air Force is producing jet fuel from algae at a total cost of under $5 per gallon. The process used to produce algal fuel is as follows: grow the algae (which use sunlight as their energy source and CO_2 as a raw material); harvest the algae; extract the fuel compounds (or precursor compounds); process as necessary (e.g., perform a transesterification reaction to make biodiesel); purify; and distribute (Figure **4.3.5**).



Figure **4.3.5**: Algae convert sunlight and carbon dioxide into oil that is harvested, extracted, purified, and transformed into a variety of renewable fuels.

Standard Enthalpy of Formation

A standard enthalpy of formation ΔH_f° is an 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.

The standard enthalpy of formation of $CO_2(g)$ is −393.5 kJ/mol. This is the enthalpy change for the exothermic reaction:

$$\mathrm{C}(s) + \mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) \quad \Delta H_f^\circ = \Delta H_{298}^\circ = -393.5\ k\mathrm{J} \tag{4.3.11}$$

starting with the reactants at a pressure of 1 atm and 25 °C (with the carbon present as graphite, the most stable form of carbon under these conditions) and ending with one mole of CO_2, also at 1 atm and 25 °C. For nitrogen dioxide, $\mathrm{NO_{2(g)}}$, ΔH_f° is 33.2 kJ/mol. This is the enthalpy change for the reaction:

$$\frac{1}{2}\mathrm{N_2}(g) + \mathrm{O_2}(g) \longrightarrow \mathrm{NO_2}(g) \quad \Delta H_f^\circ = \Delta H_{298}^\circ = +33.2\ k\mathrm{J} \tag{4.3.12}$$

A reaction equation with $\frac{1}{2}$ mole of N_2 and 1 mole of O_2 is correct in this case because the standard enthalpy of formation always refers to 1 mole of product, $NO_2(g)$.

You will find a table of standard enthalpies of formation of many common substances in Tables T1 and T2. These values indicate that formation reactions range from highly exothermic (such as −2984 kJ/mol for the formation of P_4O_{10}) to strongly endothermic (such as +226.7 kJ/mol for the formation of acetylene, C_2H_2). By definition, the standard enthalpy of formation of an element in its most stable form is equal to zero under standard conditions, which is 1 atm for gases and 1 M for solutions.

Example 4.3.4: Evaluating an Enthalpy of Formation

Ozone, $O_3(g)$, forms from oxygen, $O_2(g)$, by an endothermic process. Ultraviolet radiation is the source of the energy that drives this reaction in the upper atmosphere. Assuming that both the reactants and products of the reaction are in their standard states, determine the standard enthalpy of formation, ΔH_f° of ozone from the following information:

$$3\,O_2(g) \longrightarrow 2\,O_3(g) \quad \Delta H_{298}^\circ = +286\ k\,J$$

Solution ΔH_f° is the enthalpy change for the formation of one mole of a substance in its standard state from the elements in their standard states. Thus, ΔH_f° for $O_3(g)$ is the enthalpy change for the reaction:

$$\frac{3}{2}O_2(g) \longrightarrow O_3(g)$$

For the formation of 2 mol of $O_3(g)$, $\Delta H_{298}^\circ = +286\ k\,J$. This ratio, $\left(\frac{286\ kJ}{2\ mol\ O_3}\right)$, can be used as a conversion factor to find the heat produced when 1 mole of $O_3(g)$ is formed, which is the enthalpy of formation for $O_3(g)$:

$$\Delta H^\circ \text{ for 1 mole of } O_3(g) = 1\ \cancel{mol\ O_3} \times \frac{286\ kJ}{2\ \cancel{mol\ O_3}} = 143\ kJ$$

Therefore, $\Delta H_f^\circ[O_3(g)] = +143\ \ k\,J/mol$.

Exercise 4.3.4

Hydrogen gas, H_2, reacts explosively with gaseous chlorine, Cl_2, to form hydrogen chloride, $HCl(g)$. What is the enthalpy change for the reaction of 1 mole of $H_2(g)$ with 1 mole of $Cl_2(g)$ if both the reactants and products are at standard state conditions? The standard enthalpy of formation of $HCl(g)$ is −92.3 kJ/mol.

Answer

For the reaction

$$H_2(g) + Cl_2(g) \longrightarrow 2\,HCl(g) \quad \Delta H_{298}^\circ = -184.6\ kJ$$

Example 4.3.5: Writing Reaction Equations for ΔH_f°

Write the heat of formation reaction equations for:

a. $C_2H_5OH_{(l)}$
b. $Ca_3(PO_4)_{2(s)}$

Solution

Remembering that ΔH_f° reaction equations are for forming 1 mole of the compound from its constituent elements under standard conditions, we have:

a. $2\,C(s,\ \text{graphite}) + 3\,H_2(g) + \frac{1}{2}O_2(g) \longrightarrow C_2H_5OH(l)$
b. $3\,Ca(s) + \frac{1}{2}P_4(s) + 4\,O_2(g) \longrightarrow Ca_3(PO_4)_2(s)$

Note: The standard state of carbon is graphite, and phosphorus exists as P_4.

Exercise 4.3.5

Write the heat of formation reaction equations for:

a. $C_2H_5OC_2H_{5(l)}$
b. $Na_2CO_{3(s)}$

Answer a

$4\,C(s,\ \text{graphite}) + 5\,H_2(g) + \frac{1}{2}O_2(g) \longrightarrow C_2H_5OC_2H_5(l)$;

Answer b

$$2\,Na(s) + C(s,\ \text{graphite}) + \frac{3}{2}O_2(g) \longrightarrow Na_2CO_3(s)$$

Hess's Law

There are two ways to determine the amount of heat involved in a chemical change: measure it experimentally, or calculate it from other experimentally determined enthalpy changes. Some reactions are difficult, if not impossible, to investigate and make accurate measurements for experimentally. And even when a reaction is not hard to perform or measure, it is convenient to be able to determine the heat involved in a reaction without having to perform an experiment.

This type of calculation usually involves the use of 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. For example, we can think 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:

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \quad \Delta H^\circ_{298} = -394\ \text{kJ} \tag{4.3.13}$$

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

$$C_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{(g)} \quad \Delta H^\circ_{298} = -111\ \text{kJ} \tag{4.3.14}$$

Then, carbon monoxide reacts further to form carbon dioxide:

$$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g) \quad \Delta H^\circ_{298} = -283\ \text{kJ} \tag{4.3.15}$$

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

$$\begin{aligned}
&\text{Step 1: } C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)\\
&\underline{\text{Step 2: } CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)}\\
&\text{Sum: } C(s) + \frac{1}{2}O_2(g) + CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO(g) + CO_2(g)
\end{aligned}$$

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

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \tag{4.3.16}$$

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 **4.3.1** to find the enthalpy change of the entire reaction from its two steps:

$$\begin{aligned}
&C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g) && \Delta H^\circ_{298} = -111\ \text{kJ}\\
&\underline{CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)} && \underline{\Delta H^\circ_{298} = -283\ \text{kJ}}\\
&C(s) + O_2(g) \longrightarrow CO_2(g) && \Delta H^\circ_{298} = -394\ \text{kJ}
\end{aligned}$$

The result is shown in Figure **4.3.6**. We see that 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.

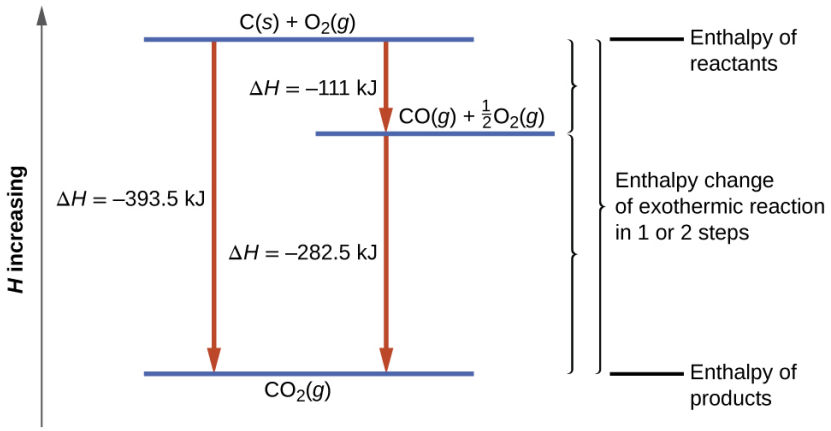


Figure **4.3.6**: The formation of CO_2(g) from its elements can be thought of as occurring in two steps, which sum to the overall reaction, as described by Hess's law. The horizontal blue lines represent enthalpies. For an exothermic process, the products are at lower enthalpy than are the reactants.

Before we further practice using Hess's law, let us recall two important features of ΔH.

1. ΔH is directly proportional to the quantities of reactants or products. For example, the enthalpy change for the reaction forming 1 mole of $NO_2(g)$ is +33.2 kJ:

$$\frac{1}{2}\mathrm{N_2}(g) + \mathrm{O_2}(g) \longrightarrow \mathrm{NO_2}(g) \quad \Delta H = +33.2\,\mathrm{kJ} \tag{4.3.17}$$

   When 2 moles of NO_2 (twice as much) are formed, the ΔH will be twice as large:

$$\mathrm{N_2}(g) + 2\,\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{NO_2}(g) \quad \Delta H = +66.4\,\mathrm{kJ} \tag{4.3.18}$$

   In general, if we multiply or divide an equation by a number, then the enthalpy change should also be multiplied or divided by the same number.

2. ΔH for a reaction in one direction is equal in magnitude and opposite in sign to ΔH for the reaction in the reverse direction. For example, given that:

$$\mathrm{H_2}(g) + \mathrm{Cl_2}(g) \longrightarrow 2\,\mathrm{HCl}(g) \quad \Delta H = -184.6\,\mathrm{kJ} \tag{4.3.19}$$

   Then, for the "reverse" reaction, the enthalpy change is also "reversed":

$$2\,\mathrm{HCl}(g) \longrightarrow \mathrm{H_2}(g) + \mathrm{Cl_2}(g) \quad \Delta H = +184.6\,\mathrm{kJ} \tag{4.3.20}$$

Example 4.3.6: Stepwise Calculation of ΔH_f°

Using Hess's Law Determine the enthalpy of formation, ΔH_f°, of $FeCl_3$(s) from the enthalpy changes of the following two-step process that occurs under standard state conditions:

$$\mathrm{Fe}(s) + \mathrm{Cl_2}(g) \longrightarrow \mathrm{FeCl_2}(s) \quad \Delta H^\circ = -341.8\,\mathrm{kJ}$$

$$\mathrm{FeCl_2}(s) + \frac{1}{2}\mathrm{Cl_2}(g) \longrightarrow \mathrm{FeCl_3}(s) \quad \Delta H^\circ = -57.7\,kJ$$

Solution

We are trying to find the standard enthalpy of formation of FeCl3(s), which is equal to ΔH° for the reaction:

$$\mathrm{Fe}(s) + \frac{3}{2}\mathrm{Cl_2}(g) \longrightarrow \mathrm{FeCl_3}(s) \quad \Delta H_f^\circ = ?$$

Looking at the reactions, we see that the reaction for which we want to find ΔH° is the sum of the two reactions with known ΔH values, so we must sum their ΔHs:

$$\begin{aligned}
&\mathrm{Fe}(s) + \mathrm{Cl_2}(g) \longrightarrow \mathrm{FeCl_2}(s) \qquad \Delta H° = -341.8\ \mathrm{kJ}\\
&\mathrm{FeCl_2}(s) + \frac{1}{2}\mathrm{Cl_2}(g) \longrightarrow \mathrm{FeCl_3}(s) \qquad \Delta H° = -57.7\ \mathrm{kJ}\\
&\overline{\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad}\\
&\mathrm{Fe}(s) + \frac{1}{2}\mathrm{Cl_2}(g) \longrightarrow \mathrm{FeCl_3}(s) \qquad \Delta H° = -399.5\ \mathrm{kJ}
\end{aligned}$$

The enthalpy of formation, ΔH_f°, of $FeCl_3$(s) is −399.5 kJ/mol.

? Exercise 4.3.6

Calculate ΔH for the process:

$$\mathrm{N_2}(g) + 2\,\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{NO_2}(g)$$

from the following information:

$$\mathrm{N_2}(g) + \mathrm{O_2}(g) \longrightarrow 2\,\mathrm{NO}(g) \quad \Delta H = 180.5\ \mathrm{kJ}$$

$$\mathrm{NO}(g) + \frac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{NO_2}(g) \quad \Delta H = -57.06\ \mathrm{kJ}$$

Answer

66.4 kJ

Here is a less straightforward example that illustrates the thought process involved in solving many Hess's law problems. It shows how we can find many standard enthalpies of formation (and other values of Δ*H*) if they are difficult to determine experimentally.

✓ Example 4.3.7: A More Challenging Problem

Using Hess's Law Chlorine monofluoride can react with fluorine to form chlorine trifluoride:

$$\text{(i)}\ \mathrm{ClF}(g) + \mathrm{F_2}(g) \longrightarrow \mathrm{ClF_3}(g) \quad \Delta H° = ?$$

Use the reactions here to determine the ΔH° for reaction (i):

$$\text{(ii)}\ 2\,\mathrm{OF_2}(g) \longrightarrow \mathrm{O_2}(g) + 2\,\mathrm{F_2}(g) \quad \Delta H^\circ_{(ii)} = -49.4\ \mathrm{kJ}$$

$$\text{(iii)}\ 2\,\mathrm{ClF}(g) + \mathrm{O_2}(g) \longrightarrow \mathrm{Cl_2O}(g) + \mathrm{OF_2}(g) \quad \Delta H^\circ_{(iii)} = +205.6\ \mathrm{kJ}$$

$$\text{(iv)}\ \mathrm{ClF_3}(g) + \mathrm{O_2}(g) \longrightarrow \tfrac{1}{2}\mathrm{Cl_2O}(g) + \frac{3}{2}\mathrm{OF_2}(g) \quad \Delta H^\circ_{(iv)} = +266.7\ \mathrm{kJ}$$

Solution

Our goal is to manipulate and combine reactions (ii), (iii), and (iv) such that they add up to reaction (i). Going from left to right in (i), we first see that $\mathrm{ClF}_{(g)}$ is needed as a reactant. This can be obtained by multiplying reaction (iii) by $\frac{1}{2}$, which means that the ΔH° change is also multiplied by $\frac{1}{2}$:

$$\mathrm{ClF}(g) + \frac{1}{2}\mathrm{O_2}(g) \longrightarrow \frac{1}{2}\mathrm{Cl_2O}(g) + \frac{1}{2}\mathrm{OF_2}(g) \quad \Delta H° = \frac{1}{2}(205.6) = +102.8\ k\,\mathrm{J}$$

Next, we see that $\mathrm{F_2}$ is also needed as a reactant. To get this, reverse and halve reaction (ii), which means that the ΔH° changes sign and is halved:

$$\frac{1}{2}\mathrm{O_2}(g) + \mathrm{F_2}(g) \longrightarrow \mathrm{OF_2}(g) \quad \Delta H° = +24.7\ k\,\mathrm{J}$$

To get ClF_3 as a product, reverse (iv), changing the sign of ΔH°:

$$\frac{1}{2}\mathrm{Cl_2O}(g) + \frac{3}{2}\mathrm{OF_2}(g) \longrightarrow \mathrm{ClF_3}(g) + \mathrm{O_2}(g) \quad \Delta H° = -266.7\ \mathrm{kJ}$$

Now check to make sure that these reactions add up to the reaction we want:

$$\begin{aligned}
&\mathrm{ClF}(g) + \frac{1}{2}\mathrm{O_2}(g) \longrightarrow \frac{1}{2}\mathrm{Cl_2O}(g) + \frac{1}{2}\mathrm{OF_2}(g) && \Delta H^\circ = +102.8\ \mathrm{kJ}\\
&\frac{1}{2}\mathrm{O_2}(g) + \mathrm{F_2}(g) \longrightarrow \mathrm{OF_2}(g) && \Delta H^\circ = +24.7\ \mathrm{kJ}\\
&\frac{1}{2}\mathrm{Cl_2O}(g) + \frac{3}{2}\mathrm{OF_2}(g) \longrightarrow \mathrm{ClF_3}(g) + \mathrm{O_2}(g) && \Delta H^\circ = -266.7\ \mathrm{kJ}\\
&\overline{\mathrm{ClF}(g) + \mathrm{F_2} \longrightarrow \mathrm{ClF_3}(g)} && \overline{\Delta H^\circ = -139.2\ \mathrm{kJ}}
\end{aligned}$$

Reactants $\frac{1}{2}\mathrm{O_2}$ and $\frac{1}{2}\mathrm{O_2}$ cancel out product O_2; product $\frac{1}{2}\mathrm{Cl_2O}$ cancels reactant $\frac{1}{2}\mathrm{Cl_2O}$; and reactant $\frac{3}{2}\mathrm{OF_2}$ is cancelled by products $\frac{1}{2}\mathrm{OF_2}$ and OF_2. This leaves only reactants ClF(g) and F_2(g) and product ClF_3(g), which are what we want. Since summing these three modified reactions yields the reaction of interest, summing the three modified ΔH° values will give the desired ΔH°:

$$\Delta H^\circ = (+102.8\ \mathrm{kJ}) + (24.7\ \mathrm{kJ}) + (-266.7\ \mathrm{kJ}) = -139.2\ \mathrm{kJ}$$

? Exercise 4.3.7

Aluminum chloride can be formed from its elements:

$$\text{(i)}\ 2\,\mathrm{Al}(s) + 3\,\mathrm{Cl_2}(g) \longrightarrow 2\,\mathrm{AlCl_3}(s) \quad \Delta H^\circ = ?$$

Use the reactions here to determine the ΔH° for reaction (i):

$$\text{(ii)}\ \mathrm{HCl}(g) \longrightarrow \mathrm{HCl}(aq) \quad \Delta H^\circ_{(ii)} = -74.8\ \mathrm{kJ}$$

$$\text{(iii)}\ \mathrm{H_2}(g) + \mathrm{Cl_2}(g) \longrightarrow 2\,\mathrm{HCl}(g) \quad \Delta H^\circ_{(iii)} = -185\ \mathrm{kJ}$$

$$\text{(iv)}\ \mathrm{AlCl_3}(aq) \longrightarrow \mathrm{AlCl_3}(s) \quad \Delta H^\circ_{(iv)} = +323\ \mathrm{kJ/mol}$$

$$\text{(v)}\ 2\,\mathrm{Al}(s) + 6\,\mathrm{HCl}(aq) \longrightarrow 2\,\mathrm{AlCl_3}(aq) + 3\,\mathrm{H_2}(g) \quad \Delta H^\circ_{(v)} = -1049\ \mathrm{kJ}$$

Answer

−1407 kJ

We also can use Hess's law to determine the enthalpy change of any reaction if the corresponding enthalpies of formation of the reactants and products are available. The stepwise reactions we consider are: (i) decompositions of the reactants into their component elements (for which the enthalpy changes are proportional to the negative of the enthalpies of formation of the reactants), followed by (ii) re-combinations of the elements to give the products (with the enthalpy changes proportional to the enthalpies of formation of the products). The standard enthalpy change of the overall reaction is therefore equal to: (ii) the sum of the standard enthalpies of formation of all the products plus (i) the sum of the negatives of the standard enthalpies of formation of the reactants. This is usually rearranged slightly to be written as follows, with $\sum$ representing "the sum of" and n standing for the stoichiometric coefficients:

$$\Delta H^\circ_{\text{reaction}} = \sum n \times \Delta H^\circ_f(\text{products}) - \sum n \times \Delta H^\circ_f(\text{reactants}) \tag{4.3.21}$$

The following example shows in detail why this equation is valid, and how to use it to calculate the enthalpy change for a reaction of interest.

✓ Example 4.3.8: Using Hess's Law

What is the standard enthalpy change for the reaction:

$$3\,\mathrm{NO_2}(g) + \mathrm{H_2O}(l) \longrightarrow 2\,\mathrm{HNO_3}(aq) + \mathrm{NO}(g) \quad \Delta H^\circ = ?$$

Solution 1: Using the Equation

Alternatively, we could use the special form of Hess's law given previously:

$$\Delta H^\circ_{\text{reaction}} = \sum n \times \Delta H^\circ_f(\text{products}) - \sum n \times \Delta H^\circ_f(\text{reactants})$$

$$= \left[2 \cancel{\text{ mol HNO}_3} \times \frac{-207.4\text{ kJ}}{\cancel{\text{mol HNO}_3\,(aq)}} + 1 \cancel{\text{ mol NO}\,(g)} \times \frac{+90.2\text{ kJ}}{\cancel{\text{mol NO}\,(g)}}\right]$$
$$- \left[3 \cancel{\text{ mol NO}_2(g)} \times \frac{+33.2\text{ kJ}}{\cancel{\text{mol NO}_2\,(g)}} + 1 \cancel{\text{ mol H}_2\text{O}\,(l)} \times \frac{-285.8\text{ kJ}}{\cancel{\text{mol H}_2\text{O}\,(l)}}\right]$$
$$= 2(-207.4\text{ kJ}) + 1(+90.2\text{ kJ}) - 3(+33.2\text{ kJ}) - 1(-285.8\text{ kJ})$$
$$= -138.4\text{ kJ}$$

Solution 2: Supporting Why the General Equation Is Valid

We can write this reaction as the sum of the decompositions of $3NO_2(g)$ and $1H_2O(l)$ into their constituent elements, and the formation of 2 $HNO_3(aq)$ and 1 $NO(g)$ from their constituent elements. Writing out these reactions, and noting their relationships to the ΔH_f° values for these compounds (from Tables T1 and T2), we have:

$$3\,NO_2(g) \longrightarrow \frac{3}{2}N_2(g) + 3O_2(g) \quad \Delta H_1^\circ = -99.6\text{ kJ}$$

$$H_2O(l) \longrightarrow H_2(g) + \frac{1}{2}O_2(g) \quad \Delta H_2^\circ = +285.8\,kJ\,[-1 \times \Delta H_f^\circ(H_2O)]$$

$$H_2(g) + N_2(g) + 3O_2(g) \longrightarrow 2\,HNO_3(aq) \quad \Delta H_3^\circ = -414.8\,kJ\,[2 \times \Delta H_f^\circ(HNO_3)]$$

$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \longrightarrow NO(g) \quad \Delta H_4^\circ = +90.2\,kJ\,[1 \times (NO)]$$

Summing these reaction equations gives the reaction we are interested in:

$$3\,NO_2(g) + H_2O(l) \longrightarrow 2\,HNO_3(aq) + NO(g)$$

Summing their enthalpy changes gives the value we want to determine:

$$\Delta H_{rxn}^\circ = \Delta H_1^\circ + \Delta H_2^\circ + \Delta H_3^\circ + \Delta H_4^\circ = (-99.6\text{ kJ}) + (+285.8\text{ kJ}) + (-414.8\text{ kJ}) + (+90.2\text{ kJ})$$
$$= -138.4\text{ kJ}$$

So the standard enthalpy change for this reaction is $\Delta H^\circ = -138.4$ kJ.

Note that this result was obtained by:

1. multiplying the ΔH_f° of each product by its stoichiometric coefficient and summing those values,
2. multiplying the ΔH_f° of each reactant by its stoichiometric coefficient and summing those values, and then
3. subtracting the result found in step 2 from the result found in step 1.

This is also the procedure in using the general equation, as shown.

? Exercise 4.3.8

Calculate the heat of combustion of 1 mole of ethanol, $C_2H_5OH(l)$, when $H_2O(l)$ and $CO_2(g)$ are formed. Use the following enthalpies of formation: $C_2H_5OH(l)$, −278 kJ/mol; $H_2O(l)$, −286 kJ/mol; and $CO_2(g)$, −394 kJ/mol.

Answer

−1368 kJ/mol

Summary

If a chemical change is carried out at constant pressure and the only work done is caused by expansion or contraction, q for the change is called the enthalpy change with the symbol ΔH, or ΔH_{298}° for reactions occurring under standard state conditions. The value of ΔH for a reaction in one direction is equal in magnitude, but opposite in sign, to ΔH for the reaction in the opposite direction, and ΔH is directly proportional to the quantity of reactants and products. Examples of enthalpy changes include enthalpy of combustion, enthalpy of fusion, enthalpy of vaporization, and standard enthalpy of formation. The standard enthalpy of formation, ΔH_f°, is the enthalpy change accompanying the formation of 1 mole of a substance from the elements in their most stable states at 1 bar (standard state). Many of the processes are carried out at 298.15 K. If the enthalpies of formation are available

for the reactants and products of a reaction, the enthalpy change can be calculated using Hess's law: 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.

Key Equations

- $\Delta U = q + w$
- $\Delta H^\circ_{\text{reaction}} = \sum n \times \Delta H^\circ_f(\text{products}) - \sum n \times \Delta H^\circ_f(\text{reactants})$

Footnotes

1. 1 For more on algal fuel, see www.theguardian.com/environme...n-fuel-problem.

Glossary

chemical thermodynamics
area of science that deals with the relationships between heat, work, and all forms of energy associated with chemical and physical processes

enthalpy (H)
sum of a system's internal energy and the mathematical product of its pressure and volume

enthalpy change (ΔH)
heat released or absorbed by a system under constant pressure during a chemical or physical process

expansion work (pressure-volume work)
work done as a system expands or contracts against external pressure

first law of thermodynamics
internal energy of a system changes due to heat flow in or out of the system or work done on or by the system

Hess's law
if a process can be represented as the sum of several steps, the enthalpy change of the process equals the sum of the enthalpy changes of the steps

hydrocarbon
compound composed only of hydrogen and carbon; the major component of fossil fuels

internal energy (U)
total of all possible kinds of energy present in a substance or substances

standard enthalpy of combustion (ΔH°_c)
heat released when one mole of a compound undergoes complete combustion under standard conditions

standard enthalpy of formation (ΔH°_f)
enthalpy change of a chemical reaction in which 1 mole of a pure substance is formed from its elements in their most stable states under standard state conditions

standard state
set of physical conditions as accepted as common reference conditions for reporting thermodynamic properties; 1 bar of pressure, and solutions at 1 molar concentrations, usually at a temperature of 298.15 K

state function
property depending only on the state of a system, and not the path taken to reach that state

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4.E: Thermochemistry (Exercises)

5.1: Energy Basics

Q5.1.1

A burning match and a bonfire may have the same temperature, yet you would not sit around a burning match on a fall evening to stay warm. Why not?

S5.1.1

The temperature of 1 gram of burning wood is approximately the same for both a match and a bonfire. This is an intensive property and depends on the material (wood). However, the overall amount of produced heat depends on the amount of material; this is an extensive property. The amount of wood in a bonfire is much greater than that in a match; the total amount of produced heat is also much greater, which is why we can sit around a bonfire to stay warm, but a match would not provide enough heat to keep us from getting cold.

Q5.1.2

Prepare a table identifying several energy transitions that take place during the typical operation of an automobile.

Q5.1.3

Explain the difference between heat capacity and specific heat of a substance.

S5.1.3

Heat capacity refers to the heat required to raise the temperature of the mass of the substance 1 degree; specific heat refers to the heat required to raise the temperature of 1 gram of the substance 1 degree. Thus, heat capacity is an extensive property, and specific heat is an intensive one.

Q5.1.4

Calculate the heat capacity, in joules and in calories per degree, of the following:

a. 28.4 g of water
b. 1.00 oz of lead

Q5.1.5

Calculate the heat capacity, in joules and in calories per degree, of the following:

a. 45.8 g of nitrogen gas
b. 1.00 pound of aluminum metal

S5.1.5

a. 47.6 J/°C; 11.38 cal $°C^{-1}$;
b. 407 J/°C; 97.3 cal $°C^{-1}$

Q5.1.6

How much heat, in joules and in calories, must be added to a 75.0–g iron block with a specific heat of 0.449 J/g °C to increase its temperature from 25 °C to its melting temperature of 1535 °C?

S5.1.6

$q = mC\Delta °T$

$q = (75.0g) \times (\frac{0.449\ J}{g\ °C}) \times (1,510°K) = 50,800J$

50,800J ; 12,200cal

Q5.1.7

How much heat, in joules and in calories, is required to heat a 28.4-g (1-oz) ice cube from −23.0 °C to −1.0 °C?

S5.1.7

1310 J; 313 cal

Q5.1.8

How much would the temperature of 275 g of water increase if 36.5 kJ of heat were added?

S5.1.8

ΔT° = 31.7° C

Q5.1.9

If 14.5 kJ of heat were added to 485 g of liquid water, how much would its temperature increase?

S5.1.9

7.15 °C

Q5.1.10

A piece of unknown substance weighs 44.7 g and requires 2110 J to increase its temperature from 23.2 °C to 89.6 °C.

a. What is the specific heat of the substance?
b. If it is one of the substances found in Table, what is its likely identity?

S5.1.10

a.) Solve for the specific heat C and compare the values with the chart

$$q = mC\Delta°T$$

$$2110J = (44.7\,g)(C)(66.4°C)$$

$$C = \frac{2110\,J}{2970\,g\,°C}$$

$$C = \frac{0.711\,J}{g\,°C}$$

b.) Silicon

Q5.1.11

A piece of unknown solid substance weighs 437.2 g, and requires 8460 J to increase its temperature from 19.3 °C to 68.9 °C.

a. What is the specific heat of the substance?
b. If it is one of the substances found in Table, what is its likely identity?

S5.1.11

a. 0.390 J/g °C;
b. Copper is a likely candidate.

Q5.1.12

An aluminum kettle weighs 1.05 kg.

a. What is the heat capacity of the kettle?
b. How much heat is required to increase the temperature of this kettle from 23.0 °C to 99.0 °C?
c. How much heat is required to heat this kettle from 23.0 °C to 99.0 °C if it contains 1.25 L of water (density of 0.997 g/mL and a specific heat of 4.184 J/g °C)?

Q5.1.13

Most people find waterbeds uncomfortable unless the water temperature is maintained at about 85 °F. Unless it is heated, a waterbed that contains 892 L of water cools from 85 °F to 72 °F in 24 hours. Estimate the amount of electrical energy required over 24 hours, in kWh, to keep the bed from cooling. Note that 1 kilowatt-hour (kWh) = 3.6×10^6 J, and assume that the density of water is 1.0 g/mL (independent of temperature). What other assumptions did you make? How did they affect your calculated result (i.e., were they likely to yield “positive” or “negative” errors)?

S5.1.13

We assume that the density of water is 1.0 g/cm^3(1 g/mL) and that it takes as much energy to keep the water at 85 °F as to heat it from 72 °F to 85 °F. We also assume that only the water is going to be heated. Energy required = 7.47 kWh

5.2: Calorimetry

Q5.2.1

A 500-mL bottle of water at room temperature and a 2-L bottle of water at the same temperature were placed in a refrigerator. After 30 minutes, the 500-mL bottle of water had cooled to the temperature of the refrigerator. An hour later, the 2-L of water had cooled to the same temperature. When asked which sample of water lost the most heat, one student replied that both bottles lost the same amount of heat because they started at the same temperature and finished at the same temperature. A second student thought that the 2-L bottle of water lost more heat because there was more water. A third student believed that the 500-mL bottle of water lost more heat because it cooled more quickly. A fourth student thought that it was not possible to tell because we do not know the initial temperature and the final temperature of the water. Indicate which of these answers is correct and describe the error in each of the other answers.

Q5.2.2

Would the amount of heat measured for the reaction in Example be greater, lesser, or remain the same if we used a calorimeter that was a poorer insulator than a coffee cup calorimeter? Explain your answer.

S5.2.2

lesser; more heat would be lost to the coffee cup and the environment and so ΔT for the water would be lesser and the calculated q would be lesser

Q5.2.3

Would the amount of heat absorbed by the dissolution in Example appear greater, lesser, or remain the same if the experimenter used a calorimeter that was a poorer insulator than a coffee cup calorimeter? Explain your answer.

Q5.2.4

Would the amount of heat absorbed by the dissolution in Example appear greater, lesser, or remain the same if the heat capacity of the calorimeter were taken into account? Explain your answer.

S5.2.4

greater, since taking the calorimeter’s heat capacity into account will compensate for the thermal energy transferred to the solution from the calorimeter; this approach includes the calorimeter itself, along with the solution, as “surroundings”: $q_{rxn} = -(q_{solution} + q_{calorimeter})$; since both $q_{solution}$ and $q_{calorimeter}$ are negative, including the latter term (q_{rxn}) will yield a greater value for the heat of the dissolution

Q5.2.5

How many milliliters of water at 23 °C with a density of 1.00 g/mL must be mixed with 180 mL (about 6 oz) of coffee at 95 °C so that the resulting combination will have a temperature of 60 °C? Assume that coffee and water have the same density and the same specific heat.

Q5.2.6

How much will the temperature of a cup (180 g) of coffee at 95 °C be reduced when a 45 g silver spoon (specific heat 0.24 J/g °C) at 25 °C is placed in the coffee and the two are allowed to reach the same temperature? Assume that the coffee has the same density and specific heat as water.

S5.2.6

The temperature of the coffee will drop 1 degree.

Q5.2.7

A 45-g aluminum spoon (specific heat 0.88 J/g °C) at 24 °C is placed in 180 mL (180 g) of coffee at 85 °C and the temperature of the two become equal.

a. What is the final temperature when the two become equal? Assume that coffee has the same specific heat as water.
b. The first time a student solved this problem she got an answer of 88 °C. Explain why this is clearly an incorrect answer.

Q5.2.8

The temperature of the cooling water as it leaves the hot engine of an automobile is 240 °F. After it passes through the radiator it has a temperature of 175 °F. Calculate the amount of heat transferred from the engine to the surroundings by one gallon of water with a specific heat of 4.184 J/g °C.

S5.2.8

$5.7 \times 10^2\ kJ$

Q5.2.8

A 70.0-g piece of metal at 80.0 °C is placed in 100 g of water at 22.0 °C contained in a calorimeter like that shown in Figure. The metal and water come to the same temperature at 24.6 °C. How much heat did the metal give up to the water? What is the specific heat of the metal?

Q5.2.9

If a reaction produces 1.506 kJ of heat, which is trapped in 30.0 g of water initially at 26.5 °C in a calorimeter like that in Figure, what is the resulting temperature of the water?

S5.2.9

38.5 °C

Q5.2.10

A 0.500-g sample of KCl is added to 50.0 g of water in a calorimeter (Figure). If the temperature decreases by 1.05 °C, what is the approximate amount of heat involved in the dissolution of the KCl, assuming the heat capacity of the resulting solution is 4.18 J/g °C? Is the reaction exothermic or endothermic?

Q5.2.11

Dissolving 3.0 g of $CaCl_2(s)$ in 150.0 g of water in a calorimeter (Figure) at 22.4 °C causes the temperature to rise to 25.8 °C. What is the approximate amount of heat involved in the dissolution, assuming the heat capacity of the resulting solution is 4.18 J/g °C? Is the reaction exothermic or endothermic?

S5.2.11

2.2 kJ; The heat produced shows that the reaction is exothermic.

Q5.2.12

When 50.0 g of 0.200 M NaCl(aq) at 24.1 °C is added to 100.0 g of 0.100 M $AgNO_3(aq)$ at 24.1 °C in a calorimeter, the temperature increases to 25.2 °C as AgCl(s) forms. Assuming the specific heat of the solution and products is 4.20 J/g °C, calculate the approximate amount of heat in joules produced.

Q5.2.13

The addition of 3.15 g of $Ba(OH)_2 \cdot 8H_2O$ to a solution of 1.52 g of NH_4SCN in 100 g of water in a calorimeter caused the temperature to fall by 3.1 °C. Assuming the specific heat of the solution and products is 4.20 J/g °C, calculate the approximate amount of heat absorbed by the reaction, which can be represented by the following equation:

$$Ba(OH)_2 \cdot 8H_2O_{(s)} + 2NH_4SCN_{(aq)} \rightarrow Ba(SCN)_{2(aq)} + 2NH_{3(aq)} + 10H_2O_{(l)} \tag{4.E.1}$$

S5.2.13

1.4 kJ

Q5.2.14

The reaction of 50 mL of acid and 50 mL of base described in Example increased the temperature of the solution by 6.9 degrees. How much would the temperature have increased if 100 mL of acid and 100 mL of base had been used in the same calorimeter starting at the same temperature of 22.0 °C? Explain your answer.

Q5.2.15

If the 3.21 g of NH_4NO_3 in Example were dissolved in 100.0 g of water under the same conditions, how much would the temperature change? Explain your answer.

S5.2.15

22.6. Since the mass and the heat capacity of the solution is approximately equal to that of the water, the two-fold increase in the amount of water leads to a two-fold decrease of the temperature change.

Q5.2.16

When 1.0 g of fructose, $C_6H_{12}O_6(s)$, a sugar commonly found in fruits, is burned in oxygen in a bomb calorimeter, the temperature of the calorimeter increases by 1.58 °C. If the heat capacity of the calorimeter and its contents is 9.90 kJ/°C, what is q for this combustion?

Q5.2.17

When a 0.740-g sample of trinitrotoluene (TNT), $C_7H_5N_2O_6$, is burned in a bomb calorimeter, the temperature increases from 23.4 °C to 26.9 °C. The heat capacity of the calorimeter is 534 J/°C, and it contains 675 mL of water. How much heat was produced by the combustion of the TNT sample?

S5.2.17

11.7 kJ

Q5.2.18

One method of generating electricity is by burning coal to heat water, which produces steam that drives an electric generator. To determine the rate at which coal is to be fed into the burner in this type of plant, the heat of combustion per ton of coal must be determined using a bomb calorimeter. When 1.00 g of coal is burned in a bomb calorimeter, the temperature increases by 1.48 °C. If the heat capacity of the calorimeter is 21.6 kJ/°C, determine the heat produced by combustion of a ton of coal (2.000×10^3 pounds).

Q5.2.19

The amount of fat recommended for someone with a daily diet of 2000 Calories is 65 g. What percent of the calories in this diet would be supplied by this amount of fat if the average number of Calories for fat is 9.1 Calories/g?

S5.2.19

30%

Q5.2.20

A teaspoon of the carbohydrate sucrose (common sugar) contains 16 Calories (16 kcal). What is the mass of one teaspoon of sucrose if the average number of Calories for carbohydrates is 4.1 Calories/g?

Q5.2.21

What is the maximum mass of carbohydrate in a 6-oz serving of diet soda that contains less than 1 Calorie per can if the average number of Calories for carbohydrates is 4.1 Calories/g?

S5.2.21

0.24 g

Q5.2.22

A pint of premium ice cream can contain 1100 Calories. What mass of fat, in grams and pounds, must be produced in the body to store an extra 1.1×10^3 Calories if the average number of Calories for fat is 9.1 Calories/g?

Q5.2.23

A serving of a breakfast cereal contains 3 g of protein, 18 g of carbohydrates, and 6 g of fat. What is the Calorie content of a serving of this cereal if the average number of Calories for fat is 9.1 Calories/g, for carbohydrates is 4.1 Calories/g, and for protein is 4.1 Calories/g?

S5.2.23

1.4×10^2 Calories

Q5.2.24

Which is the least expensive source of energy in kilojoules per dollar: a box of breakfast cereal that weighs 32 ounces and costs $4.23, or a liter of isooctane (density, 0.6919 g/mL) that costs $0.45? Compare the nutritional value of the cereal with the heat produced by combustion of the isooctane under standard conditions. A 1.0-ounce serving of the cereal provides 130 Calories.

5.3: Enthalpy

Q5.3.1

Explain how the heat measured in [link] differs from the enthalpy change for the exothermic reaction described by the following equation:

$$\mathrm{HCl}(aq) + \mathrm{NaOH}(aq) \longrightarrow \mathrm{NaCl}(aq) + \mathrm{H_2O}(l) \tag{4.E.2}$$

The enthalpy change of the indicated reaction is for exactly 1 mol HCL and 1 mol NaOH; the heat in the example is produced by 0.0500 mol HCl and 0.0500 mol NaOH. Using the data in the check your learning section of [link], calculate ΔH in kJ/mol of $AgNO_3(aq)$ for the reaction:

$$\mathrm{NaCl}(aq) + \mathrm{AgNO_3}(aq) \longrightarrow \mathrm{AgCl}(s) + \mathrm{NaNO_3}(aq) \tag{4.E.3}$$

Q5.3.2

Calculate the enthalpy of solution (ΔH for the dissolution) per mole of NH_4NO_3 under the conditions described in [link].

S5.3.2

25 kJ mol^{-1}

Q5.3.3

Calculate ΔH for the reaction described by the equation.

$$\mathrm{Ba(OH)_2 \cdot 8\,H_2O}(s) + 2\,\mathrm{NH_4SCN}(aq) \longrightarrow \mathrm{Ba(SCN)_2}(aq) + 2\,\mathrm{NH_3}(aq) + 10\,\mathrm{H_2O}(l)$$

Q5.3.4

Calculate the enthalpy of solution (ΔH for the dissolution) per mole of $CaCl_2$.

S5.3.4

81 kJ mol^{-1}

Q5.3.5

Although the gas used in an oxyacetylene torch is essentially pure acetylene, the heat produced by combustion of one mole of acetylene in such a torch is likely not equal to the enthalpy of combustion of acetylene listed in Table. Considering the conditions for which the tabulated data are reported, suggest an explanation.

Q5.3.6

How much heat is produced by burning 4.00 moles of acetylene under standard state conditions?

S5.3.6

5204.4 kJ

Q5.3.7

How much heat is produced by combustion of 125 g of methanol under standard state conditions?

Q5.3.8

How many moles of isooctane must be burned to produce 100 kJ of heat under standard state conditions?

S5.3.8

1.83×10^{-2} mol

Q5.3.9

What mass of carbon monoxide must be burned to produce 175 kJ of heat under standard state conditions?

Q5.3.10

When 2.50 g of methane burns in oxygen, 125 kJ of heat is produced. What is the enthalpy of combustion per mole of methane under these conditions?

S5.3.10

802 kJ mol^{-1}

Q5.3.11

How much heat is produced when 100 mL of 0.250 M HCl (density, 1.00 g/mL) and 200 mL of 0.150 M NaOH (density, 1.00 g/mL) are mixed?

$$\mathrm{HCl}(aq) + \mathrm{NaOH}(aq) \longrightarrow \mathrm{NaCl}(aq) + \mathrm{H_2O}(l) \quad \Delta H^\circ_{298} = -58\ \mathrm{kJ} \tag{4.E.4}$$

If both solutions are at the same temperature and the heat capacity of the products is 4.19 J/g °C, how much will the temperature increase? What assumption did you make in your calculation?

Q5.3.12

A sample of 0.562 g of carbon is burned in oxygen in a bomb calorimeter, producing carbon dioxide. Assume both the reactants and products are under standard state conditions, and that the heat released is directly proportional to the enthalpy of combustion of graphite. The temperature of the calorimeter increases from 26.74 °C to 27.93 °C. What is the heat capacity of the calorimeter and its contents?

S5.3.12

15.5 kJ/°C

Q5.3.13

Before the introduction of chlorofluorocarbons, sulfur dioxide (enthalpy of vaporization, 6.00 kcal/mol) was used in household refrigerators. What mass of SO_2 must be evaporated to remove as much heat as evaporation of 1.00 kg of CCl_2F_2 (enthalpy of vaporization is 17.4 kJ/mol)?

The vaporization reactions for SO_2 and CCl_2F_2 are

$$\mathrm{SO_2}(l) \longrightarrow \mathrm{SO_2}(g) \text{ and } \mathrm{CCl_2F}(l) \longrightarrow \mathrm{CCl_2F_2}(g), \text{ respectively.}$$

Q5.3.14

Homes may be heated by pumping hot water through radiators. What mass of water will provide the same amount of heat when cooled from 95.0 to 35.0 °C, as the heat provided when 100 g of steam is cooled from 110 °C to 100 °C.

S5.3.14

7.43 g

Q5.3.15

Which of the enthalpies of combustion in Table the table are also standard enthalpies of formation?

Q5.3.16

Does the standard enthalpy of formation of $H_2O(g)$ differ from $\Delta H°$ for the reaction $\mathrm{2\,H_2}(g) + \mathrm{O_2}(g) \longrightarrow \mathrm{2\,H_2O}(g)$?

S5.3.16

No.

Q5.3.17

Joseph Priestly prepared oxygen in 1774 by heating red mercury(II) oxide with sunlight focused through a lens. How much heat is required to decompose exactly 1 mole of red HgO(s) to Hg(l) and $O_2(g)$ under standard conditions?

Q5.3.18

How many kilojoules of heat will be released when exactly 1 mole of manganese, Mn, is burned to form $Mn_3O_4(s)$ at standard state conditions?

S5.3.18

459.6 kJ

Q5.3.19

How many kilojoules of heat will be released when exactly 1 mole of iron, Fe, is burned to form $Fe_2O_3(s)$ at standard state conditions?

Q5.3.20

The following sequence of reactions occurs in the commercial production of aqueous nitric acid:

$$\mathrm{4\,NH_3}(g) + \mathrm{5\,O_2}(g) \longrightarrow \mathrm{4\,NO}(g) + \mathrm{6\,H_2O}(l) \quad \Delta H = -907\ \mathrm{kJ}$$

$$\mathrm{2\,NO}(g) + \mathrm{O_2}(g) \longrightarrow \mathrm{2\,NO_2}(g) \quad \Delta H = -113\ \mathrm{kJ}$$

$$\mathrm{3\,NO_2} + \mathrm{H_2O}(l) \longrightarrow \mathrm{2\,HNO_2}(aq) + \mathrm{NO}(g) \quad \Delta H = -139\ \mathrm{kJ}$$

Determine the total energy change for the production of one mole of aqueous nitric acid by this process.

S5.3.20

495 kJ/mol

Q5.3.21

Both graphite and diamond burn.

$$\mathrm{C}(s,\ \text{diamond}) + \mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g)$$

For the conversion of graphite to diamond:

$$\mathrm{C}(s,\ \text{graphite}) \longrightarrow \mathrm{C}(s,\ \text{diamond}) \quad \Delta H^\circ_{298} = 1.90\ \mathrm{kJ}$$

Which produces more heat, the combustion of graphite or the combustion of diamond?

Q5.3.22

From the molar heats of formation in Appendix G, determine how much heat is required to evaporate one mole of water: $\mathrm{H_2O}(l) \longrightarrow \mathrm{H_2O}(g)$

S5.3.22

44.01 kJ/mol

Q5.3.23

Which produces more heat?

$$\mathrm{Os}(s) \longrightarrow 2\,\mathrm{O_2}(g) \longrightarrow \mathrm{OsO_4}(s)$$

or

$$\mathrm{Os}(s) \longrightarrow 2\,\mathrm{O_2}(g) \longrightarrow \mathrm{OsO_4}(g)$$

for the phase change $\mathrm{OsO_4}(s) \longrightarrow \mathrm{OsO_4}(g) \quad \Delta H = 56.4\ \mathrm{kJ}$

Q5.3.24

Calculate ΔH°_{298} for the process

$$\mathrm{Sb}(s) + \frac{5}{2}\mathrm{Cl_2}(g) \longrightarrow \mathrm{SbCl_5}(g)$$

from the following information:

$$\mathrm{Sb}(s) + \frac{3}{2}\mathrm{Cl_2}(g) \longrightarrow \mathrm{SbCl_3}(g) \quad \Delta H^\circ_{298} = -314\ \mathrm{kJ}$$

$$\mathrm{SbCl_3}(s) + \mathrm{Cl_2}(g) \longrightarrow \mathrm{SbCl_5}(g) \quad \Delta H^\circ_{298} = -80\ \mathrm{kJ}$$

S5.3.24

394 kJ

Q5.3.25

Calculate ΔH°_{298} for the process $\mathrm{Zn}(s) + \mathrm{S}(s) + 2\,\mathrm{O_2}(g) \longrightarrow \mathrm{ZnSO_4}(s)$

from the following information:

$$\mathrm{Zn}(s) + \mathrm{S}(s) \longrightarrow \mathrm{ZnS}(s) \quad \Delta H^\circ_{298} = -206.0\ \mathrm{kJ}$$

$$\mathrm{ZnS}(s) + 2\,\mathrm{O_2}(g) \longrightarrow \mathrm{ZnSO_4}(s) \quad \Delta H^\circ_{298} = -776.8\ \mathrm{kJ}$$

Q5.3.26

Calculate ΔH for the process

$$\mathrm{Hg_2Cl_2}(s) \longrightarrow 2\,\mathrm{Hg}(l) + \mathrm{Cl_2}(g)$$

from the following information:

$$\mathrm{Hg}(l) + \mathrm{Cl_2}(g) \longrightarrow \mathrm{HgCl_2}(s) \quad \Delta H = -224\ \mathrm{kJ}$$

$$\mathrm{Hg}(l) + \mathrm{HgCl_2}(s) \longrightarrow \mathrm{Hg_2Cl_2}(s) \quad \Delta H = -41.2\ \mathrm{kJ}$$

S5.3.26

265 kJ

Q5.3.27

Calculate ΔH°_{298} for the process

$$\mathrm{Co_3O_4}(s) \longrightarrow 3\,\mathrm{Co}(s) + 2\,\mathrm{O_2}(g)$$

from the following information:

$$\mathrm{Co}(s) + \frac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{CoO}(s) \quad \Delta H^\circ_{298} = -237.9\ \mathrm{kJ}$$

$$3\,\mathrm{Co}(s) + \mathrm{O_2}(g) \longrightarrow \mathrm{Co_3O_4}(s) \quad \Delta H^\circ_{298} = -177.5\ \mathrm{kJ}$$

Q5.3.28

Calculate the standard molar enthalpy of formation of NO(g) from the following data:

$$\mathrm{N_2}(g) + 2\,\mathrm{O_2} \longrightarrow 2\,\mathrm{NO_2}(g) \quad \Delta H^\circ_{298} = 66.4\ \mathrm{kJ}$$

$$2\,\mathrm{NO}(g) + \mathrm{O_2} \longrightarrow 2\,\mathrm{NO_2}(g) \quad \Delta H^\circ_{298} = -114.1\ \mathrm{kJ}$$

S5.3.28

90.3 mol^{-1} of NO

Q5.3.29

Using the data in Appendix G, calculate the standard enthalpy change for each of the following reactions:

a. $\mathrm{N_2}(g) + \mathrm{O_2}(g) \longrightarrow 2\,\mathrm{NO}(g)$
b. $\mathrm{Si}(s) + 2\,\mathrm{Cl_2}(g) \longrightarrow \mathrm{SiCl_4}(g)$
c. $\mathrm{Fe_2O_3}(s) + 3\,\mathrm{H_2}(g) \longrightarrow 2\,\mathrm{Fe}(s) + 3\,\mathrm{H_2O}(l)$
d. $2\,\mathrm{LiOH}(s) + \mathrm{CO_2}(g) \longrightarrow \mathrm{Li_2CO_3}(s) + \mathrm{H_2O}(g)$

Q5.3.30

Using the data in Appendix G, calculate the standard enthalpy change for each of the following reactions:

a. $\mathrm{Si}(s) + 2\,\mathrm{F_2}(g) \longrightarrow \mathrm{SiF_4}(g)$
b. $2\,\mathrm{C}(s) + 2\,\mathrm{H_2}(g) + \mathrm{O_2}(g) \longrightarrow \mathrm{CH_3CO_2H}(l)$
c. $\mathrm{CH_4}(g) + \mathrm{N_2}(g) \longrightarrow \mathrm{HCN}(g) + \mathrm{NH_3}(g)$;
d. $\mathrm{CS_2}(g) + 3\,\mathrm{Cl_2}(g) \longrightarrow \mathrm{CCl_4}(g) + \mathrm{S_2Cl_2}(g)$

S5.3.30

a. −1615.0 kJ mol^{-1};
b. −484.3 kJ mol^{-1};
c. 164.2 kJ;
d. −232.1 kJ

Q5.3.31

The following reactions can be used to prepare samples of metals. Determine the enthalpy change under standard state conditions for each.

a. $2\,\mathrm{Ag_2O}(s) \longrightarrow 4\,\mathrm{Ag}(s) + \mathrm{O_2}(g)$
b. $\mathrm{SnO}(s) + \mathrm{CO}(g) \longrightarrow \mathrm{Sn}(s) + \mathrm{CO_2}(g)$
c. $\mathrm{Cr_2O_3}(s) + 3\,\mathrm{H_2}(g) \longrightarrow 2\,\mathrm{Cr}(s) + 3\,\mathrm{H_2O}(l)$

d. $2\,Al(s) + Fe_2O_3(s) \longrightarrow Al_2O_3(s) + 2\,Fe(s)$

Q5.3.32

The decomposition of hydrogen peroxide, H_2O_2, has been used to provide thrust in the control jets of various space vehicles. Using the data in Appendix G, determine how much heat is produced by the decomposition of exactly 1 mole of H_2O_2 under standard conditions.

$$2\,H_2O_2(l) \longrightarrow 2\,H_2O(g) + O_2(g)$$

S5.3.32

-54.04 kJ mol^{-1}

Q5.3.33

Calculate the enthalpy of combustion of propane, $C_3H_8(g)$, for the formation of $H_2O(g)$ and $CO_2(g)$. The enthalpy of formation of propane is −104 kJ/mol.

Q5.3.34

Calculate the enthalpy of combustion of butane, $C_4H_{10}(g)$ for the formation of $H_2O(g)$ and $CO_2(g)$. The enthalpy of formation of butane is −126 kJ/mol.

S5.3.34

2660 kJ mol^{-1}

Q5.3.35

Both propane and butane are used as gaseous fuels. Which compound produces more heat per gram when burned?

Q5.3.36

The white pigment TiO_2 is prepared by the reaction of titanium tetrachloride, $TiCl_4$, with water vapor in the gas phase:

$$TiCl_4(g) + 2\,H_2O(g) \longrightarrow TiO_2(s) + 4\,HCl(g).$$

How much heat is evolved in the production of exactly 1 mole of $TiO_2(s)$ under standard state conditions?

S5.3.36

67.1 kJ

Q5.3.37

Water gas, a mixture of H_2 and CO, is an important industrial fuel produced by the reaction of steam with red hot coke, essentially pure carbon:

$$C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g).$$

a. Assuming that coke has the same enthalpy of formation as graphite, calculate ΔH°_{298} for this reaction.
b. Methanol, a liquid fuel that could possibly replace gasoline, can be prepared from water gas and additional hydrogen at high temperature and pressure in the presence of a suitable catalyst:

$$2\,H_2(g) + CO(g) \longrightarrow CH_3OH(g). \tag{4.E.5}$$

Under the conditions of the reaction, methanol forms as a gas. Calculate ΔH°_{298} for this reaction and for the condensation of gaseous methanol to liquid methanol.
c. Calculate the heat of combustion of 1 mole of liquid methanol to $H_2O(g)$ and $CO_2(g)$.

Q5.3.38

In the early days of automobiles, illumination at night was provided by burning acetylene, C_2H_2. Though no longer used as auto headlamps, acetylene is still used as a source of light by some cave explorers. The acetylene is (was) prepared in the lamp by the reaction of water with calcium carbide, CaC_2:

$\mathrm{CaC_2}(s) + \mathrm{H_2O}(l) \longrightarrow \mathrm{Ca(OH)_2}(s) + \mathrm{C_2H_2}(g)$.

Calculate the standard enthalpy of the reaction. The ΔH_f° of CaC_2 is −15.14 kcal/mol.

S5.3.38

122.8 kJ

Q5.3.39

From the data in Table, determine which of the following fuels produces the greatest amount of heat per gram when burned under standard conditions: $CO(g)$, $CH_4(g)$, or $C_2H_2(g)$.

Q5.3.40

The enthalpy of combustion of hard coal averages −35 kJ/g, that of gasoline, 1.28×10^5 kJ/gal. How many kilograms of hard coal provide the same amount of heat as is available from 1.0 gallon of gasoline? Assume that the density of gasoline is 0.692 g/mL (the same as the density of isooctane).

S5.3.40

3.7 kg

Q5.3.41

Ethanol, C_2H_5OH, is used as a fuel for motor vehicles, particularly in Brazil.

a. Write the balanced equation for the combustion of ethanol to $CO_2(g)$ and $H_2O(g)$, and, using the data in Appendix G, calculate the enthalpy of combustion of 1 mole of ethanol.
b. The density of ethanol is 0.7893 g/mL. Calculate the enthalpy of combustion of exactly 1 L of ethanol.
c. Assuming that an automobile's mileage is directly proportional to the heat of combustion of the fuel, calculate how much farther an automobile could be expected to travel on 1 L of gasoline than on 1 L of ethanol. Assume that gasoline has the heat of combustion and the density of n–octane, C_8H_{18} ($\Delta H_f^\circ = -208.4\ \mathrm{kJ/mol}$; density = 0.7025 g/mL).

Q5.3.42

Among the substances that react with oxygen and that have been considered as potential rocket fuels are diborane [B_2H_6, produces $B_2O_3(s)$ and $H_2O(g)$], methane [CH_4, produces $CO_2(g)$ and $H_2O(g)$], and hydrazine [N_2H_4, produces $N_2(g)$ and $H_2O(g)$]. On the basis of the heat released by 1.00 g of each substance in its reaction with oxygen, which of these compounds offers the best possibility as a rocket fuel? The ΔH_f° of $B_2H_6(g)$, $CH_4(g)$, and $N_2H_4(l)$ may be found in Appendix G.

S5.3.42

On the assumption that the best rocket fuel is the one that gives off the most heat, B_2H_6 is the prime candidate.

Q5.3.43

How much heat is produced when 1.25 g of chromium metal reacts with oxygen gas under standard conditions?

Ethylene, C_2H_2, a byproduct from the fractional distillation of petroleum, is fourth among the 50 chemical compounds produced commercially in the largest quantities. About 80% of synthetic ethanol is manufactured from ethylene by its reaction with water in the presence of a suitable catalyst.

$$\mathrm{C_2H_4}(g) + \mathrm{H_2O}(g) \longrightarrow \mathrm{C_2H_5OH}(l)$$

Using the data in the table in Appendix G, calculate $\Delta H°$ for the reaction.

S5.3.43

88.2 kJ

Q5.3.44

The oxidation of the sugar glucose, $C_6H_{12}O_6$, is described by the following equation:

$$C_6H_{12}O_6(s) + 6\,O_2(g) \longrightarrow 6\,CO_2(g) + 6\,H_2O(l) \quad \Delta H = -2816\ \text{kJ}$$

The metabolism of glucose gives the same products, although the glucose reacts with oxygen in a series of steps in the body.

a. How much heat in kilojoules can be produced by the metabolism of 1.0 g of glucose?
b. How many Calories can be produced by the metabolism of 1.0 g of glucose?

Q5.3.45

Propane, C_3H_8, is a hydrocarbon that is commonly used as a fuel.

a. Write a balanced equation for the complete combustion of propane gas.
b. Calculate the volume of air at 25 °C and 1.00 atmosphere that is needed to completely combust 25.0 grams of propane. Assume that air is 21.0 percent O_2 by volume. (Hint: we will see how to do this calculation in a later chapter on gases—for now use the information that 1.00 L of air at 25 °C and 1.00 atm contains 0.275 g of O_2 per liter.)
c. The heat of combustion of propane is −2,219.2 kJ/mol. Calculate the heat of formation, ΔH_f° of propane given that ΔH_f° of $H_2O(l)$ = −285.8 kJ/mol and ΔH_f° of $CO_2(g)$ = −393.5 kJ/mol.
d. Assuming that all of the heat released in burning 25.0 grams of propane is transferred to 4.00 kilograms of water, calculate the increase in temperature of the water.

S5.3.45

a. $C_3H_8(g) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(l)$;
b. 330 L;
c. −104.5 kJ mol^{-1};
d. 75.4 °C

Q5.3.46

During a recent winter month in Sheboygan, Wisconsin, it was necessary to obtain 3500 kWh of heat provided by a natural gas furnace with 89% efficiency to keep a small house warm (the efficiency of a gas furnace is the percent of the heat produced by combustion that is transferred into the house).

a. Assume that natural gas is pure methane and determine the volume of natural gas in cubic feet that was required to heat the house. The average temperature of the natural gas was 56 °F; at this temperature and a pressure of 1 atm, natural gas has a density of 0.681 g/L.
b. How many gallons of LPG (liquefied petroleum gas) would be required to replace the natural gas used? Assume the LPG is liquid propane [C_3H_8: density, 0.5318 g/mL; enthalpy of combustion, 2219 kJ/mol for the formation of $CO_2(g)$ and $H_2O(l)$] and the furnace used to burn the LPG has the same efficiency as the gas furnace.
c. What mass of carbon dioxide is produced by combustion of the methane used to heat the house?
d. What mass of water is produced by combustion of the methane used to heat the house?
e. What volume of air is required to provide the oxygen for the combustion of the methane used to heat the house? Air contains 23% oxygen by mass. The average density of air during the month was 1.22 g/L.
f. How many kilowatt–hours (1 kWh = 3.6×10^6 J) of electricity would be required to provide the heat necessary to heat the house? Note electricity is 100% efficient in producing heat inside a house.
g. Although electricity is 100% efficient in producing heat inside a house, production and distribution of electricity is not 100% efficient. The efficiency of production and distribution of electricity produced in a coal-fired power plant is about 40%. A certain type of coal provides 2.26 kWh per pound upon combustion. What mass of this coal in kilograms will be required to produce the electrical energy necessary to heat the house if the efficiency of generation and distribution is 40%?

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CHAPTER OVERVIEW

5: Electronic Structure and Periodic Properties

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General Chemistry

The study of chemistry must at some point extend to the molecular level, for the physical and chemical properties of a substance are ultimately explained in terms of the structure and bonding of molecules. This module introduces some basic facts and principles that are needed for a discussion of organic molecules.

5.1: Electromagnetic Energy

5.2: Electronic Structure of Atoms (Electron Configurations)

5.3: Periodic Variations in Element Properties

5.E: Electronic Structure and Periodic Properties (Exercises)

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5.1: Electromagnetic Energy

Learning Objectives

- Explain the basic behavior of waves, including traveling waves and standing waves
- Describe the wave nature of light
- Use appropriate equations to calculate related light-wave properties such as period, frequency, wavelength, and energy
- Distinguish between line and continuous emission spectra
- Describe the particle nature of light

The nature of light has been a subject of inquiry since antiquity. In the seventeenth century, Isaac Newton performed experiments with lenses and prisms and was able to demonstrate that white light consists of the individual colors of the rainbow combined together. Newton explained his optics findings in terms of a "corpuscular" view of light, in which light was composed of streams of extremely tiny particles travelling at high speeds according to Newton's laws of motion. Others in the seventeenth century, such as Christiaan Huygens, had shown that optical phenomena such as reflection and refraction could be equally well explained in terms of light as waves travelling at high speed through a medium called "luminiferous aether" that was thought to permeate all space. Early in the nineteenth century, Thomas Young demonstrated that light passing through narrow, closely spaced slits produced interference patterns that could not be explained in terms of Newtonian particles but could be easily explained in terms of waves. Later in the nineteenth century, after James Clerk Maxwell developed his theory of electromagnetic radiation and showed that light was the visible part of a vast spectrum of electromagnetic waves, the particle view of light became thoroughly discredited. By the end of the nineteenth century, scientists viewed the physical universe as roughly comprising two separate domains: matter composed of particles moving according to Newton's laws of motion, and electromagnetic radiation consisting of waves governed by Maxwell's equations. Today, these domains are referred to as classical mechanics and classical electrodynamics (or classical electromagnetism). Although there were a few physical phenomena that could not be explained within this framework, scientists at that time were so confident of the overall soundness of this framework that they viewed these aberrations as puzzling paradoxes that would ultimately be resolved somehow within this framework. As we shall see, these paradoxes led to a contemporary framework that intimately connects particles and waves at a fundamental level called wave-particle duality, which has superseded the classical view.

Visible light and other forms of electromagnetic radiation play important roles in chemistry, since they can be used to infer the energies of electrons within atoms and molecules. Much of modern technology is based on electromagnetic radiation. For example, radio waves from a mobile phone, X-rays used by dentists, the energy used to cook food in your microwave, the radiant heat from red-hot objects, and the light from your television screen are forms of electromagnetic radiation that all exhibit wavelike behavior.

Waves

A wave is an oscillation or periodic movement that can transport energy from one point in space to another. Common examples of waves are all around us. Shaking the end of a rope transfers energy from your hand to the other end of the rope, dropping a pebble into a pond causes waves to ripple outward along the water's surface, and the expansion of air that accompanies a lightning strike generates sound waves (thunder) that can travel outward for several miles. In each of these cases, kinetic energy is transferred through matter (the rope, water, or air) while the matter remains essentially in place. An insightful example of a wave occurs in sports stadiums when fans in a narrow region of seats rise simultaneously and stand with their arms raised up for a few seconds before sitting down again while the fans in neighboring sections likewise stand up and sit down in sequence. While this wave can quickly encircle a large stadium in a few seconds, none of the fans actually travel with the wave-they all stay in or above their seats.

Waves need not be restricted to travel through matter. As Maxwell showed, electromagnetic waves consist of an electric field oscillating in step with a perpendicular magnetic field, both of which are perpendicular to the direction of travel. These waves can travel through a vacuum at a constant speed of 2.998×10^8 m/s, the speed of light (denoted by c).

All waves, including forms of electromagnetic radiation, are characterized by, a wavelength (denoted by λ, the lowercase Greek letter lambda), a frequency (denoted by ν, the lowercase Greek letter nu), and an amplitude. As can be seen in Figure **5.1.1**, the wavelength is the distance between two consecutive peaks or troughs in a wave (measured in meters in the SI system).

Electromagnetic waves have wavelengths that fall within an enormous range-wavelengths of kilometers (10^3 m) to picometers (10^{-12} m) have been observed. The frequency is the number of wave cycles that pass a specified point in space in a specified amount of time (in the SI system, this is measured in seconds). A cycle corresponds to one complete wavelength. The unit for frequency, expressed as cycles per second [s^{-1}], is the hertz (Hz). Common multiples of this unit are megahertz, (1 MHz = 1×10^6 Hz) and gigahertz (1 GHz = 1×10^9 Hz). The amplitude corresponds to the magnitude of the wave's displacement and so, in Figure, this corresponds to one-half the height between the peaks and troughs. The amplitude is related to the intensity of the wave, which for light is the brightness, and for sound is the loudness.

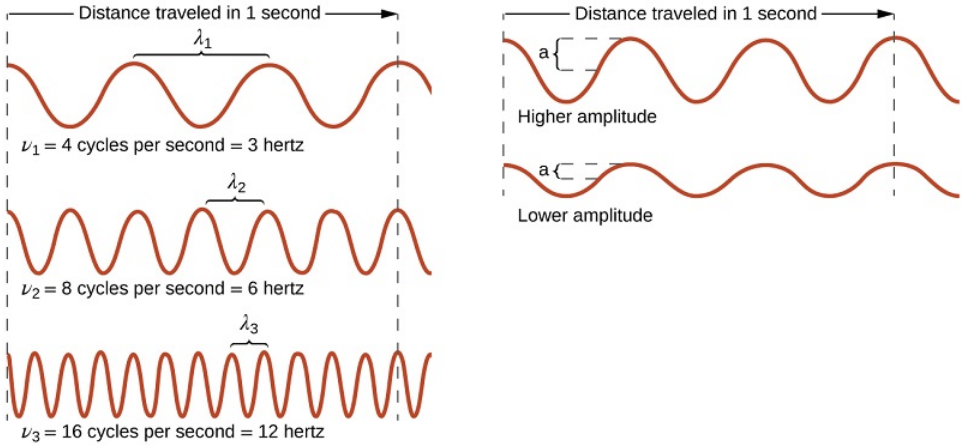


Figure **5.1.1**: One-dimensional sinusoidal waves show the relationship among wavelength, frequency, and speed. The wave with the shortest wavelength has the highest frequency. Amplitude is one-half the height of the wave from peak to trough. (CC by 4.0; OpenStax)

This figure includes 5 one-dimensional sinusoidal waves in two columns. The column on the left includes three waves, and the column on the right includes two waves. In each column, dashed vertical line segments extend down the left and right sides of the column. A right pointing arrow extends from the left dashed line to the right dashed line in both columns and is labeled, “Distance traveled in 1 second.” The waves all begin on the left side at a crest. The wave at the upper left shows 3 peaks to the right of the starting point. A bracket labeled, “lambda subscript 1,” extends upward from the second and third peaks. Beneath this wave is the label, “nu subscript 1 equals 4 cycles per second equals 3 hertz.” The wave below has six peaks to the right of the starting point with a bracket similarly connecting the third and fourth peaks which is labeled, “lambda subscript 2.” Beneath this wave is the label, “nu subscript 2 equals 8 cycles per second equals 6 hertz” The third wave in the column has twelve peaks to the right of the starting point with a bracket similarly connecting the seventh and eighth peaks which is labeled, “lambda subscript 3.” Beneath this wave is the label, “nu subscript 3 equals 12 cycles per second equals 12 hertz.” All waves in this column appear to have the same vertical distance from peak to trough. In the second column, the two waves are similarly shown, but lack the lambda labels. The top wave in this column has a greater vertical distance between the peaks and troughs and is labeled, “Higher amplitude.” The wave beneath it has a lesser distance between the peaks and troughs and is labeled, “Lower amplitude.”

The product of a wave's wavelength (λ) and its frequency (ν), $\lambda\nu$, is the speed of the wave. Thus, for electromagnetic radiation in a vacuum:

$$c = 2.998 \times 10^8\ \mathrm{ms}^{-1} = \lambda\nu \tag{5.1.1}$$

Wavelength and frequency are inversely proportional: As the wavelength increases, the frequency decreases. The inverse proportionality is illustrated in Figure **5.1.2**. This figure also shows the electromagnetic spectrum, the range of all types of electromagnetic radiation. Each of the various colors of visible light has specific frequencies and wavelengths associated with them, and you can see that visible light makes up only a small portion of the electromagnetic spectrum. Because the technologies developed to work in various parts of the electromagnetic spectrum are different, for reasons of convenience and historical legacies, different units are typically used for different parts of the spectrum. For example, radio waves are usually specified as frequencies (typically in units of MHz), while the visible region is usually specified in wavelengths (typically in units of nm or angstroms).

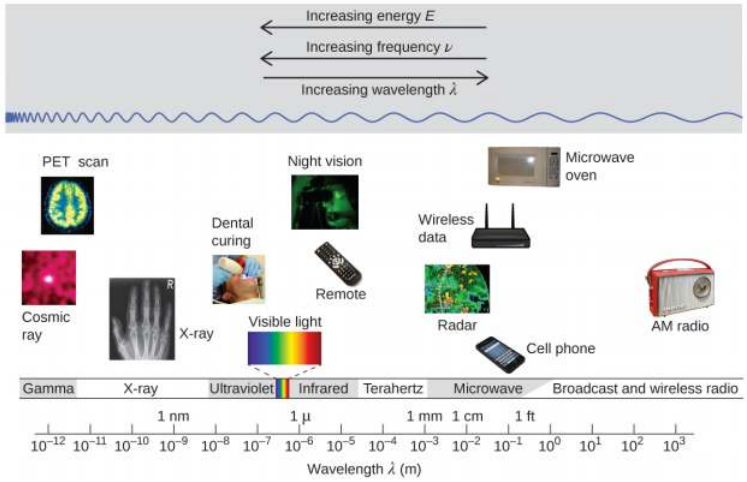


Figure 5.1.2: Portions of the electromagnetic spectrum are shown in order of decreasing frequency and increasing wavelength. Examples of some applications for various wavelengths include positron emission tomography (PET) scans, X-ray imaging, remote controls, wireless Internet, cellular telephones, and radios. (credit "Cosmic ray": modification of work by NASA; credit "PET scan": modification of work by the National Institute of Health; credit "X-ray": modification of work by Dr. Jochen Lengerke; credit "Dental curing": modification of work by the Department of the Navy; credit "Night vision": modification of work by the Department of the Army; credit "Remote": modification of work by Emilian Robert Vicol; credit "Cell phone": modification of work by Brett Jordan; credit "Microwave oven": modification of work by Billy Mabray; credit "Ultrasound": modification of work by Jane Whitney; credit "AM radio": modification of work by Dave Clausen)

✔ Example 5.1.1: Determining the Frequency and Wavelength of Radiation

A sodium streetlight gives off yellow light that has a wavelength of 589 nm (1 nm = 1×10^{-9} m). What is the frequency of this light?

Solution

We can rearrange the Equation 5.1.1 to solve for the frequency:

$$\nu = \frac{c}{\lambda}$$

Since c is expressed in meters per second, we must also convert 589 nm to meters.

$$\nu = \left(\frac{2.998 \times 10^{8}\ \cancel{\text{m}}\ \text{s}^{-1}}{589\ \cancel{\text{nm}}}\right)\left(\frac{1 \times 10^{9}\ \cancel{\text{nm}}}{1\ \cancel{\text{m}}}\right) = 5.09 \times 10^{14}\ \text{s}^{-1}$$

? Exercise 5.1.1

One of the frequencies used to transmit and receive cellular telephone signals in the United States is 850 MHz. What is the wavelength in meters of these radio waves?

Answer

0.353 m = 35.3 cm

Wireless Communication

Many valuable technologies operate in the radio (3 kHz-300 GHz) frequency region of the electromagnetic spectrum. At the low frequency (low energy, long wavelength) end of this region are AM (amplitude modulation) radio signals (540-2830 kHz) that can travel long distances. FM (frequency modulation) radio signals are used at higher frequencies (87.5-108.0 MHz). In AM radio, the information is transmitted by varying the amplitude of the wave (Figure 5.1.5). In FM radio, by contrast, the amplitude is constant and the instantaneous frequency varies.



Figure 5.1.3: Radio and cell towers are typically used to transmit long-wavelength electromagnetic radiation. Increasingly, cell towers are designed to blend in with the landscape, as with the Tucson, Arizona, cell tower (right) disguised as a palm tree. (credit left: modification of work by Sir Mildred Pierce; credit middle: modification of work by M.O. Stevens)

Other technologies also operate in the radio-wave portion of the electromagnetic spectrum. For example, 4G cellular telephone signals are approximately 880 MHz, while Global Positioning System (GPS) signals operate at 1.228 and 1.575 GHz, local area wireless technology (Wi-Fi) networks operate at 2.4 to 5 GHz, and highway toll sensors operate at 5.8 GHz. The frequencies associated with these applications are convenient because such waves tend not to be absorbed much by common building materials.

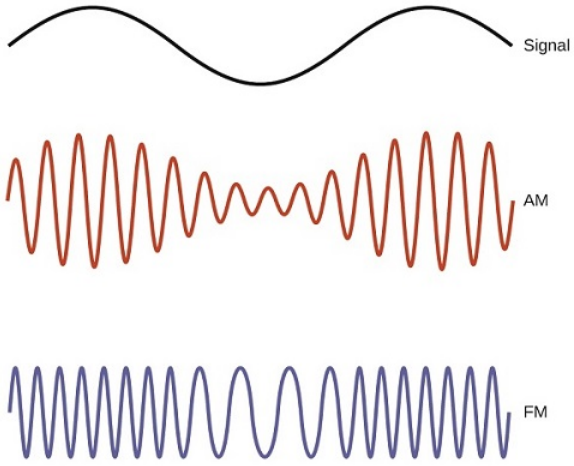


Figure 5.1.4: This schematic depicts how amplitude modulation (AM) and frequency modulation (FM) can be used to transmit a radio wave.

One particularly characteristic phenomenon of waves results when two or more waves come into contact: They interfere with each other. Figure 5.1.5 shows the interference patterns that arise when light passes through narrow slits closely spaced about a wavelength apart. The fringe patterns produced depend on the wavelength, with the fringes being more closely spaced for shorter wavelength light passing through a given set of slits. When the light passes through the two slits, each slit effectively acts as a new source, resulting in two closely spaced waves coming into contact at the detector (the camera in this case). The dark regions in Figure 5.1.5 correspond to regions where the peaks for the wave from one slit happen to coincide with the troughs for the wave from the other slit (destructive interference), while the brightest regions correspond to the regions where the peaks for the two waves (or their two troughs) happen to coincide (constructive interference). Likewise, when two stones are tossed close together into a pond, interference patterns are visible in the interactions between the waves produced by the stones. Such interference patterns cannot be explained by particles moving according to the laws of classical mechanics.

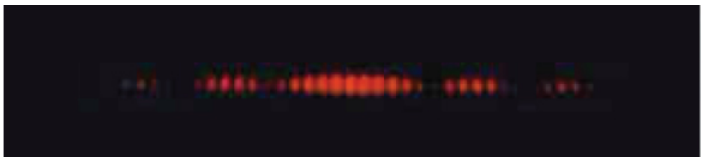


Figure **5.1.5**: Interference fringe patterns are shown for light passing through two closely spaced, narrow slits. The spacing of the fringes depends on the wavelength, with the fringes being more closely spaced for the shorter-wavelength blue light. (credit: PASCO)

Dorothy Hodgkin

Because the wavelengths of X-rays (10-10,000 picometers [pm]) are comparable to the size of atoms, X-rays can be used to determine the structure of molecules. When a beam of X-rays is passed through molecules packed together in a crystal, the X-rays collide with the electrons and scatter. Constructive and destructive interference of these scattered X-rays creates a specific diffraction pattern. Calculating backward from this pattern, the positions of each of the atoms in the molecule can be determined very precisely. One of the pioneers who helped create this technology was Dorothy Crowfoot Hodgkin.

She was born in Cairo, Egypt, in 1910, where her British parents were studying archeology. Even as a young girl, she was fascinated with minerals and crystals. When she was a student at Oxford University, she began researching how X-ray crystallography could be used to determine the structure of biomolecules. She invented new techniques that allowed her and her students to determine the structures of vitamin B_{12}, penicillin, and many other important molecules. Diabetes, a disease that affects 382 million people worldwide, involves the hormone insulin. Hodgkin began studying the structure of insulin in 1934, but it required several decades of advances in the field before she finally reported the structure in 1969. Understanding the structure has led to better understanding of the disease and treatment options.

Not all waves are travelling waves. Standing waves (also known as stationary waves) remain constrained within some region of space. As we shall see, standing waves play an important role in our understanding of the electronic structure of atoms and molecules. The simplest example of a standing wave is a one-dimensional wave associated with a vibrating string that is held fixed at its two end points. Figure **5.1.6** shows the four lowest-energy standing waves (the fundamental wave and the lowest three harmonics) for a vibrating string at a particular amplitude. Although the string's motion lies mostly within a plane, the wave itself is considered to be one dimensional, since it lies along the length of the string. The motion of string segments in a direction perpendicular to the string length generates the waves and so the amplitude of the waves is visible as the maximum displacement of the curves seen in Figure **5.1.6**. The key observation from the figure is that only those waves having an integer number, n, of half-wavelengths between the end points can form. A system with fixed end points such as this restricts the number and type of the possible waveforms. This is an example of quantization, in which only discrete values from a more general set of continuous values of some property are observed. Another important observation is that the harmonic waves (those waves displaying more than one-half wavelength) all have one or more points between the two end points that are not in motion. These special points are nodes. The energies of the standing waves with a given amplitude in a vibrating string increase with the number of half-wavelengths *n*. Since the number of nodes is $n - 1$, the energy can also be said to depend on the number of nodes, generally increasing as the number of nodes increases.

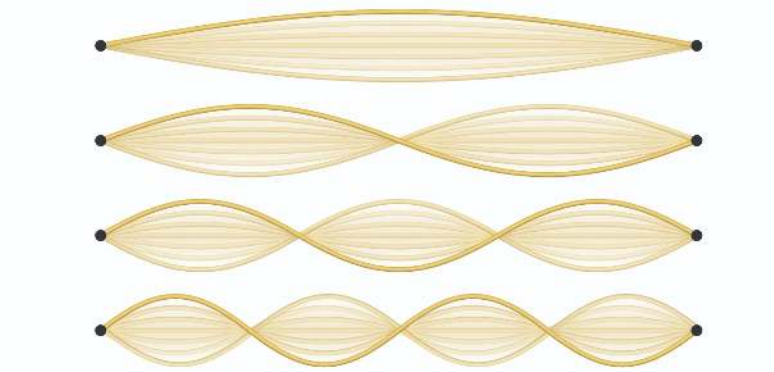


Figure 5.1.6: A vibrating string shows some one-dimensional standing waves. Since the two end points of the string are held fixed, only waves having an integer number of half-wavelengths can form. The points on the string between the end points that are not moving are called the nodes.

An example of two-dimensional standing waves is shown in Figure 5.1.7 which shows the vibrational patterns on a flat surface. Although the vibrational amplitudes cannot be seen like they could in the vibrating string, the nodes have been made visible by sprinkling the drum surface with a powder that collects on the areas of the surface that have minimal displacement. For one-dimensional standing waves, the nodes were points on the line, but for two-dimensional standing waves, the nodes are lines on the surface (for three-dimensional standing waves, the nodes are two-dimensional surfaces within the three-dimensional volume). Because of the circular symmetry of the drum surface, its boundary conditions (the drum surface being tightly constrained to the circumference of the drum) result in two types of nodes: radial nodes that sweep out all angles at constant radii and, thus, are seen as circles about the center, and angular nodes that sweep out all radii at constant angles and, thus, are seen as lines passing through the center. The upper left image in Figure 5.1.7 shows two radial nodes, while the image in the lower right shows the vibrational pattern associated with three radial nodes and two angular nodes.

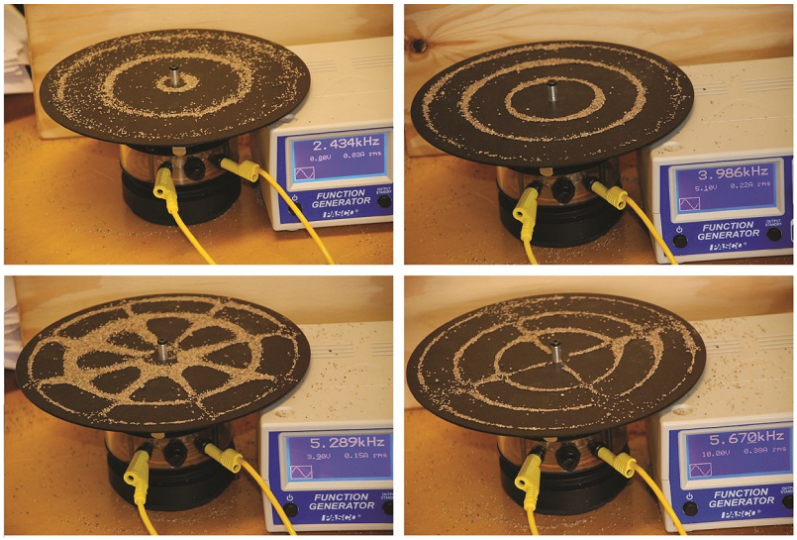


Figure 5.1.7: *Two-dimensional standing waves can be visualized on a vibrating surface. The surface has been sprinkled with a powder that collects near the nodal lines. There are two types of nodes visible: radial nodes (circles) and angular nodes (radii). For a more animated video, check this link out.*

Blackbody Radiation and the Ultraviolet Catastrophe

The last few decades of the nineteenth century witnessed intense research activity in commercializing newly discovered electric lighting. This required obtaining a better understanding of the distributions of light emitted from various sources being considered. Artificial lighting is usually designed to mimic natural sunlight within the limitations of the underlying technology. Such lighting consists of a range of broadly distributed frequencies that form a continuous spectrum. Figure 5.1.8 shows the wavelength

distribution for sunlight. The most intense radiation is in the visible region, with the intensity dropping off rapidly for shorter wavelength ultraviolet (UV) light, and more slowly for longer wavelength infrared (IR) light.

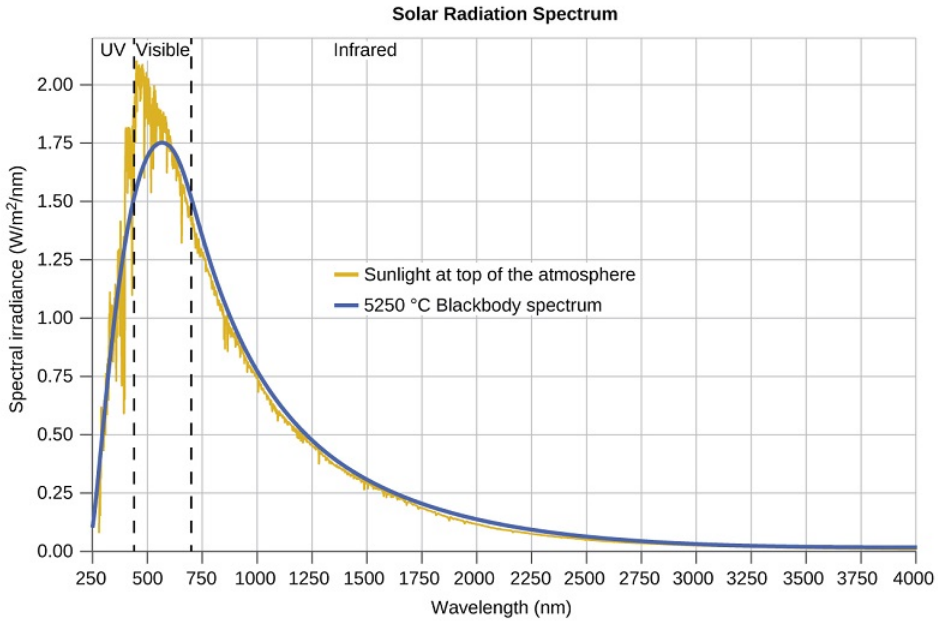


Figure **5.1.8**: The spectral distribution (light intensity vs. wavelength) of sunlight reaches the Earth's atmosphere as UV light, visible light, and IR light. The unabsorbed sunlight at the top of the atmosphere has a distribution that approximately matches the theoretical distribution of a blackbody at 5250 °C, represented by the blue curve. (credit: modification of work by American Society for Testing and Materials (ASTM) Terrestrial Reference Spectra for Photovoltaic Performance Evaluation)

In Figure **5.1.8**, the solar distribution is compared to a representative distribution, called a blackbody spectrum, that corresponds to a temperature of 5250 °C. The blackbody spectrum matches the solar spectrum quite well. A blackbody is a convenient, ideal emitter that approximates the behavior of many materials when heated. It is “ideal” in the same sense that an ideal gas is a convenient, simple representation of real gases that works well, provided that the pressure is not too high nor the temperature too low. A good approximation of a blackbody that can be used to observe blackbody radiation is a metal oven that can be heated to very high temperatures. The oven has a small hole allowing for the light being emitted within the oven to be observed with a spectrometer so that the wavelengths and their intensities can be measured. Figure **5.1.8** shows the resulting curves for some representative temperatures. Each distribution depends only on a single parameter: the temperature. The maxima in the blackbody curves, λ_{max}, shift to shorter wavelengths as the temperature increases, reflecting the observation that metals being heated to high temperatures begin to glow a darker red that becomes brighter as the temperature increases, eventually becoming white hot at very high temperatures as the intensities of all of the visible wavelengths become appreciable. This common observation was at the heart of the first paradox that showed the fundamental limitations of classical physics that we will examine.

Physicists derived mathematical expressions for the blackbody curves using well-accepted concepts from the theories of classical mechanics and classical electromagnetism. The theoretical expressions as functions of temperature fit the observed experimental blackbody curves well at longer wavelengths, but showed significant discrepancies at shorter wavelengths. Not only did the theoretical curves not show a peak, they absurdly showed the intensity becoming infinitely large as the wavelength became smaller, which would imply that everyday objects at room temperature should be emitting large amounts of UV light. This became known as the “ultraviolet catastrophe” because no one could find any problems with the theoretical treatment that could lead to such unrealistic short-wavelength behavior. Finally, around 1900, Max Planck derived a theoretical expression for blackbody radiation that fit the experimental observations exactly (within experimental error). Planck developed his theoretical treatment by extending the earlier work that had been based on the premise that the atoms composing the oven vibrated at increasing frequencies (or decreasing wavelengths) as the temperature increased, with these vibrations being the source of the emitted electromagnetic radiation. But where the earlier treatments had allowed the vibrating atoms to have any energy values obtained from a continuous set of energies (perfectly reasonable, according to classical physics), Planck found that by restricting the vibrational energies to discrete values for each frequency, he could derive an expression for blackbody radiation that correctly had the intensity dropping rapidly for the short wavelengths in the UV region.

$$E = nh\nu,\ n = 1, 2, 3,\ \ldots$$

The quantity h is a constant now known as Planck's constant, in his honor. Although Planck was pleased he had resolved the blackbody radiation paradox, he was disturbed that to do so, he needed to assume the vibrating atoms required quantized energies, which he was unable to explain. The value of Planck's constant is very small, 6.626×10^{-34} joule seconds (J s), which helps explain why energy quantization had not been observed previously in macroscopic phenomena.

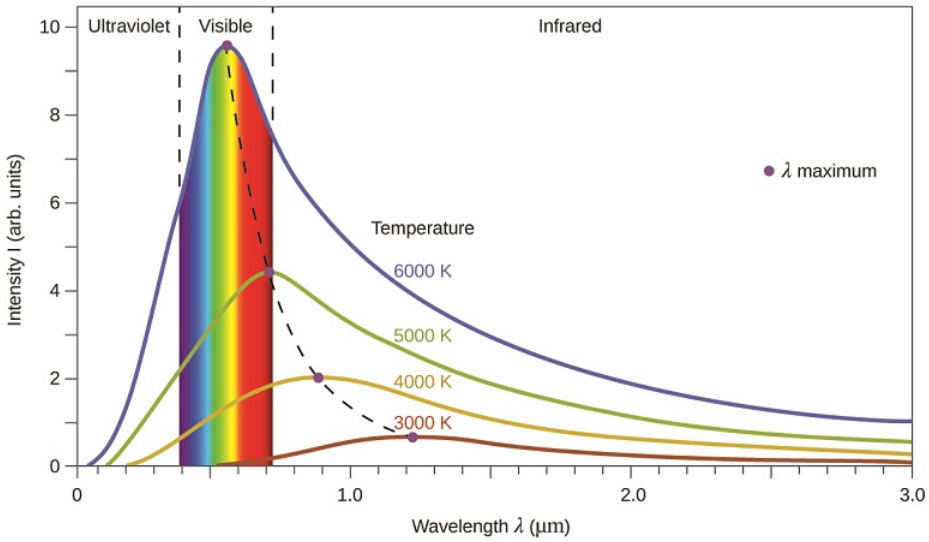


Figure 5.1.9: Blackbody spectral distribution curves are shown for some representative temperatures.

A graph is shown with a horizontal axis labeled, “Wavelength lambda (micrometers)” and a vertical axis labeled, “Intensity I (a r b. units).” The horizontal axis begins at 0 and extends to 3.0 with markings provided every 0.1 micrometer. Similarly, the vertical axis begins at 0 and extends to 10 with markings every 1 unit. Two vertical dashed lines are drawn. The first appears at about 0.39 micrometers and the second at about 0.72 micrometers. To the left of the first of these lines, the label, “Ultraviolet,” appears at the top of the graph. Between these lines, the label, “Visible,” appears at the top of the graph. To the right of the second of these lines, the label, “Infrared,” appears at the top of the graph. To the far right of the graph in open space a purple dot is placed which is labeled, “lambda maximum.” A “Temperature” label is located in a central region of the graph. A blue curve begins on the horizontal axis at about 0.05 micrometers. This curve increases steeply to a maximum value between the two vertical line segments of approximately 9.5 at about 0.55 micrometers. This curve decreases rapidly at first, then tapers off to reach a value of about 1.5 at the far right end of the graph. This blue curve is labeled 6000 K beneath the “Temperature” label. Curves are similarly drawn in green for 5000 K, orange for 4000 K, and red for 3000 K. As the temperature decreases, the height of the peak is lower and shifted right on the graph. The maximum value for the green curve is around 4.5 at 7.2 micrometers. This curve tapers at the right end of the graph to a value around 0.6. The maximum for the orange curve is around 2 at about 0.9 micrometers. This curve tapers at the right end of the graph to a value around 0.2. The maximum for the red curve is around 0.7 at about 1.2 micrometers. This curve tapers at the right end of the graph to a value around 0.1. The entire region under the blue curve that is between the two dashed lines, indicating the visible region, is shaded with vertical bands of color. The colors extending left to right across this region are violet, indigo, blue, green, yellow, orange, and red. A purple dot is placed at the peak of each of the four colored curves. These peaks are connected with a dashed curve.

The Photoelectric Effect

The next paradox in the classical theory to be resolved concerned the photoelectric effect (Figure 5.1.10). It had been observed that electrons could be ejected from the clean surface of a metal when light having a frequency greater than some threshold frequency was shone on it. Surprisingly, the kinetic energy of the ejected electrons did not depend on the brightness of the light, but increased with increasing frequency of the light. Since the electrons in the metal had a certain amount of binding energy keeping them there, the incident light needed to have more energy to free the electrons. According to classical wave theory, a wave's energy depends on its intensity (which depends on its amplitude), not its frequency. One part of these observations was that the number of electrons ejected within in a given time period was seen to increase as the brightness increased. In 1905, Albert Einstein was able to resolve the paradox by incorporating Planck's quantization findings into the discredited particle view of light (Einstein actually won his Nobel prize for this work, and not for his theories of relativity for which he is most famous).

Einstein argued that the quantized energies that Planck had postulated in his treatment of blackbody radiation could be applied to the light in the photoelectric effect so that the light striking the metal surface should not be viewed as a wave, but instead as a stream of particles (later called photons) whose energy depended on their frequency, according to Planck's formula, $E = h\nu$ (or, in terms of wavelength using $c = \nu\lambda$, $E = \frac{hc}{\lambda}$). Electrons were ejected when hit by photons having sufficient energy (a frequency greater than the threshold). The greater the frequency, the greater the kinetic energy imparted to the escaping electrons by the collisions. Einstein also argued that the light intensity did not depend on the amplitude of the incoming wave, but instead corresponded to the number of photons striking the surface within a given time period. This explains why the number of ejected electrons increased with increasing brightness, since the greater the number of incoming photons, the greater the likelihood that they would collide with some of the electrons.

With Einstein's findings, the nature of light took on a new air of mystery. Although many light phenomena could be explained either in terms of waves or particles, certain phenomena, such as the interference patterns obtained when light passed through a double slit, were completely contrary to a particle view of light, while other phenomena, such as the photoelectric effect, were completely contrary to a wave view of light. Somehow, at a deep fundamental level still not fully understood, light is both wavelike and particle-like. This is known as wave-particle duality.

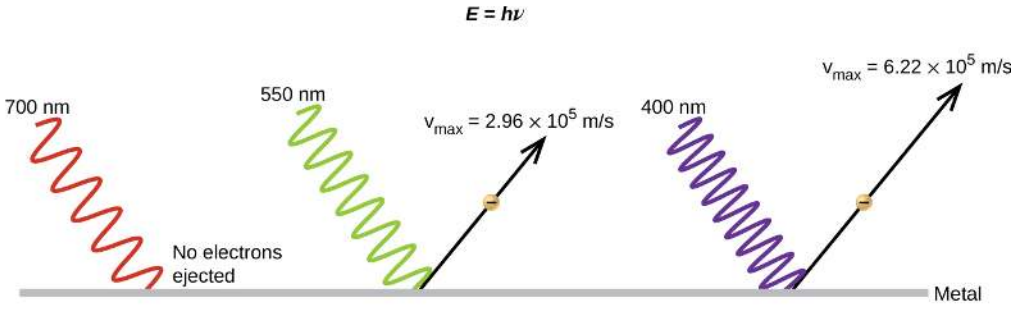


Figure **5.1.10**: Photons with low frequencies do not have enough energy to cause electrons to be ejected via the photoelectric effect. For any frequency of light above the threshold frequency, the kinetic energy of an ejected electron will increase linearly with the energy of the incoming photon.

The figure includes three diagrams of waves approaching a flat, horizontal surface that is labeled, “Metal,” from an angle around 45 degrees above and to the left relative to the surface. At the top of the diagram at the center is the label, “E equals h nu.” At the left, a sinusoidal wave reaches the surface and stops. The portion of the diagram near the flat metal surface is labeled, “No electrons ejected,” and the wave is labeled, “700 n m.” To the right, a second similar, more compressed wave, which is labeled, “550 n m,” reaches the flat surface. This time, an arrow extends up and to the right at an angle of approximately 45 degrees. A tiny yellow circle with a negative sign in it is at the center of the arrow shaft. Above this arrow is the equation, “v subscript max equals 2.96 times 10 superscript 5 m per s.” To the far right, a third similar, even more compressed wave, which is labeled “400 n m” reaches the flat surface. This time, an arrow extends up and to the right at an angle of approximately 45 degrees. A tiny yellow circle with a negative sign in it is at the center of the arrow shaft. Above this arrow is the equation “v subscript max equals 6.22 times 10 superscript 5 m per s.”

Example 5.1.2: Calculating the Energy of Radiation

When we see light from a neon sign, we are observing radiation from excited neon atoms. If this radiation has a wavelength of 640 nm, what is the energy of the photon being emitted?

Solution

We use the part of Planck's equation that includes the wavelength, λ, and convert units of nanometers to meters so that the units of λ and c are the same.

$$E = \frac{hc}{\lambda}$$

$$= \frac{(6.626 \times 10^{-34}\ \text{J}\cancel{\text{s}})(2.998 \times 10^{8}\ \text{m}\cancel{\text{s}^{-1}})}{(640\ \cancel{\text{nm}})\left(\frac{1\ \text{m}}{10^{9}\ \cancel{\text{nm}}}\right)}$$

$$= 3.10 \times 10^{-19}\ \text{J}$$

? Exercise 5.1.2

The microwaves in an oven are of a specific frequency that will heat the water molecules contained in food. (This is why most plastics and glass do not become hot in a microwave oven-they do not contain water molecules.) This frequency is about 3×10^9 Hz. What is the energy of one photon in these microwaves?

Answer

2×10^{-24} J

✓ Example 5.1.3: Photoelectric Effect

Identify which of the following statements are false and, where necessary, change the italicized word or phrase to make them true, consistent with Einstein's explanation of the photoelectric effect.

a. Increasing the brightness of incoming light *increases* the kinetic energy of the ejected electrons.
b. Increasing the *wavelength* of incoming light increases the kinetic energy of the ejected electrons.
c. Increasing the brightness of incoming light *increases* the number of ejected electrons.
d. Increasing the *frequency* of incoming light can increase the number of ejected electrons.

Solution

a. False. Increasing the brightness of incoming light *has no effect* on the kinetic energy of the ejected electrons. Only energy, not the number or amplitude, of the photons influences the kinetic energy of the electrons.
b. False. Increasing the *frequency* of incoming light increases the kinetic energy of the ejected electrons. Frequency is proportional to energy and inversely proportional to wavelength. Frequencies above the threshold value transfer the excess energy into the kinetic energy of the electrons.
c. True. Because the number of collisions with photons increases with brighter light, the number of ejected electrons increases.
d. True with regard to the threshold energy binding the electrons to the metal. Below this threshold, electrons are not emitted and above it they are. Once over the threshold value, further increasing the frequency does not increase the number of ejected electrons

? Exercise 5.1.3

Calculate the threshold energy in kJ/mol of electrons in aluminum, given that the lowest frequency photon for which the photoelectric effect is observed is $9.87 \times 10^{14}\ Hz$.

Answer

$3.94\ kJ/mol$

Line Spectra

Another paradox within the classical electromagnetic theory that scientists in the late nineteenth century struggled with concerned the light emitted from atoms and molecules. When solids, liquids, or condensed gases are heated sufficiently, they radiate some of the excess energy as light. Photons produced in this manner have a range of energies, and thereby produce a continuous spectrum in which an unbroken series of wavelengths is present. Most of the light generated from stars (including our sun) is produced in this fashion. You can see all the visible wavelengths of light present in sunlight by using a prism to separate them. As can be seen in Figure 5.1.8, sunlight also contains UV light (shorter wavelengths) and IR light (longer wavelengths) that can be detected using instruments but that are invisible to the human eye. Incandescent (glowing) solids such as tungsten filaments in incandescent lights also give off light that contains all wavelengths of visible light. These continuous spectra can often be approximated by blackbody radiation curves at some appropriate temperature, such as those shown in Figure 5.1.9.

In contrast to continuous spectra, light can also occur as discrete or line spectra having very narrow line widths interspersed throughout the spectral regions such as those shown in Figure **5.1.5**. Exciting a gas at low partial pressure using an electrical current, or heating it, will produce line spectra. Fluorescent light bulbs and neon signs operate in this way (Figure **5.1.11**). Each element displays its own characteristic set of lines, as do molecules, although their spectra are generally much more complicated.



Figure **5.1.11**: Neon signs operate by exciting a gas at low partial pressure using an electrical current. This sign shows the elaborate artistic effects that can be achieved. (credit: Dave Shaver)

Each emission line consists of a single wavelength of light, which implies that the light emitted by a gas consists of a set of discrete energies. For example, when an electric discharge passes through a tube containing hydrogen gas at low pressure, the H_2 molecules are broken apart into separate H atoms, and we see a blue-pink color. Passing the light through a prism produces a line spectrum, indicating that this light is composed of photons of four visible wavelengths, as shown in Figure **5.1.12**.

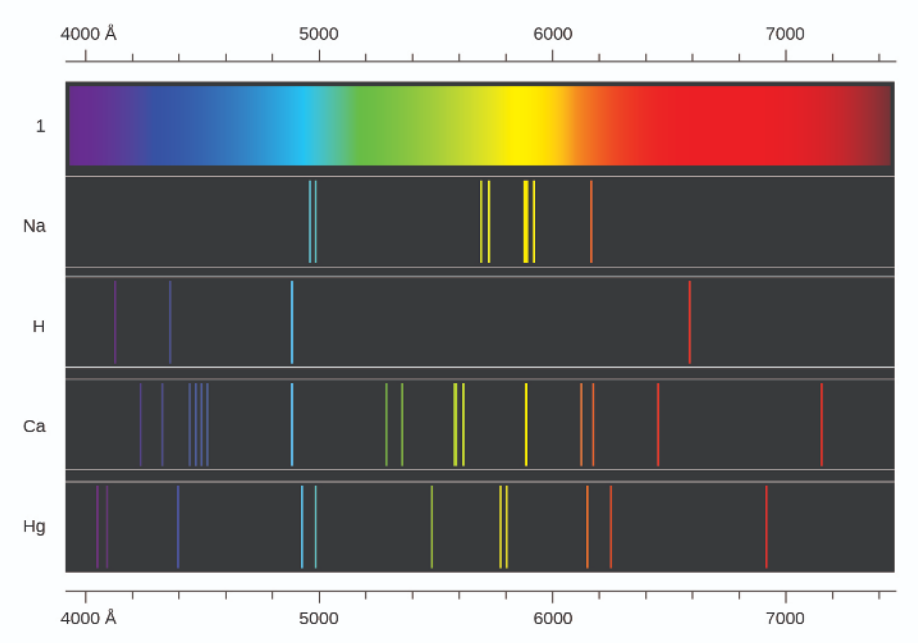


Figure 5.1.12: Line spectra of select gas. Compare the two types of emission spectra: continuous spectrum of white light (top) and the line spectra of the light from excited sodium, hydrogen, calcium, and mercury atoms.

An image is shown with 5 rows. Across the top and bottom of the image is a scale that begins at 4000 angstroms at the left and extends to 740 angstroms at the far right. The top row is a continuous band of the visible spectrum, showing the colors from violet at the far left through indigo, blue, green, yellow, orange, and red at the far right. The second row, labeled, “N a,” shows the emission spectrum for the element sodium, which includes two narrow vertical bands in the blue range, two narrow bands in the yellow-green range, two narrow bands in the yellow range, and one narrow band in the orange range. The third row, labeled, “H,” shows the emission spectrum for hydrogen. This spectrum shows single bands in the violet, indigo, blue, and orange regions. The fourth row, labeled, “C a,” shows the emission spectrum for calcium. This spectrum shows bands in the following colors and frequencies; one violet, five indigo, one blue, two green, two yellow-green, one yellow, two yellow-orange, one orange, and one red. The fifth row, labeled, “H g,” shows the emission spectrum for mercury. This spectrum shows bands in the following colors and frequencies; two violet, one indigo, two blue, one green, two yellow, two orange, and one orange-red. It is important to note that each of the color bands for the emission spectra of the elements matches to a specific wavelength of light. Extending a vertical line from the bands to the scale above or below the diagram will match the band to a specific measurement on the scale.

The origin of discrete spectra in atoms and molecules was extremely puzzling to scientists in the late nineteenth century, since according to classical electromagnetic theory, only continuous spectra should be observed. Even more puzzling, in 1885, Johann Balmer was able to derive an empirical equation that related the four visible wavelengths of light emitted by hydrogen atoms to whole integers. That equation is the following one, in which k is a constant:

$$\frac{1}{\lambda} = k\left(\frac{1}{4} - \frac{1}{n^2}\right), \; n = 3,\, 4,\, 5,\, 6$$

Other discrete lines for the hydrogen atom were found in the UV and IR regions. Johannes Rydberg generalized Balmer's work and developed an empirical formula that predicted all of hydrogen's emission lines, not just those restricted to the visible range, where, n_1 and n_2 are integers, $n_1 < n_2$, and R_∞ is the Rydberg constant ($1.097 \times 10^7\ \mathrm{m}^{-1}$).

$$\frac{1}{\lambda} = R_\infty\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Even in the late nineteenth century, spectroscopy was a very precise science, and so the wavelengths of hydrogen were measured to very high accuracy, which implied that the Rydberg constant could be determined very precisely as well. That such a simple formula as the Rydberg formula could account for such precise measurements seemed astounding at the time, but it was the eventual explanation for emission spectra by Neils Bohr in 1913 that ultimately convinced scientists to abandon classical physics and spurred the development of modern quantum mechanics.

Summary

Light and other forms of electromagnetic radiation move through a vacuum with a constant speed, c, of 2.998×10^8 m s^{-1}. This radiation shows wavelike behavior, which can be characterized by a frequency, ν, and a wavelength, λ, such that $c = \lambda\nu$. Light is an example of a travelling wave. Other important wave phenomena include standing waves, periodic oscillations, and vibrations. Standing waves exhibit quantization, since their wavelengths are limited to discrete integer multiples of some characteristic lengths. Electromagnetic radiation that passes through two closely spaced narrow slits having dimensions roughly similar to the wavelength will show an interference pattern that is a result of constructive and destructive interference of the waves. Electromagnetic radiation also demonstrates properties of particles called photons. The energy of a photon is related to the frequency (or alternatively, the wavelength) of the radiation as $E = h\nu$ (or $\boldsymbol{E = \frac{hc}{\lambda}}$), where h is Planck's constant. That light demonstrates both wavelike and particle-like behavior is known as wave-particle duality. All forms of electromagnetic radiation share these properties, although various forms including X-rays, visible light, microwaves, and radio waves interact differently with matter and have very different practical applications. Electromagnetic radiation can be generated by exciting matter to higher energies, such as by heating it. The emitted light can be either continuous (incandescent sources like the sun) or discrete (from specific types of excited atoms). Continuous spectra often have distributions that can be approximated as blackbody radiation at some appropriate temperature. The line spectrum of hydrogen can be obtained by passing the light from an electrified tube of hydrogen gas through a prism. This line spectrum was simple enough that an empirical formula called the Rydberg formula could be derived from the spectrum. Three historically important paradoxes from the late 19th and early 20th centuries that could not be explained within the existing framework of classical mechanics and classical electromagnetism were the blackbody problem, the photoelectric effect, and the discrete spectra of atoms. The resolution of these paradoxes ultimately led to quantum theories that superseded the classical theories.

Key Equations

- $c = \lambda\nu$
- $\boldsymbol{E = h\nu = \frac{hc}{\lambda}}$, where $h = 6.626 \times 10^{-34}$ J s
- $\boldsymbol{\frac{1}{\lambda} = R_\infty \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)}$

Glossary

amplitude
extent of the displacement caused by a wave (for sinusoidal waves, it is one-half the difference from the peak height to the trough depth, and the intensity is proportional to the square of the amplitude)

blackbody
idealized perfect absorber of all incident electromagnetic radiation; such bodies emit electromagnetic radiation in characteristic continuous spectra called blackbody radiation

continuous spectrum
electromagnetic radiation given off in an unbroken series of wavelengths (e.g., white light from the sun)

electromagnetic radiation
energy transmitted by waves that have an electric-field component and a magnetic-field component

electromagnetic spectrum
range of energies that electromagnetic radiation can comprise, including radio, microwaves, infrared, visible, ultraviolet, X-rays, and gamma rays; since electromagnetic radiation energy is proportional to the frequency and inversely proportional to the wavelength, the spectrum can also be specified by ranges of frequencies or wavelengths

frequency (ν)
number of wave cycles (peaks or troughs) that pass a specified point in space per unit time

hertz (Hz)
the unit of frequency, which is the number of cycles per second, s^{-1}

intensity
property of wave-propagated energy related to the amplitude of the wave, such as brightness of light or loudness of sound

interference pattern
pattern typically consisting of alternating bright and dark fringes; it results from constructive and destructive interference of waves

line spectrum
electromagnetic radiation emitted at discrete wavelengths by a specific atom (or atoms) in an excited state

node
any point of a standing wave with zero amplitude

photon
smallest possible packet of electromagnetic radiation, a particle of light

quantization
occurring only in specific discrete values, not continuous

standing wave
(also, stationary wave) localized wave phenomenon characterized by discrete wavelengths determined by the boundary conditions used to generate the waves; standing waves are inherently quantized

wave
oscillation that can transport energy from one point to another in space

wavelength (λ)
distance between two consecutive peaks or troughs in a wave

wave-particle duality
term used to describe the fact that elementary particles including matter exhibit properties of both particles (including localized position, momentum) and waves (including nonlocalization, wavelength, frequency)

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5.2: Electronic Structure of Atoms (Electron Configurations)

Learning Objectives

- Derive the predicted ground-state electron configurations of atoms
- Identify and explain exceptions to predicted electron configurations for atoms and ions
- Relate electron configurations to element classifications in the periodic table

Having introduced the basics of atomic structure and quantum mechanics, we can use our understanding of quantum numbers to determine how atomic orbitals relate to one another. This allows us to determine which orbitals are occupied by electrons in each atom. The specific arrangement of electrons in orbitals of an atom determines many of the chemical properties of that atom.

Orbital Energies and Atomic Structure

The energy of atomic orbitals increases as the principal quantum number, n, increases. In any atom with two or more electrons, the repulsion between the electrons makes energies of subshells with different values of l differ so that the energy of the orbitals increases within a shell in the order $s < p < d < f$. Figure 5.2.1 depicts how these two trends in increasing energy relate. The 1*s* orbital at the bottom of the diagram is the orbital with electrons of lowest energy. The energy increases as we move up to the 2*s* and then 2*p*, 3*s*, and 3*p* orbitals, showing that the increasing *n* value has more influence on energy than the increasing *l* value for small atoms. However, this pattern does not hold for larger atoms. The 3*d* orbital is higher in energy than the 4*s* orbital. Such overlaps continue to occur frequently as we move up the chart.

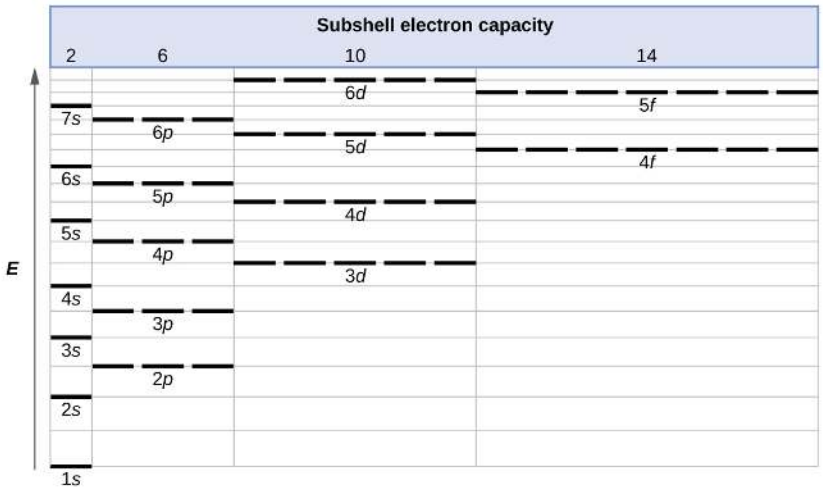


Figure 5.2.1: Generalized energy-level diagram for atomic orbitals in an atom with two or more electrons (not to scale).

Electrons in successive atoms on the periodic table tend to fill low-energy orbitals first. Thus, many students find it confusing that, for example, the 5*p* orbitals fill immediately after the 4*d*, and immediately before the 6*s*. The filling order is based on observed experimental results, and has been confirmed by theoretical calculations. As the principal quantum number, *n*, increases, the size of the orbital increases and the electrons spend more time farther from the nucleus. Thus, the attraction to the nucleus is weaker and the energy associated with the orbital is higher (less stabilized). But this is not the only effect we have to take into account. Within each shell, as the value of *l* increases, the electrons are less penetrating (meaning there is less electron density found close to the nucleus), in the order $s > p > d > f$. Electrons that are closer to the nucleus slightly repel electrons that are farther out, offsetting the more dominant electron–nucleus attractions slightly (recall that all electrons have −1 charges, but nuclei have +*Z* charges). This phenomenon is called shielding and will be discussed in more detail in the next section. Electrons in orbitals that experience more shielding are less stabilized and thus higher in energy. For small orbitals (1*s* through 3*p*), the increase in energy due to *n* is more significant than the increase due to *l*; however, for larger orbitals the two trends are comparable and cannot be simply predicted. We will discuss methods for remembering the observed order.

The arrangement of electrons in the orbitals of an atom is called the electron configuration of the atom. We describe an electron configuration with a symbol that contains three pieces of information (Figure 5.2.2):

1. The number of the principal quantum shell, n,
2. The letter that designates the orbital type (the subshell, l), and
3. A superscript number that designates the number of electrons in that particular subshell.

For example, the notation $2p^4$ (read "two–p–four") indicates four electrons in a p subshell (l = 1) with a principal quantum number (n) of 2. The notation $3d^8$ (read "three–d–eight") indicates eight electrons in the d subshell (i.e., l = 2) of the principal shell for which n = 3.

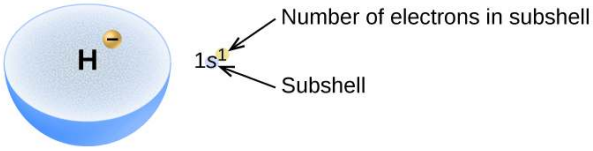


Figure **5.2.2**: The diagram of an electron configuration specifies the subshell (n and l value, with letter symbol) and superscript number of electrons.

The Aufbau Principle

To determine the electron configuration for any particular atom, we can “build” the structures in the order of atomic numbers. Beginning with hydrogen, and continuing across the periods of the periodic table, we add one proton at a time to the nucleus and one electron to the proper subshell until we have described the electron configurations of all the elements. This procedure is called the Aufbau principle, from the German word *Aufbau* (“to build up”). Each added electron occupies the subshell of lowest energy available (in the order shown in Figure **5.2.3**), subject to the limitations imposed by the allowed quantum numbers according to the Pauli exclusion principle. Electrons enter higher-energy subshells only after lower-energy subshells have been filled to capacity. Figure **5.2.3** illustrates the traditional way to remember the filling order for atomic orbitals.

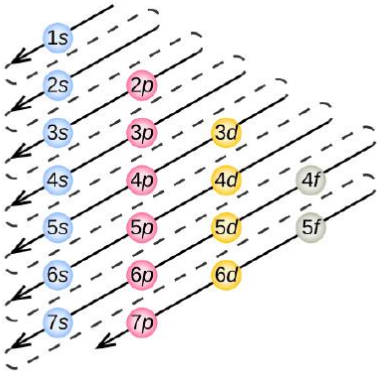


Figure **5.2.3**: The arrow leads through each subshell in the appropriate filling order for electron configurations. This chart is straightforward to construct. Simply make a column for all the s orbitals with each n shell on a separate row. Repeat for p, d, and f. Be sure to only include orbitals allowed by the quantum numbers (no 1p or 2d, and so forth). Finally, draw diagonal lines from top to bottom as shown.

Since the arrangement of the periodic table is based on the electron configurations, Figure **5.2.4** provides an alternative method for determining the electron configuration. The filling order simply begins at hydrogen and includes each subshell as you proceed in increasing Z order. For example, after filling the 3p block up to Ar, we see the orbital will be 4s (K, Ca), followed by the 3d orbitals.

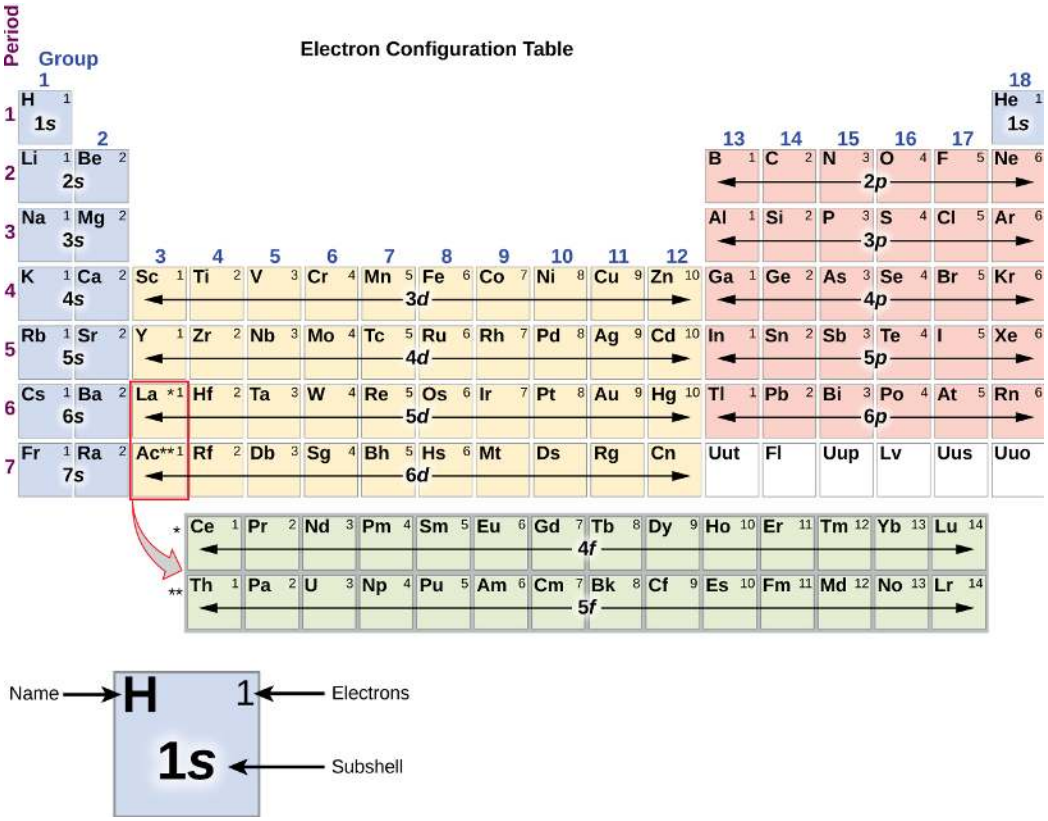
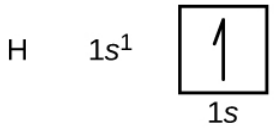
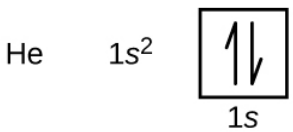


Figure 5.2.4: This periodic table shows the electron configuration for each subshell. By "building up" from hydrogen, this table can be used to determine the electron configuration for any atom on the periodic table.

We will now construct the ground-state electron configuration and orbital diagram for a selection of atoms in the first and second periods of the periodic table. Orbital diagrams are pictorial representations of the electron configuration, showing the individual orbitals and the pairing arrangement of electrons. We start with a single hydrogen atom (atomic number 1), which consists of one proton and one electron. Referring to either Figure 5.2.3 or 5.2.4, we would expect to find the electron in the 1*s* orbital. By convention, the $m_s = +\frac{1}{2}$ value is usually filled first. The electron configuration and the orbital diagram are:



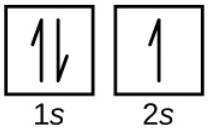
Following hydrogen is the noble gas helium, which has an atomic number of 2. The helium atom contains two protons and two electrons. The first electron has the same four quantum numbers as the hydrogen atom electron (n = 1, l = 0, m_l = 0, $m_s = +\frac{1}{2}$). The second electron also goes into the 1*s* orbital and fills that orbital. The second electron has the same n, l, and m_l quantum numbers, but must have the opposite spin quantum number, $m_s = -\frac{1}{2}$. This is in accord with the Pauli exclusion principle: No two electrons in the same atom can have the same set of four quantum numbers. For orbital diagrams, this means two arrows go in each box (representing two electrons in each orbital) and the arrows must point in opposite directions (representing paired spins). The electron configuration and orbital diagram of helium are:



The n = 1 shell is completely filled in a helium atom.

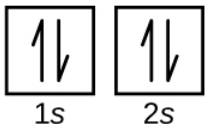
The next atom is the alkali metal lithium with an atomic number of 3. The first two electrons in lithium fill the 1*s* orbital and have the same sets of four quantum numbers as the two electrons in helium. The remaining electron must occupy the orbital of next lowest energy, the 2*s* orbital (Figure **5.2.3** or **5.2.4**). Thus, the electron configuration and orbital diagram of lithium are:

Li $1s^2 2s^1$



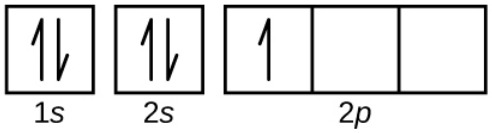
An atom of the alkaline earth metal beryllium, with an atomic number of 4, contains four protons in the nucleus and four electrons surrounding the nucleus. The fourth electron fills the remaining space in the 2*s* orbital.

Be $1s^2 2s^2$



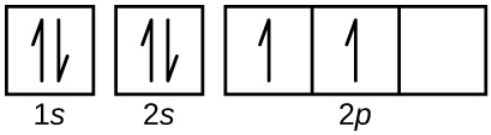
An atom of boron (atomic number 5) contains five electrons. The $n = 1$ shell is filled with two electrons and three electrons will occupy the $n = 2$ shell. Because any *s* subshell can contain only two electrons, the fifth electron must occupy the next energy level, which will be a 2*p* orbital. There are three degenerate 2*p* orbitals ($m_l = -1, 0, +1$) and the electron can occupy any one of these *p* orbitals. When drawing orbital diagrams, we include empty boxes to depict any empty orbitals in the same subshell that we are filling.

B $1s^2 2s^2 2p^1$



Carbon (atomic number 6) has six electrons. Four of them fill the 1*s* and 2*s* orbitals. The remaining two electrons occupy the 2*p* subshell. We now have a choice of filling one of the 2*p* orbitals and pairing the electrons or of leaving the electrons unpaired in two different, but degenerate, *p* orbitals. The orbitals are filled as described by Hund's rule: the lowest-energy configuration for an atom with electrons within a set of degenerate orbitals is that having the maximum number of unpaired electrons. Thus, the two electrons in the carbon 2*p* orbitals have identical *n*, *l*, and m_s quantum numbers and differ in their m_l quantum number (in accord with the Pauli exclusion principle). The electron configuration and orbital diagram for carbon are:

C $1s^2 2s^2 2p^2$



Nitrogen (atomic number 7) fills the 1*s* and 2*s* subshells and has one electron in each of the three 2*p* orbitals, in accordance with Hund's rule. These three electrons have unpaired spins. Oxygen (atomic number 8) has a pair of electrons in any one of the 2*p* orbitals (the electrons have opposite spins) and a single electron in each of the other two. Fluorine (atomic number 9) has only one 2*p* orbital containing an unpaired electron. All of the electrons in the noble gas neon (atomic number 10) are paired, and all of the orbitals in the $n = 1$ and the $n = 2$ shells are filled. The electron configurations and orbital diagrams of these four elements are:

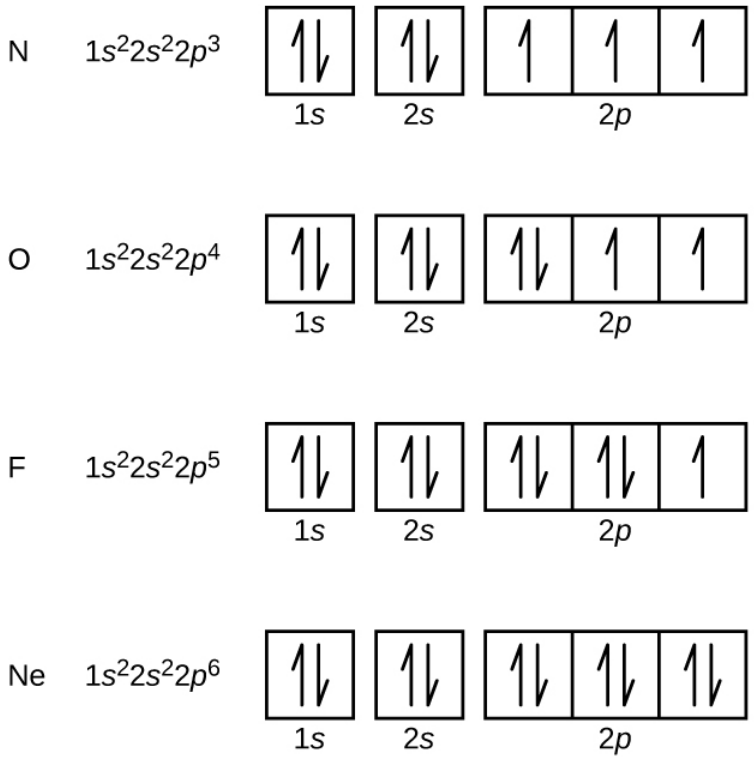


Figure 5.2.5: Since the core electron shells correspond to noble gas electron configurations, we can abbreviate electron configurations by writing the noble gas that matches the core electron configuration, along with the valence electrons in a condensed format. For our sodium example, the symbol [Ne] represents core electrons, ($1s^2 2s^2 2p^6$) and our abbreviated or condensed configuration is [Ne]$3s^1$.

The alkali metal sodium (atomic number 11) has one more electron than the neon atom. This electron must go into the lowest-energy subshell available, the 3*s* orbital, giving a $1s^2 2s^2 2p^6 3s^1$ configuration. The electrons occupying the outermost shell orbital(s) (highest value of *n*) are called valence electrons, and those occupying the inner shell orbitals are called core electrons (Figure \PageIndex5\PageIndex5). Since the core electron shells correspond to noble gas electron configurations, we can abbreviate electron configurations by writing the noble gas that matches the core electron configuration, along with the valence electrons in a condensed format. For our sodium example, the symbol [Ne] represents core electrons, ($1s^2 2s^2 2p^6$) and our abbreviated or condensed configuration is [Ne]$3s^1$.

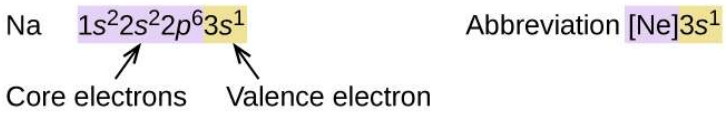


Figure 5.2.5: A core-abbreviated electron configuration (right) replaces the core electrons with the noble gas symbol whose configuration matches the core electron configuration of the other element.

Similarly, the abbreviated configuration of lithium can be represented as [He]$2s^1$, where [He] represents the configuration of the helium atom, which is identical to that of the filled inner shell of lithium. Writing the configurations in this way emphasizes the similarity of the configurations of lithium and sodium. Both atoms, which are in the alkali metal family, have only one electron in a valence *s* subshell outside a filled set of inner shells.

$$\textbf{Li : [He]}\ 2s^1$$
$$\textbf{Na : [Ne]}\ 3s^1$$

The alkaline earth metal magnesium (atomic number 12), with its 12 electrons in a [Ne]$3s^2$ configuration, is analogous to its family member beryllium, [He]$2s^2$. Both atoms have a filled *s* subshell outside their filled inner shells. Aluminum (atomic number 13), with 13 electrons and the electron configuration [Ne]$3s^2 3p^1$, is analogous to its family member boron, [He]$2s^2 2p^1$.

The electron configurations of silicon (14 electrons), phosphorus (15 electrons), sulfur (16 electrons), chlorine (17 electrons), and argon (18 electrons) are analogous in the electron configurations of their outer shells to their corresponding family members carbon, nitrogen, oxygen, fluorine, and neon, respectively, except that the principal quantum number of the outer shell of the heavier elements has increased by one to $n = 3$. Figure **5.2.6** shows the lowest energy, or ground-state, electron configuration for these elements as well as that for atoms of each of the known elements.

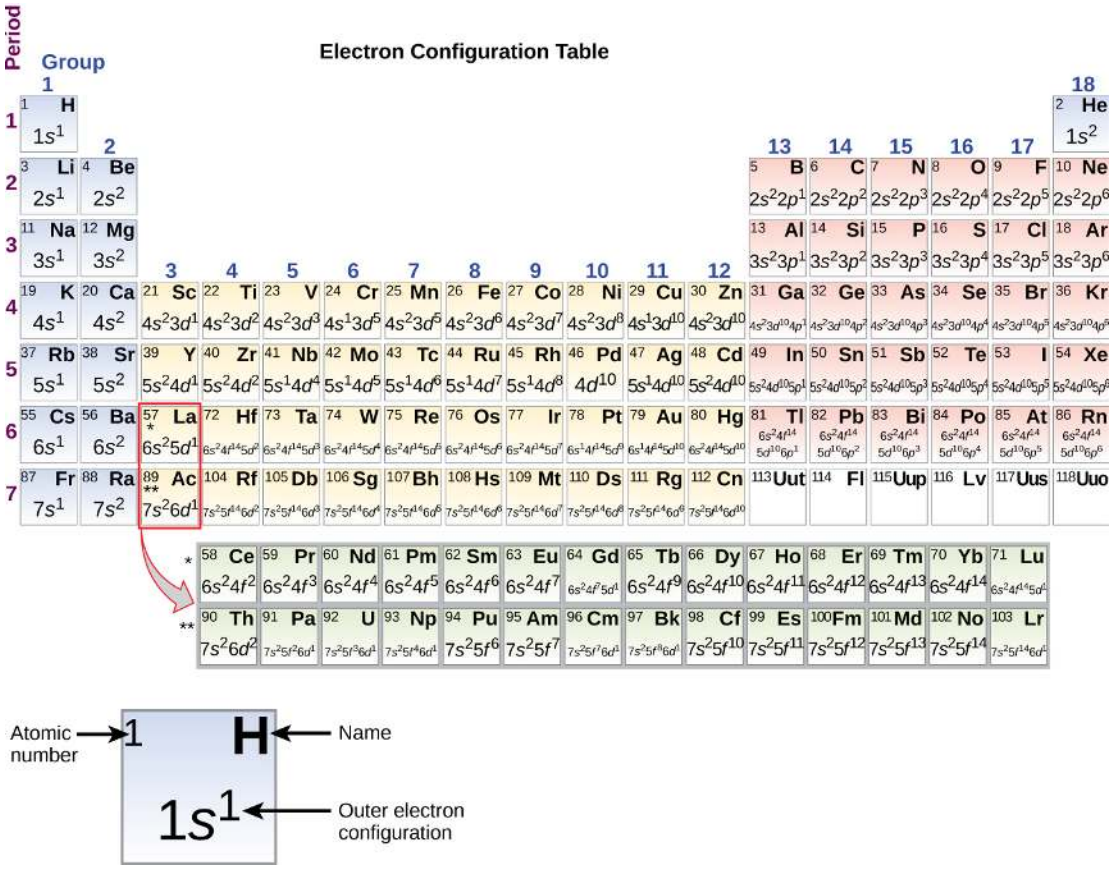


Figure **5.2.6**: This version of the periodic table shows the outer-shell electron configuration of each element. Note that down each group, the configuration is often similar.

When we come to the next element in the periodic table, the alkali metal potassium (atomic number 19), we might expect that we would begin to add electrons to the 3*d* subshell. However, all available chemical and physical evidence indicates that potassium is like lithium and sodium, and that the next electron is not added to the 3*d* level but is, instead, added to the 4*s* level (Figure **5.2.3** or **5.2.4**). As discussed previously, the 3*d* orbital with no radial nodes is higher in energy because it is less penetrating and more shielded from the nucleus than the 4*s*, which has three radial nodes. Thus, potassium has an electron configuration of $[Ar]4s^1$. Hence, potassium corresponds to Li and Na in its valence shell configuration. The next electron is added to complete the 4*s* subshell and calcium has an electron configuration of $[Ar]4s^2$. This gives calcium an outer-shell electron configuration corresponding to that of beryllium and magnesium.

Beginning with the transition metal scandium (atomic number 21), additional electrons are added successively to the 3*d* subshell. This subshell is filled to its capacity with 10 electrons (remember that for $l = 2$ [*d* orbitals], there are $2l + 1 = 5$ values of m_l, meaning that there are five *d* orbitals that have a combined capacity of 10 electrons). The 4*p* subshell fills next. Note that for three series of elements, scandium (Sc) through copper (Cu), yttrium (Y) through silver (Ag), and lutetium (Lu) through gold (Au), a total of 10 *d* electrons are successively added to the $(n - 1)$ shell next to the *n* shell to bring that $(n - 1)$ shell from 8 to 18 electrons. For two series, lanthanum (La) through lutetium (Lu) and actinium (Ac) through lawrencium (Lr), 14 *f* electrons ($l = 3$, $2l + 1 = 7$ m_l values; thus, seven orbitals with a combined capacity of 14 electrons) are successively added to the $(n - 2)$ shell to bring that shell from 18 electrons to a total of 32 electrons.

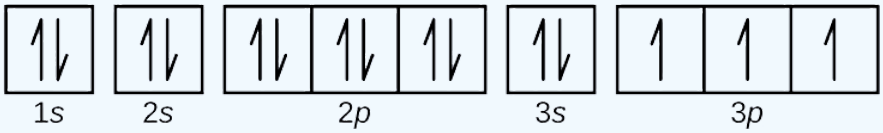
Example 5.2.1: Quantum Numbers and Electron Configurations

What is the electron configuration and orbital diagram for a phosphorus atom? What are the four quantum numbers for the last electron added?

Solution

The atomic number of phosphorus is 15. Thus, a phosphorus atom contains 15 electrons. The order of filling of the energy levels is 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, . . . The 15 electrons of the phosphorus atom will fill up to the 3*p* orbital, which will contain three electrons:

P $1s^2 2s^2 2p^6 3s^2 3p^3$



The last electron added is a 3*p* electron. Therefore, $n = 3$ and, for a *p*-type orbital, $l = 1$. The m_l value could be –1, 0, or +1. The three *p* orbitals are degenerate, so any of these m_l values is correct. For unpaired electrons, convention assigns the value of $+\frac{1}{2}$ for the spin quantum number; thus, $m_s = +\frac{1}{2}$.

Exercise 5.2.1

Identify the atoms from the electron configurations given:

a. $[Ar]4s^2 3d^5$
b. $[Kr]5s^2 4d^{10} 5p^6$

Answer a

Mn

Answer b

Xe

The periodic table can be a powerful tool in predicting the electron configuration of an element. However, we do find exceptions to the order of filling of orbitals that are shown in Figure **5.2.3** or **5.2.4**. For instance, the electron configurations of the transition metals chromium (Cr; atomic number 24) and copper (Cu; atomic number 29), among others, are not those we would expect. In general, such exceptions involve subshells with very similar energy, and small effects can lead to changes in the order of filling.

In the case of Cr and Cu, we find that half-filled and completely filled subshells apparently represent conditions of preferred stability. This stability is such that an electron shifts from the 4*s* into the 3*d* orbital to gain the extra stability of a half-filled 3*d* subshell (in Cr) or a filled 3*d* subshell (in Cu). Other exceptions also occur. For example, niobium (Nb, atomic number 41) is predicted to have the electron configuration $[Kr]5s^2 4d^3$. Experimentally, we observe that its ground-state electron configuration is actually $[Kr]5s^1 4d^4$. We can rationalize this observation by saying that the electron–electron repulsions experienced by pairing the electrons in the 5*s* orbital are larger than the gap in energy between the 5*s* and 4*d* orbitals. There is no simple method to predict the exceptions for atoms where the magnitude of the repulsions between electrons is greater than the small differences in energy between subshells.

Electron Configurations and the Periodic Table

As described earlier, the periodic table arranges atoms based on increasing atomic number so that elements with the same chemical properties recur periodically. When their electron configurations are added to the table (Figure **5.2.6**), we also see a periodic recurrence of similar electron configurations in the outer shells of these elements. Because they are in the outer shells of an atom, valence electrons play the most important role in chemical reactions. The outer electrons have the highest energy of the electrons in

an atom and are more easily lost or shared than the core electrons. Valence electrons are also the determining factor in some physical properties of the elements.

Elements in any one group (or column) have the same number of valence electrons; the alkali metals lithium and sodium each have only one valence electron, the alkaline earth metals beryllium and magnesium each have two, and the halogens fluorine and chlorine each have seven valence electrons. The similarity in chemical properties among elements of the same group occurs because they have the same number of valence electrons. It is the loss, gain, or sharing of valence electrons that defines how elements react.

It is important to remember that the periodic table was developed on the basis of the chemical behavior of the elements, well before any idea of their atomic structure was available. Now we can understand why the periodic table has the arrangement it has—the arrangement puts elements whose atoms have the same number of valence electrons in the same group. This arrangement is emphasized in Figure **5.2.6**, which shows in periodic-table form the electron configuration of the last subshell to be filled by the Aufbau principle. The colored sections of Figure **5.2.6** show the three categories of elements classified by the orbitals being filled: main group, transition, and inner transition elements. These classifications determine which orbitals are counted in the valence shell, or highest energy level orbitals of an atom.

1. **Main group elements** (sometimes called **representative elements**) are those in which the last electron added enters an *s* or a *p* orbital in the outermost shell, shown in blue and red in Figure **5.2.6**. This category includes all the nonmetallic elements, as well as many metals and the intermediate semimetallic elements. The valence electrons for main group elements are those with the highest *n* level. For example, gallium (Ga, atomic number 31) has the electron configuration [Ar]$\underline{4s^2}3d^{10}\underline{4p^1}$, which contains three valence electrons (underlined). The completely filled *d* orbitals count as core, not valence, electrons.
2. **Transition elements or transition metals**. These are metallic elements in which the last electron added enters a *d* orbital. The valence electrons (those added after the last noble gas configuration) in these elements include the *ns* and $(n - 1)$ *d* electrons. The official IUPAC definition of transition elements specifies those with partially filled *d* orbitals. Thus, the elements with completely filled orbitals (Zn, Cd, Hg, as well as Cu, Ag, and Au in Figure **5.2.6**) are not technically transition elements. However, the term is frequently used to refer to the entire *d* block (colored yellow in Figure **5.2.6**), and we will adopt this usage in this textbook.
3. **Inner transition elements** are metallic elements in which the last electron added occupies an *f* orbital. They are shown in green in Figure **5.2.6**. The valence shells of the inner transition elements consist of the $(n - 2)f$, the $(n - 1)d$, and the *ns* subshells. There are two inner transition series:
    1. The lanthanide series: lanthanide (La) through lutetium (Lu)
    2. The actinide series: actinide (Ac) through lawrencium (Lr)

Lanthanum and actinium, because of their similarities to the other members of the series, are included and used to name the series, even though they are transition metals with no *f* electrons.

Electron Configurations of Ions

We have seen that ions are formed when atoms gain or lose electrons. A cation (positively charged ion) forms when one or more electrons are removed from a parent atom. For main group elements, the electrons that were added last are the first electrons removed. For transition metals and inner transition metals, however, electrons in the *s* orbital are easier to remove than the *d* or *f* electrons, and so the highest *ns* electrons are lost, and then the $(n - 1)d$ or $(n - 2)f$ electrons are removed. An anion (negatively charged ion) forms when one or more electrons are added to a parent atom. The added electrons fill in the order predicted by the Aufbau principle.

✔ Example **5.2.2**: Predicting Electron Configurations of Ions

What is the electron configuration and orbital diagram of:

a. Na^+
b. P^{3-}
c. Al^{2+}
d. Fe^{2+}

e. Sm^{3+}

Solution

First, write out the electron configuration for each parent atom. We have chosen to show the full, unabbreviated configurations to provide more practice for students who want it, but listing the core-abbreviated electron configurations is also acceptable.

Next, determine whether an electron is gained or lost. Remember electrons are negatively charged, so ions with a positive charge have *lost* an electron. For main group elements, the last orbital gains or loses the electron. For transition metals, the last *s* orbital loses an electron before the *d* orbitals.

a. Na: $1s^2 2s^2 2p^6 3s^1$. Sodium cation loses one electron, so Na^+: $1s^2 2s^2 2p^6 3s^1 = Na^+$: $1s^2 2s^2 2p^6$.
b. P: $1s^2 2s^2 2p^6 3s^2 3p^3$. Phosphorus trianion gains three electrons, so P^{3-}: $1s^2 2s^2 2p^6 3s^2 3p^6$.
c. Al: $1s^2 2s^2 2p^6 3s^2 3p^1$. Aluminum dication loses two electrons Al^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^1 = Al^{2+}$: $1s^2 2s^2 2p^6 3s^1$.
d. Fe: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$. Iron(II) loses two electrons and, since it is a transition metal, they are removed from the 4*s* orbital Fe^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6 = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$.
e. Sm: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^6$. Samarium trication loses three electrons. The first two will be lost from the 6*s* orbital, and the final one is removed from the 4*f* orbital. Sm^{3+}: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^6 = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 4f^5$.

? Exercise 5.2.2

a. Which ion with a +2 charge has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^5$?
b. Which ion with a +3 charge has this configuration?

Answer a

Tc^{2+}

Answer b

Ru^{3+}

Summary

The relative energy of the subshells determine the order in which atomic orbitals are filled (1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, and so on). Electron configurations and orbital diagrams can be determined by applying the Pauli exclusion principle (no two electrons can have the same set of four quantum numbers) and Hund's rule (whenever possible, electrons retain unpaired spins in degenerate orbitals).

Electrons in the outermost orbitals, called valence electrons, are responsible for most of the chemical behavior of elements. In the periodic table, elements with analogous valence electron configurations usually occur within the same group. There are some exceptions to the predicted filling order, particularly when half-filled or completely filled orbitals can be formed. The periodic table can be divided into three categories based on the orbital in which the last electron to be added is placed: main group elements (*s* and *p* orbitals), transition elements (*d* orbitals), and inner transition elements (*f* orbitals).

Glossary

Aufbau principle
procedure in which the electron configuration of the elements is determined by "building" them in order of atomic numbers, adding one proton to the nucleus and one electron to the proper subshell at a time

core electron
electron in an atom that occupies the orbitals of the inner shells

electron configuration

electronic structure of an atom in its ground state given as a listing of the orbitals occupied by the electrons

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

orbital diagram

pictorial representation of the electron configuration showing each orbital as a box and each electron as an arrow

valence electrons

electrons in the outermost or valence shell (highest value of *n*) of a ground-state atom; determine how an element reacts

valence shell

outermost shell of electrons in a ground-state atom; for main group elements, the orbitals with the highest *n* level (*s* and *p* subshells) are in the valence shell, while for transition metals, the highest energy *s* and *d* subshells make up the valence shell and for inner transition elements, the highest *s*, *d*, and *f* subshells are included

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5.3: Periodic Variations in Element Properties

Learning Objectives

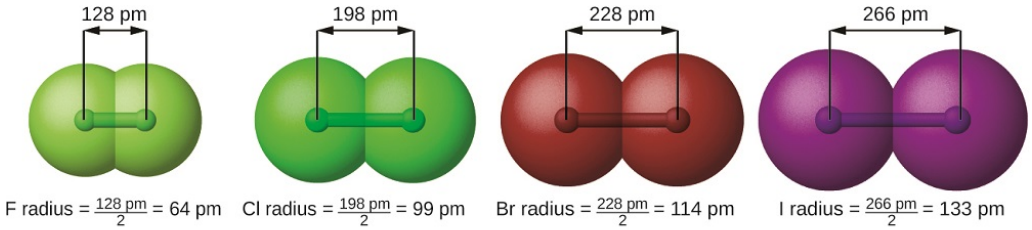
- Describe and explain the observed trends in atomic size, ionization energy, and electron affinity of the elements

The elements in groups (vertical columns) of the periodic table exhibit similar chemical behavior. This similarity occurs because the members of a group have the same number and distribution of electrons in their valence shells. However, there are also other patterns in chemical properties on the periodic table. For example, as we move down a group, the metallic character of the atoms increases. Oxygen, at the top of Group 16 (6A), is a colorless gas; in the middle of the group, selenium is a semiconducting solid; and, toward the bottom, polonium is a silver-grey solid that conducts electricity.

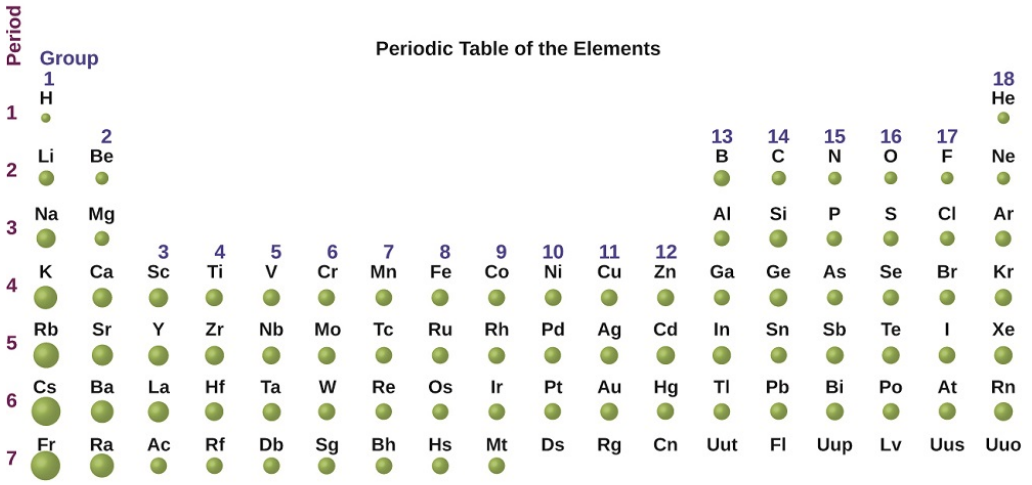
As we go across a period from left to right, we add a proton to the nucleus and an electron to the valence shell with each successive element. As we go down the elements in a group, the number of electrons in the valence shell remains constant, but the principal quantum number increases by one each time. An understanding of the electronic structure of the elements allows us to examine some of the properties that govern their chemical behavior. These properties vary periodically as the electronic structure of the elements changes. They are (1) size (radius) of atoms and ions, (2) ionization energies, and (3) electron affinities.

Variation in Covalent Radius

The quantum mechanical picture makes it difficult to establish a definite size of an atom. However, there are several practical ways to define the radius of atoms and, thus, to determine their relative sizes that give roughly similar values. We will use the covalent radius (Figure **5.3.1**), which is defined as one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond (this measurement is possible because atoms within molecules still retain much of their atomic identity).



(a)



(b)

Figure **5.3.1**: (a) The radius of an atom is defined as one-half the distance between the nuclei in a molecule consisting of two identical atoms joined by a covalent bond. The atomic radius for the halogens increases down the group as n increases. (b) Covalent radii of the elements are shown to scale. The general trend is that radii increase down a group and decrease across a period.

This figure has two parts: a and b. In figure a, 4 diatomic molecules are shown to illustrate the method of determining the atomic radius of an atom. The first model, in light green, is used to find the F atom radius. Two spheres are pushed very tightly together. The distance between the centers of the two atoms is indicated above the diagram with a double headed arrow labeled, “128 p m.” The endpoints of this arrow connect to line segments that extend to the atomic radii below. Beneath the molecule is the label, “F radius equals 128 p m divided by 2 equals 64 p m.” The next three models are similarly used to show the atomic radii of additional atoms. The second diatomic molecule is in a darker shade of green. The distance between the radii is 198 p m. Beneath the molecule is the label, “C l radius equals 198 p m divided by 2 equals 99 pm.” The third diatomic molecule is in red. The distance between the radii is 228 p m. Beneath the molecule is the label, “B r radius equals 228 p m divided by 2 equals 114 pm.” The fourth diatomic molecule is in purple. The distance between the radii is 266 p m. Beneath the molecule is the label, “I radius equals 266 p m divided by 2 equals 133 p m.” In figure b, a periodic table layout is used to compare relative sizes of atoms using green spheres. No spheres are provided for the noble or inert gas, group 18 elements. General trends noted are increasing circle size moving from top to bottom in a group, with a general tendency toward increasing atomic radii toward the lower left corner of the periodic table.

We know that as we scan down a group, the principal quantum number, *n*, increases by one for each element. Thus, the electrons are being added to a region of space that is increasingly distant from the nucleus. Consequently, the size of the atom (and its covalent radius) must increase as we increase the distance of the outermost electrons from the nucleus. This trend is illustrated for the covalent radii of the halogens in Table **5.3.1** and Figure **5.3.1**. The trends for the entire periodic table can be seen in Figure **5.3.2**.

Table **5.3.1**: Covalent Radii of the Halogen Group Elements

Atom	Covalent radius (pm)	Nuclear charge
F	64	+9
Cl	99	+17
Br	114	+35
I	133	+53
At	148	+85

As shown in Figure **5.3.2**, as we move across a period from left to right, we generally find that each element has a smaller covalent radius than the element preceding it. This might seem counterintuitive because it implies that atoms with more electrons have a smaller atomic radius. This can be explained with the concept of effective nuclear charge, Z_{eff}. This is the pull exerted on a specific electron by the nucleus, taking into account any electron–electron repulsions. For hydrogen, there is only one electron and so the nuclear charge (Z) and the effective nuclear charge (Z_{eff}) are equal. For all other atoms, the inner electrons partially *shield* the outer electrons from the pull of the nucleus, and thus:

$$Z_{\text{eff}} = Z - shielding$$

Shielding is determined by the probability of another electron being between the electron of interest and the nucleus, as well as by the electron–electron repulsions the electron of interest encounters. Core electrons are adept at shielding, while electrons in the same valence shell do not block the nuclear attraction experienced by each other as efficiently. Thus, each time we move from one element to the next across a period, Z increases by one, but the shielding increases only slightly. Thus, Z_{eff} increases as we move from left to right across a period. The stronger pull (higher effective nuclear charge) experienced by electrons on the right side of the periodic table draws them closer to the nucleus, making the covalent radii smaller.

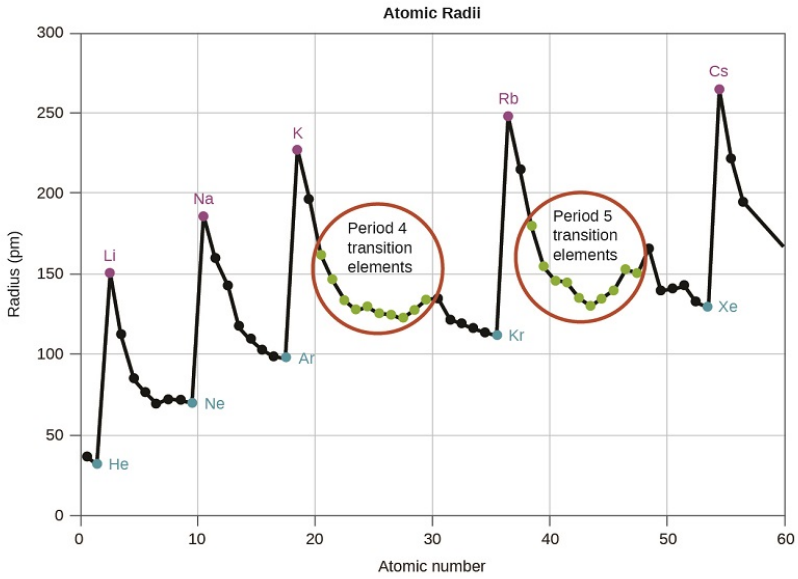


Figure **5.3.2**: Within each period, the trend in atomic radius decreases as Z increases; for example, from K to Kr. Within each group (e.g., the alkali metals shown in purple), the trend is that atomic radius increases as Z increases.

This graph is labeled Atomic Number on the horizontal axis and Radius (p m) on the vertical axis. A black jagged line connects the radii values for elements with atomic numbers 1 through 60 on the graph. Peaks are evident at the locations of the alkali metals: L i, N a, K, R b, and C s. Similarly, minima exist at the locations of noble or inert gases: H e, N e, A r, K r, X e, and R n. The locations of period 4 and period 5 transition elements are provided with green dots.

Thus, as we would expect, the outermost or valence electrons are easiest to remove because they have the highest energies, are shielded more, and are farthest from the nucleus. As a general rule, when the representative elements form cations, they do so by the loss of the *ns* or *np* electrons that were added last in the Aufbau process. The transition elements, on the other hand, lose the *ns* electrons before they begin to lose the $(n - 1)d$ electrons, even though the *ns* electrons are added first, according to the Aufbau principle.

✔ Example **5.3.1**: Sorting Atomic Radii

Predict the order of increasing covalent radius for Ge, Fl, Br, Kr.

Solution

Radius increases as we move down a group, so Ge < Fl (Note: Fl is the symbol for flerovium, element 114, NOT fluorine). Radius decreases as we move across a period, so Kr < Br < Ge. Putting the trends together, we obtain Kr < Br < Ge < Fl.

? Exercise 5.3.1

Give an example of an atom whose size is smaller than fluorine.

Answer

Ne or He

Variation in Ionic Radii

Ionic radius is the measure used to describe the size of an ion. A cation always has fewer electrons and the same number of protons as the parent atom; it is smaller than the atom from which it is derived (Figure **5.3.3**). For example, the covalent radius of an aluminum atom ($1s^2 2s^2 2p^6 3s^2 3p^1$) is 118 pm, whereas the ionic radius of an Al^{3+} ($1s^2 2s^2 2p^6$) is 68 pm. As electrons are removed from the outer valence shell, the remaining core electrons occupying smaller shells experience a greater effective nuclear charge Z_{eff} (as discussed) and are drawn even closer to the nucleus.



Figure **5.3.3**: The radius for a cation is smaller than the parent atom (Al), due to the lost electrons; the radius for an anion is larger than the parent (S), due to the gained electrons.

The figure includes spheres in green to represent the relative sizes of A l and S atoms. Beneath each of these spheres is a red sphere. The red sphere represents the ionic states of aluminum and sulfur respectively. While radius for the aluminum cation is smaller than aluminum, the sulfur anion has a greater radius than sulfur.

Cations with larger charges are smaller than cations with smaller charges (e.g., V^{2+} has an ionic radius of 79 pm, while that of V^{3+} is 64 pm). Proceeding down the groups of the periodic table, we find that cations of successive elements with the same charge generally have larger radii, corresponding to an increase in the principal quantum number, *n*.

An anion (negative ion) is formed by the addition of one or more electrons to the valence shell of an atom. This results in a greater repulsion among the electrons and a decrease in Z_{eff} per electron. Both effects (the increased number of electrons and the decreased Z_{eff}) cause the radius of an anion to be larger than that of the parent atom (Figure **5.3.3**). For example, a sulfur atom ($[Ne]3s^2 3p^4$) has a covalent radius of 104 pm, whereas the ionic radius of the sulfide anion ($[Ne]3s^2 3p^6$) is 170 pm. For consecutive elements proceeding down any group, anions have larger principal quantum numbers and, thus, larger radii.

Atoms and ions that have the same electron configuration are said to be isoelectronic. Examples of isoelectronic species are N^{3-}, O^{2-}, F^-, Ne, Na^+, Mg^{2+}, and Al^{3+} ($1s^2 2s^2 2p^6$). Another isoelectronic series is P^{3-}, S^{2-}, Cl^-, Ar, K^+, Ca^{2+}, and Sc^{3+} ($[Ne]3s^2 3p^6$). For atoms or ions that are isoelectronic, the number of protons determines the size. The greater the nuclear charge, the smaller the radius in a series of isoelectronic ions and atoms.

Variation in Ionization Energies

The amount of energy required to remove the most loosely bound electron from a gaseous atom in its ground state is called its first ionization energy (IE_1). The first ionization energy for an element, X, is the energy required to form a cation with +1 charge:

$$\mathbf{X}(g) \longrightarrow \mathbf{X}^+(g) + \mathbf{e}^- \quad \mathbf{IE}_1$$

The energy required to remove the second most loosely bound electron is called the second ionization energy (IE_2).

$$\mathbf{X}^+(g) \longrightarrow \mathbf{X}^{2+}(g) + \mathbf{e}^- \quad \mathbf{IE}_2$$

The energy required to remove the third electron is the third ionization energy, and so on. Energy is always required to remove electrons from atoms or ions, so ionization processes are endothermic and IE values are always positive. For larger atoms, the most loosely bound electron is located farther from the nucleus and so is easier to remove. Thus, as size (atomic radius) increases, the

ionization energy should decrease. Relating this logic to what we have just learned about radii, we would expect first ionization energies to decrease down a group and to increase across a period.

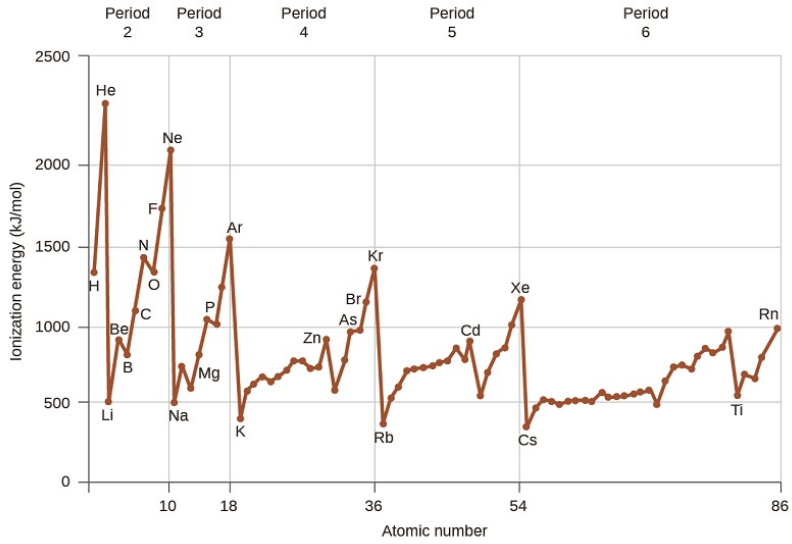


Figure 5.3.4: The first ionization energy of the elements in the first five periods are plotted against their atomic number.

This figure includes Atomic Number on the horizontal axis and, Ionization Energy (k J divided by mol) on the vertical axis. A red jagged line connects the ionization energies for elements with atomic numbers 1 through 86 on the graph. Peaks are evident at the locations of the noble or inert gases: H e, N e, A r, K r, X e, and R n. Similarly, minima exist at the locations of the alkali metals: L i, N a, K, R b, and C s.

Figure 5.3.4 graphs the relationship between the first ionization energy and the atomic number of several elements. Within a period, the values of first ionization energy for the elements (IE_1) generally increases with increasing Z. Down a group, the IE_1 value generally decreases with increasing Z. There are some systematic deviations from this trend, however. Note that the ionization energy of boron (atomic number 5) is less than that of beryllium (atomic number 4) even though the nuclear charge of boron is greater by one proton. This can be explained because the energy of the subshells increases as l increases, due to penetration and shielding (as discussed previously in this chapter). Within any one shell, the s electrons are lower in energy than the p electrons. This means that an s electron is harder to remove from an atom than a p electron in the same shell. The electron removed during the ionization of beryllium ($[He]2s^2$) is an s electron, whereas the electron removed during the ionization of boron ($[He]2s^22p^1$) is a p electron; this results in a lower first ionization energy for boron, even though its nuclear charge is greater by one proton. Thus, we see a small deviation from the predicted trend occurring each time a new subshell begins.

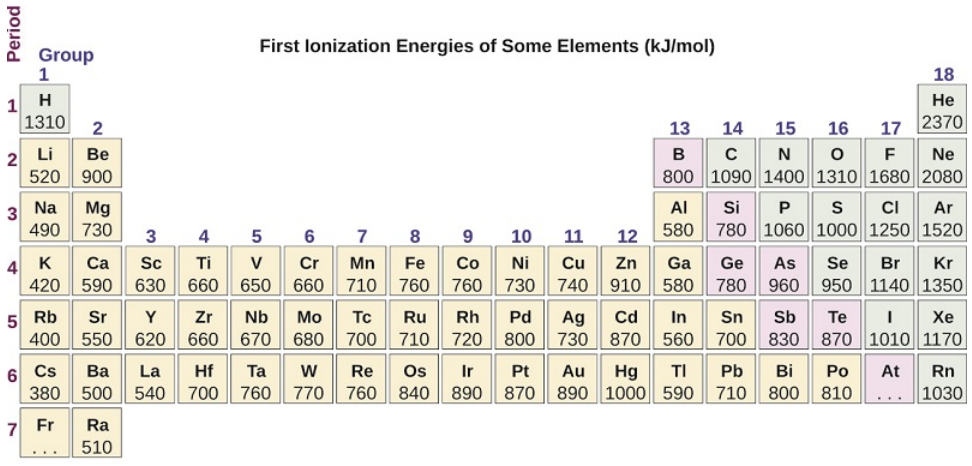
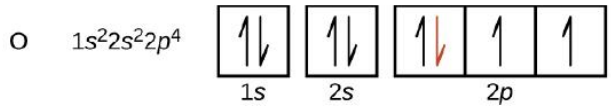


Figure 5.3.5: This version of the periodic table shows the first ionization energy of (IE: $_1$), in kJ/mol, of selected elements.

The trends for first ionization energies across periods and down groups are shown in this version of the periodic table.

Another deviation occurs as orbitals become more than one-half filled. The first ionization energy for oxygen is slightly less than that for nitrogen, despite the trend in increasing IE_1 values across a period. Looking at the orbital diagram of oxygen, we can see that removing one electron will eliminate the electron–electron repulsion caused by pairing the electrons in the 2*p* orbital and will result in a half-filled orbital (which is energetically favorable). Analogous changes occur in succeeding periods (note the dip for sulfur after phosphorus in Figure **5.3.4**.



The electronic configuration for oxygen is 1s superscript 2, 2s superscript, 2p superscript 4. An orbital diagram shows 2 squares each filled with a pair of opposite pointing arrows to represent the 1s ans 2s orbitals. Each of the three connected square which represents the 2p orbitals are filled with one arrow respectively with the addition of 1 red arrow in the first of the three squares.

Removing an electron from a cation is more difficult than removing an electron from a neutral atom because of the greater electrostatic attraction to the cation. Likewise, removing an electron from a cation with a higher positive charge is more difficult than removing an electron from an ion with a lower charge. Thus, successive ionization energies for one element always increase. As seen in Table **5.3.2**, there is a large increase in the ionization energies (color change) for each element. This jump corresponds to removal of the core electrons, which are harder to remove than the valence electrons. For example, Sc and Ga both have three valence electrons, so the rapid increase in ionization energy occurs after the third ionization.

Table 5.3.2: Successive Ionization Energies for Selected Elements (kJ/mol)

Element	IE_1	IE_2	IE_3	IE_4	IE_5	IE_6	IE_7
K	418.8	3051.8	4419.6	5876.9	7975.5	9590.6	11343
Ca	589.8	1145.4	4912.4	6490.6	8153.0	10495.7	12272.9
Sc	633.1	1235.0	2388.7	7090.6	8842.9	10679.0	13315.0
Ga	578.8	1979.4	2964.6	6180	8298.7	10873.9	13594.8
Ge	762.2	1537.5	3302.1	4410.6	9021.4	Not available	Not available
As	944.5	1793.6	2735.5	4836.8	6042.9	12311.5	Not available

Example 5.3.2: Ranking Ionization Energies

Predict the order of increasing energy for the following processes: IE_1 for Al, IE_1 for Tl, IE_2 for Na, IE_3 for Al.

Solution

Removing the $6p^1$ electron from Tl is easier than removing the $3p^1$ electron from Al because the higher *n* orbital is farther from the nucleus, so $IE_1(Tl) < IE_1(Al)$. Ionizing the third electron from

$$\mathbf{Al} \quad (\mathbf{Al^{2+} \longrightarrow Al^{3+} + e^-})$$

requires more energy because the cation Al^{2+} exerts a stronger pull on the electron than the neutral Al atom, so $IE_1(Al) < IE_3(Al)$. The second ionization energy for sodium removes a core electron, which is a much higher energy process than removing valence electrons. Putting this all together, we obtain:

$$IE_1(Tl) < IE_1(Al) < IE_3(Al) < IE_2(Na).$$

Exercise 5.3.2

Which has the lowest value for IE_1: O, Po, Pb, or Ba?

Answer

Ba

Variation in Electron Affinities

The electron affinity [EA] is the energy change for the process of adding an electron to a gaseous atom to form an anion (negative ion).

$$X(g) + e^- \longrightarrow X^-(g) \quad EA_1$$

This process can be either endothermic or exothermic, depending on the element. The EA of some of the elements is given in Figure 5.3.6. You can see that many of these elements have negative values of EA, which means that energy is released when the gaseous atom accepts an electron. However, for some elements, energy is required for the atom to become negatively charged and the value of their EA is positive. Just as with ionization energy, subsequent EA values are associated with forming ions with more charge. The second EA is the energy associated with adding an electron to an anion to form a –2 ion, and so on.

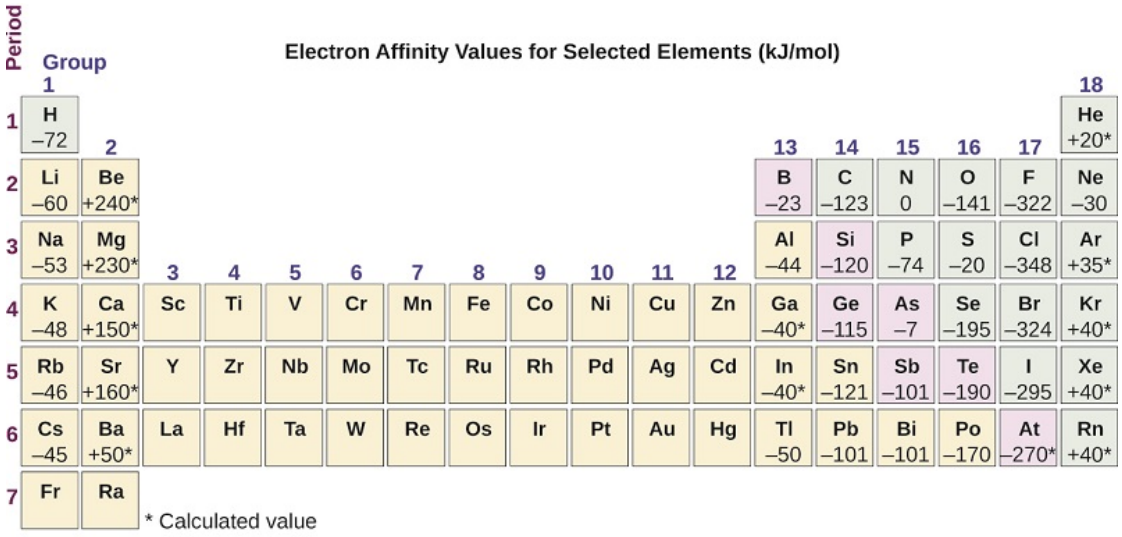


Figure 5.3.6: This version of the periodic table displays the electron affinity values (in kJ/mol) for selected elements.:
The trend for electron affinity values across periods and down groups is shown in this version of the periodic table. Values are not shown for groups 3 to 12 as well as period 7.

As we might predict, it becomes easier to add an electron across a series of atoms as the effective nuclear charge of the atoms increases. We find, as we go from left to right across a period, EAs tend to become more negative. The exceptions found among the elements of group 2 (2A), group 15 (5A), and group 18 (8A) can be understood based on the electronic structure of these groups. The noble gases, group 18 (8A), have a completely filled shell and the incoming electron must be added to a higher *n* level, which is more difficult to do. Group 2 (2A) has a filled *ns* subshell, and so the next electron added goes into the higher energy *np*, so, again, the observed EA value is not as the trend would predict. Finally, group 15 (5A) has a half-filled *np* subshell and the next electron must be paired with an existing *np* electron. In all of these cases, the initial relative stability of the electron configuration disrupts the trend in EA.

We also might expect the atom at the top of each group to have the largest EA; their first ionization potentials suggest that these atoms have the largest effective nuclear charges. However, as we move down a group, we see that the second element in the group most often has the greatest EA. The reduction of the EA of the first member can be attributed to the small size of the $n = 2$ shell and the resulting large electron–electron repulsions. For example, chlorine, with an EA value of –348 kJ/mol, has the highest value of any element in the periodic table. The EA of fluorine is –322 kJ/mol. When we add an electron to a fluorine atom to form a fluoride anion (F^-), we add an electron to the $n = 2$ shell. The electron is attracted to the nucleus, but there is also significant repulsion from the other electrons already present in this small valence shell. The chlorine atom has the same electron configuration in the valence shell, but because the entering electron is going into the $n = 3$ shell, it occupies a considerably larger region of space and the

electron–electron repulsions are reduced. The entering electron does not experience as much repulsion and the chlorine atom accepts an additional electron more readily.

The properties discussed in this section (size of atoms and ions, effective nuclear charge, ionization energies, and electron affinities) are central to understanding chemical reactivity. For example, because fluorine has an energetically favorable EA and a large energy barrier to ionization (IE), it is much easier to form fluorine anions than cations. Metallic properties including conductivity and malleability (the ability to be formed into sheets) depend on having electrons that can be removed easily. Thus, metallic character increases as we move down a group and decreases across a period in the same trend observed for atomic size because it is easier to remove an electron that is farther away from the nucleus.

Summary

Electron configurations allow us to understand many periodic trends. Covalent radius increases as we move down a group because the *n* level (orbital size) increases. Covalent radius mostly decreases as we move left to right across a period because the effective nuclear charge experienced by the electrons increases, and the electrons are pulled in tighter to the nucleus. Anionic radii are larger than the parent atom, while cationic radii are smaller, because the number of valence electrons has changed while the nuclear charge has remained constant. Ionization energy (the energy associated with forming a cation) decreases down a group and mostly increases across a period because it is easier to remove an electron from a larger, higher energy orbital. Electron affinity (the energy associated with forming an anion) is more favorable (exothermic) when electrons are placed into lower energy orbitals, closer to the nucleus. Therefore, electron affinity becomes increasingly negative as we move left to right across the periodic table and decreases as we move down a group. For both IE and electron affinity data, there are exceptions to the trends when dealing with completely filled or half-filled subshells.

Glossary

covalent radius
: one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond

effective nuclear charge
: charge that leads to the Coulomb force exerted by the nucleus on an electron, calculated as the nuclear charge minus shielding

electron affinity
: energy required to add an electron to a gaseous atom to form an anion

ionization energy
: energy required to remove an electron from a gaseous atom or ion. The associated number (e.g., second ionization energy) corresponds to the charge of the ion produced (X^{2+})

isoelectronic
: group of ions or atoms that have identical electron configurations

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5.E: Electronic Structure and Periodic Properties (Exercises)

6.1: Electromagnetic Energy

Q6.1.1

The light produced by a red neon sign is due to the emission of light by excited neon atoms. Qualitatively describe the spectrum produced by passing light from a neon lamp through a prism.

S6.1.1

The spectrum consists of colored lines, at least one of which (probably the brightest) is red.

Q6.1.2

An FM radio station found at 103.1 on the FM dial broadcasts at a frequency of 1.031×10^8 s^{-1} (103.1 MHz). What is the wavelength of these radio waves in meters?

S6.1.2

$$\lambda = \frac{c}{\nu}$$

$$\lambda = \frac{2.998 \times 10^8 \frac{m}{s}}{1.031 \times 10^8 \frac{1}{s}} = 2.908\, m$$

Q6.1.3

FM-95, an FM radio station, broadcasts at a frequency of 9.51×10^7 s^{-1} (95.1 MHz). What is the wavelength of these radio waves in meters?

S6.1.3

$$\lambda = \frac{c}{\nu}$$

$$\lambda = \frac{2.998 \times 10^8 \frac{m}{s}}{9.51 \times 10^7 \frac{1}{s}} = 3.15\, m$$

Q6.1.4

A bright violet line occurs at 435.8 nm in the emission spectrum of mercury vapor. What amount of energy, in joules, must be released by an electron in a mercury atom to produce a photon of this light?

S6.1.4

$$E = \frac{hc}{\lambda}$$

$$E = \frac{(2.998 \times 10^8 \frac{m}{s})\,(6.6262 \times 10^{-34} Js)}{4.358 \times 10^{-7} m}$$

$$= 4.56 \times 10^{-19} J$$

Q6.1.5

Light with a wavelength of 614.5 nm looks orange. What is the energy, in joules, per photon of this orange light? What is the energy in eV (1 eV = 1.602×10^{-19} J)?

S6.1.5

1.) First convert 614.5 nm into meters

$6.145 nm = 6.145 \times 10^{-7} m$

2.) Then calculate the amount of energy this wavelength of light contains using the equations:

$E = h\nu$ and $\nu = \frac{c}{\lambda}$ which can be manipulated algebraically into: $E = \frac{hc}{\lambda}$

- h = Plancks constant → $6.6262 \times 10^{-34} Js$
- c = Speed of light → $2.998 \times 10^{8} \frac{m}{s}$
- λ = wavelength of photon → $6.145 \times 10^{-7} m$

$$= \frac{(6.6262 \times 10^{-34}\ Js)\ (2.998 \times 10^{8}\ \frac{m}{s})}{6.145 \times 10^{-7} m} = 3.233 \times 10^{-19} J \quad (5.E.1)$$

3.) Then convert Joules into eV:

$$= (3.233 \times 10^{-19} J) \times \frac{1eV}{1.602 \times 10^{-19} J} \quad (5.E.2)$$

$$= 2.018eV \quad (5.E.3)$$

Q6.1.6

Heated lithium atoms emit photons of light with an energy of 2.961 × 10^{-19} J. Calculate the frequency and wavelength of one of these photons. What is the total energy in 1 mole of these photons? What is the color of the emitted light?

S6.1.6

1.) $E = h\nu$ and $\nu = \frac{E}{h}$

- h = Plancks constant → $6.6262 \times 10^{-34} Js$

Frequency: $\nu = \frac{2.961 \times 10^{-19} J}{6.6262 \times 10^{-34} Js} = 4.469 \times 10^{14} Hz$

2.) $\lambda = \frac{c}{\nu}$

c = Speed of light → $2.998 \times 10^{8}\ \frac{m}{s}$

Wavelength: $\lambda = \frac{2.998 \times 10^{8} \frac{m}{s}}{4.469 \times 10^{14} \frac{1}{s}} = 6.709 \times 10^{-7} m$ = **Red Light**

Total energy:

$$E = \frac{2.961 \times 10^{-19} J}{1\ photon} \times \frac{6.022 \times 10^{23}\ photons}{1\ mole} = 1.783 \times 10^{5} J$$

Q6.1.7

A photon of light produced by a surgical laser has an energy of 3.027 × 10^{-19} J. Calculate the frequency and wavelength of the photon. What is the total energy in 1 mole of photons? What is the color of the emitted light?

S6.1.7

ν = 4.568 × 10^{14} s; λ = 656.3 nm; Energy mol^{-1} = 1.823 × 10^{5} J mol^{-1}; red

Q6.1.8

When rubidium ions are heated to a high temperature, two lines are observed in its line spectrum at wavelengths (a) 7.9 × 10^{-7} m and (b) 4.2 × 10^{-7} m. What are the frequencies of the two lines? What color do we see when we heat a rubidium compound?

Q6.1.9

The emission spectrum of cesium contains two lines whose frequencies are (a) 3.45 × 10^{14} Hz and (b) 6.53 × 10^{14} Hz. What are the wavelengths and energies per photon of the two lines? What color are the lines?

S6.1.9

(a) $\lambda = 8.69 \times 10^{-7}$ m; $E = 2.29 \times 10^{-19}$ J; (b) $\lambda = 4.59 \times 10^{-7}$ m; $E = 4.33 \times 10^{-19}$ J; The color of (a) is red; (b) is blue.

Q6.1.10

Photons of infrared radiation are responsible for much of the warmth we feel when holding our hands before a fire. These photons will also warm other objects. How many infrared photons with a wavelength of 1.5×10^{-6} m must be absorbed by the water to warm a cup of water (175 g) from 25.0 °C to 40 °

S6.1.10

1.) First we must use the equation: $q=mC\Delta T^{\circ}$ to calculate the amount of Energy in Joules (J) to warm 175g of H_2O a total of 15° Celsius

- m = mass in grams(g) → 175g
- C = Specific heat of $H_2O_{(l)}$ → $\frac{4.184J}{g°C}$
- ΔT° = Difference in temperature → 40 - 25 =15°

$$q = 175g \times \frac{4.184J}{g°C} \times 15°C \tag{5.E.4}$$

q= 11,000 J

2.) Now we need to calculate the amount of energy in Joules (J) that one Photon with a wavelength of $1.5x10^{-6}$ m contains. We will use the equations:

$E = h\nu$ and $\nu = \frac{c}{\lambda}$ which can be manipulated algebraically into: $E = \frac{hc}{\lambda}$

- h = Plancks constant → $6.6262 \times 10^{-34} Js$
- c = Speed of light → $2.998 \times 10^{8} \frac{m}{s}$
- λ = wavelength of photon → $1.5 \times 10^{-6} m$

$$= \frac{(6.6262 \times 10^{-34}\ Js)\ (2.998 \times 10^{8}\ \frac{m}{s})}{1.5 \times 10^{-6} m} = 1.3 \times 10^{-19} J \tag{5.E.5}$$

This is the energy in one photon, so now we have to see how many times $1.3x10^{-19}$ J fits into the 11,000 J from our first calculation:

$$= \frac{11,000\ J}{1.3 \times 10^{-19}\ \frac{J}{photon}} = 8.3 \times 10^{22} photons \tag{5.E.6}$$

$$= 8.3 \times 10^{22} photons \tag{5.E.7}$$

Q6.1.11

One of the radiographic devices used in a dentist's office emits an X-ray of wavelength 2.090×10^{-11} m. What is the energy, in joules, and frequency of this X-ray?

S6.1.11

$E = 9.502 \times 10^{-15}$ J; $\nu = 1.434 \times 10^{19}$ s^{-1}

Q6.1.12

The eyes of certain reptiles pass a single visual signal to the brain when the visual receptors are struck by photons of a wavelength of 850 nm. If a total energy of 3.15×10^{-14} J is required to trip the signal, what is the minimum number of photons that must strike the receptor?

S6.1.12

1.) First we need to convert nanometers to meters

850nm = 8.5 x 10^{-7} m

2. Then calculate Energy in Joules a photon of this wavelength (λ) produces:

$$(E = \frac{hc}{\lambda}) = \frac{(6.6262 \times 10^{-34}\ Js)\ (2.998 \times 10^{8}\ \frac{m}{s})}{8.5 \times 10^{-7} m} = 2.3 \times 10^{-19} \frac{J}{photon} \tag{5.E.8}$$

3.) Then we need to find out how many of these photons it will take to trip the visual signal to the brain:

$$= \frac{3.15 \times 10^{-14}\ \cancel{J}}{2.3 \times 10^{-19}\ \frac{\cancel{J}}{photon}} \tag{5.E.9}$$

$$= 1.3 \times 10^{5}\ photons \tag{5.E.10}$$

Q6.1.13

RGB color television and computer displays use cathode ray tubes that produce colors by mixing red, green, and blue light. If we look at the screen with a magnifying glass, we can see individual dots turn on and off as the colors change. Using a spectrum of visible light, determine the approximate wavelength of each of these colors. What is the frequency and energy of a photon of each of these colors?

S6.1.13

- Red: 660 nm; 4.54 × 10^{14} Hz; 3.01 × 10^{-19} J.
- Green: 520 nm; 5.77 × 10^{14} Hz; 3.82 × 10^{-19} J.
- Blue: 440 nm; 6.81 × 10^{14} Hz; 4.51 × 10^{-19} J.

Somewhat different numbers are also possible.

Q6.1.14

Answer the following questions about a Blu-ray laser:

a. The laser on a Blu-ray player has a wavelength of 405 nm. In what region of the electromagnetic spectrum is this radiation? What is its frequency?
b. A Blu-ray laser has a power of 5 milliwatts (1 watt = 1 J s^{-1}). How many photons of light are produced by the laser in 1 hour?
c. The ideal resolution of a player using a laser (such as a Blu-ray player), which determines how close together data can be stored on a compact disk, is determined using the following formula: Resolution = 0.60(λ/NA), where λ is the wavelength of the laser and NA is the numerical aperture. Numerical aperture is a measure of the size of the spot of light on the disk; the larger the NA, the smaller the spot. In a typical Blu-ray system, NA = 0.95. If the 405-nm laser is used in a Blu-ray player, what is the closest that information can be stored on a Blu-ray disk?
d. The data density of a Blu-ray disk using a 405-nm laser is 1.5 × 10^{7} bits mm^{-2}. Disks have an outside diameter of 120 mm and a hole of 15-mm diameter. How many data bits can be contained on the disk? If a Blu-ray disk can hold 9,400,000 pages of text, how many data bits are needed for a typed page? (Hint: Determine the area of the disk that is available to hold data. The area inside a circle is given by A = πr^2, where the radius r is one-half of the diameter.)

Q6.1.15

What is the threshold frequency for sodium metal if a photon with frequency 6.66 × 10^{14} s^{-1} ejects a photon with 7.74 × 10^{-20} J kinetic energy? Will the photoelectric effect be observed if sodium is exposed to orange light?

S6.1.15

5.49 × 10^{14} s^{-1}; no

6.2: The Bohr Model

Q6.2.1

Why is the electron in a Bohr hydrogen atom bound less tightly when it has a quantum number of 3 than when it has a quantum number of 1?

Q6.2.2

What does it mean to say that the energy of the electrons in an atom is quantized?

S6.2.2

Quantized energy means that the electrons can possess only certain discrete energy values; values between those quantized values are not permitted.

Q6.2.3

Using the Bohr model, determine the energy, in joules, necessary to ionize a ground-state hydrogen atom. Show your calculations.

Q6.2.4

The electron volt (eV) is a convenient unit of energy for expressing atomic-scale energies. It is the amount of energy that an electron gains when subjected to a potential of 1 volt; $1\ eV = 1.602 \times 10^{-19}\ J$. Using the Bohr model, determine the energy, in electron volts, of the photon produced when an electron in a hydrogen atom moves from the orbit with $n = 5$ to the orbit with $n = 2$. Show your calculations.

S6.2.4

$$E = E_2 - E_5 = 2.179 \times 10^{-18} \left(\frac{1}{n_2^2} - \frac{1}{n_5^2} \right) J \tag{5.E.11}$$

$$= 2.179 \times 10^{-18} \left(\frac{1}{2^2} - \frac{1}{5^2} \right) = 4.576 \times 10^{-19}\ J \tag{5.E.12}$$

$$= \frac{4.576 \times 10^{-19}\ J}{1.602 \times 10^{-19}\ J\ eV^{-1}} = 2.856\ eV \tag{5.E.13}$$

Q6.2.5

Using the Bohr model, determine the lowest possible energy for the electron in the He^+ ion.

Q6.2.6

Using the Bohr model, determine the energy of an electron with $n = 6$ in a hydrogen atom.

S6.2.6

−8.716 × 10−18 J

Q6.2.7

Using the Bohr model, determine the energy of an electron with $n = 8$ in a hydrogen atom.

Q6.2.8

How far from the nucleus in angstroms (1 angstrom = 1×10^{-10} m) is the electron in a hydrogen atom if it has an energy of -8.72×10^{-20} J?

S6.2.8

$-3.405 \times 10^{-20} J$

Q6.2.9

What is the radius, in angstroms, of the orbital of an electron with n = 8 in a hydrogen atom?

Q6.2.10

Using the Bohr model, determine the energy in joules of the photon produced when an electron in a He^+ ion moves from the orbit with n = 5 to the orbit with n = 2.

Q6.2.11

Using the Bohr model, determine the energy in joules of the photon produced when an electron in a Li2+ ion moves from the orbit with n = 2 to the orbit with n = 1.

S6.2.11

1.471 × 10−17 J

Q6.2.12

Consider a large number of hydrogen atoms with electrons randomly distributed in the n = 1, 2, 3, and 4 orbits

a. How many different wavelengths of light are emitted by these atoms as the electrons fall into lower-energy orbitals?
b. Calculate the lowest and highest energies of light produced by the transitions described in part (a).
c. Calculate the frequencies and wavelengths of the light produced by the transitions described in part (b).

Q6.2.13

How are the Bohr model and the Rutherford model of the atom similar? How are they different?

Q6.2.14

The spectra of hydrogen and of calcium are shown in[link]. What causes the lines in these spectra? Why are the colors of the lines different? Suggest a reason for the observation that the spectrum of calcium is more complicated than the spectrum of hydrogen

S6.2.14

Both involve a relatively heavy nucleus with electrons moving around it, although strictly speaking, the Bohr model works only for one-electron atoms or ions. According to classical mechanics, the Rutherford model predicts a miniature “solar system” with electrons moving about the nucleus in circular or elliptical orbits that are confined to planes. If the requirements of classical electromagnetic theory that electrons in such orbits would emit electromagnetic radiation are ignored, such atoms would be stable, having constant energy and angular momentum, but would not emit any visible light (contrary to observation). If classical electromagnetic theory is applied, then the Rutherford atom would emit electromagnetic radiation of continually increasing frequency (contrary to the observed discrete spectra), thereby losing energy until the atom collapsed in an absurdly short time (contrary to the observed long-term stability of atoms). The Bohr model retains the classical mechanics view of circular orbits confined to planes having constant energy and angular momentum, but restricts these to quantized values dependent on a single quantum number, n. The orbiting electron in Bohr’s model is assumed not to emit any electromagnetic radiation while moving about the nucleus in its stationary orbits, but the atom can emit or absorb electromagnetic radiation when the electron changes from one orbit to another. Because of the quantized orbits, such “quantum jumps” will produce discrete spectra, in agreement with observations.

6.3: Development of Quantum Theory

Q6.3.1

How are the Bohr model and the quantum mechanical model of the hydrogen atom similar? How are they different?

S6.3.1

Both models have a central positively charged nucleus with electrons moving about the nucleus in accordance with the Coulomb electrostatic potential. The Bohr model *assumes* that the electrons move in circular orbits that have quantized energies, angular momentum, and radii that are specified by a single quantum number, n = 1, 2, 3, …, but this quantization is an ad hoc assumption made by Bohr to incorporate quantization into an essentially classical mechanics description of the atom. Bohr also assumed that electrons orbiting the nucleus normally do not emit or absorb electromagnetic radiation, but do so when the electron switches to a

different orbit. In the quantum mechanical model, the electrons do not move in precise orbits (such orbits violate the Heisenberg uncertainty principle) and, instead, a probabilistic interpretation of the electron's position at any given instant is used, with a mathematical function ψ called a wavefunction that can be used to determine the electron's spatial probability distribution. These wavefunctions, or orbitals, are three-dimensional stationary waves that can be specified by three quantum numbers that arise naturally from their underlying mathematics (no ad hoc assumptions required): the principal quantum number, n (the same one used by Bohr), which specifies shells such that orbitals having the same n all have the same energy and approximately the same spatial extent; the angular momentum quantum number l, which is a measure of the orbital's angular momentum and corresponds to the orbitals' general shapes, as well as specifying subshells such that orbitals having the same l (and n) all have the same energy; and the orientation quantum number m, which is a measure of the z component of the angular momentum and corresponds to the orientations of the orbitals. The Bohr model gives the same expression for the energy as the quantum mechanical expression and, hence, both properly account for hydrogen's discrete spectrum (an example of getting the right answers for the wrong reasons, something that many chemistry students can sympathize with), but gives the wrong expression for the angular momentum (Bohr orbits necessarily all have non-zero angular momentum, but some quantum orbitals [s orbitals] can have zero angular momentum).

Q6.3.2

What are the allowed values for each of the four quantum numbers: n, l, m_l, and m_s?

Q6.3.3

Describe the properties of an electron associated with each of the following four quantum numbers: n, l, m_l, and m_s.

S6.3.3

n determines the general range for the value of energy and the probable distances that the electron can be from the nucleus. l determines the shape of the orbital. m_l determines the orientation of the orbitals of the same l value with respect to one another. m_s determines the spin of an electron.

Q6.3.4

Answer the following questions:

a. Without using quantum numbers, describe the differences between the shells, subshells, and orbitals of an atom.
b. How do the quantum numbers of the shells, subshells, and orbitals of an atom differ?

Q6.3.5

Identify the subshell in which electrons with the following quantum numbers are found:

a. $n = 2$, $l = 1$
b. $n = 4$, $l = 2$
c. $n = 6$, $l = 0$

S6.3.5

(a) 2*p*; (b) 4*d*; (c) 6*s*

Q6.3.6

Which of the subshells described in Question 5 contain degenerate orbitals? How many degenerate orbitals are in each?

Q6.3.7

Identify the subshell in which electrons with the following quantum numbers are found:

a. $n = 3$, $l = 2$
b. $n = 1$, $l = 0$
c. $n = 4$, $l = 3$

S6.3.7

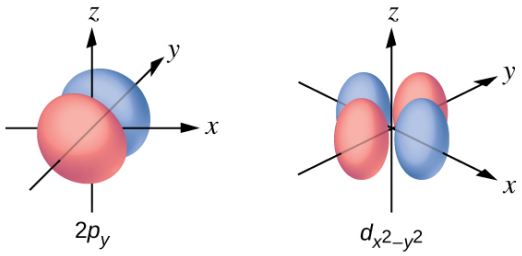
(a) 3*d;* (b) 1*s;* (c) 4*f*

Q6.3.8

Which of the subshells described in Question 7 contain degenerate orbitals? How many degenerate orbitals are in each?

Q6.3.9

Sketch the boundary surface of a $d_{x^2-y^2}$ and a p_y orbital. Be sure to show and label the axes.

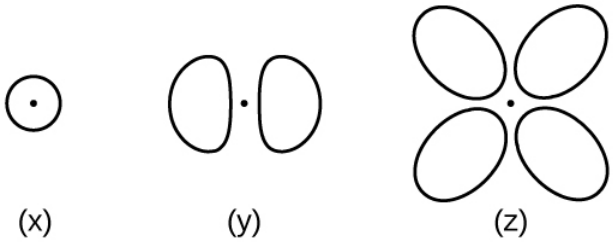


Q6.3.10

Sketch the p_x and d_{xz} orbitals. Be sure to show and label the coordinates.

Q6.3.11

Consider the orbitals shown here in outline.



a. What is the maximum number of electrons contained in an orbital of type (x)? Of type (y)? Of type (z)?
b. How many orbitals of type (x) are found in a shell with $n = 2$? How many of type (y)? How many of type (z)?
c. Write a set of quantum numbers for an electron in an orbital of type (x) in a shell with $n = 4$. Of an orbital of type (y) in a shell with $n = 2$. Of an orbital of type (z) in a shell with $n = 3$.
d. What is the smallest possible n value for an orbital of type (x)? Of type (y)? Of type (z)?
e. What are the possible l and m_l values for an orbital of type (x)? Of type (y)? Of type (z)?

S6.3.11

(a) x. 2, y. 2, z. 2; (b) x. 1, y. 3, z. 0; (c) x. 4 0 0 $\frac{1}{2}$, y. 2 1 0 $\frac{1}{2}$, z. 3 2 0 $\frac{1}{2}$; (d) x. 1, y. 2, z. 3; (e) x. $l = 0$, $m_l = 0$, y. $l = 1$, $m_l = –1$, 0, or +1, z. $l = 2$, $m_l = –2$, –1, 0, +1, +2

Q6.3.12

State the Heisenberg uncertainty principle. Describe briefly what the principle implies.

Q6.3.13

How many electrons could be held in the second shell of an atom if the spin quantum number m_s could have three values instead of just two? (Hint: Consider the Pauli exclusion principle.)

S6.3.13

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Q6.3.14

Which of the following equations describe particle-like behavior? Which describe wavelike behavior? Do any involve both types of behavior? Describe the reasons for your choices.

a. $c = \lambda\nu$
b. $E = \frac{m\nu^2}{2}$
c. $r = \frac{n^2 a_0}{Z}$
d. $E = h\nu$
e. $\lambda = \frac{h}{m\nu}$

Q6.3.15

Write a set of quantum numbers for each of the electrons with an *n* of 4 in a Se atom.

S6.3.15

n	l	m_l	s
4	0	0	$+\frac{1}{2}$
4	0	0	$-\frac{1}{2}$
4	1	−1	$+\frac{1}{2}$
4	1	0	$+\frac{1}{2}$
4	1	+1	$+\frac{1}{2}$
4	1	−1	$-\frac{1}{2}$

6.4: Electronic Structure of Atoms (Electron Configurations)

Q6.4.1

Read the labels of several commercial products and identify monatomic ions of at least four transition elements contained in the products. Write the complete electron configurations of these cations.

Q6.4.2

Read the labels of several commercial products and identify monatomic ions of at least six main group elements contained in the products. Write the complete electron configurations of these cations and anions.

S6.4.2

For example, Na^+: $1s^2 2s^2 2p^6$; Ca^{2+}: $1s^2 2s^2 2p^6$; Sn^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2$; F^-: $1s^2 2s^2 2p^6$; O^{2-}: $1s^2 2s^2 2p^6$; Cl^-: $1s^2 2s^2 2p^6 3s^2 3p^6$.

Q6.4.3

Using complete subshell notation (not abbreviations, $1s^2 2s^2 2p^6$, and so forth), predict the electron configuration of each of the following atoms:

a. C
b. P
c. V
d. Sb
e. Sm

S6.4.3

a.) $1s^2 2s^2 2p^2$

b.) $1s^2 2s^2 2p^6 3s^2 3p^3$

c.) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$

d.) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^3$

e.) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^6 5s^2 5p^6 6s^2$

Q6.4.4

Using complete subshell notation ($1s^2 2s^2 2p^6$, and so forth), predict the electron configuration of each of the following atoms:

a. N
b. Si
c. Fe
d. Te
e. Tb

S6.4.4

a. $1s^2 2s^2 2p^3$;
b. $1s^2 2s^2 2p^6 3s^2 3p^2$;
c. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$;
d. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^4$;
e. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^9$

Q6.4.5

Is $1s^2 2s^2 2p^6$ the symbol for a macroscopic property or a microscopic property of an element? Explain your answer.

Q6.4.6

What additional information do we need to answer the question “Which ion has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6$”?

S6.4.6

The charge on the ion.

Q6.4.7

Draw the orbital diagram for the valence shell of each of the following atoms:

a. C
b. P
c. V
d. Sb
e. Ru

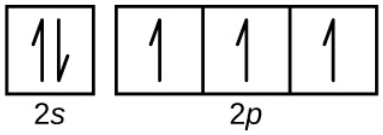
Q6.4.8

Use an orbital diagram to describe the electron configuration of the valence shell of each of the following atoms:

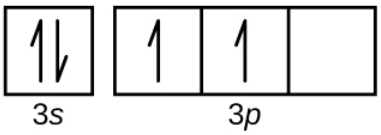
a. N
b. Si
c. Fe
d. Te
e. Mo

S6.4.8

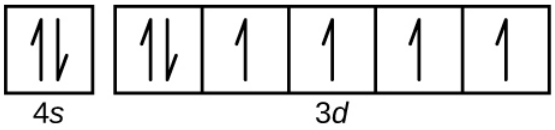
(a)



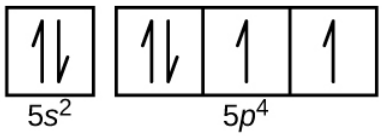
(b)



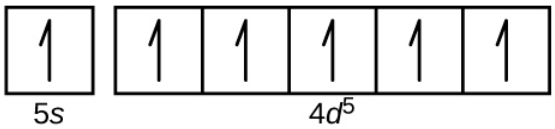
(c)



(d)



(e)



Q6.4.9

Using complete subshell notation ($1s^2 2s^2 2p^6$, and so forth), predict the electron configurations of the following ions.

a. N^{3-}
b. Ca^{2+}
c. S^{-}
d. Cs^{2+}
e. Cr^{2+}
f. Gd^{3+}

Q6.4.10

Which atom has the electron configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^2$?

S6.4.10

Zr

Q6.4.11

Which atom has the electron configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$?

https://chem.libretexts.org/@go/page/242831

S6.4.11

Co ; Cobalt

Q6.4.12

Which ion with a +1 charge has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$? Which ion with a –2 charge has this configuration?

S6.4.12

Rb^+, Se^{2-}

Q6.4.13

Which of the following atoms contains only three valence electrons: Li, B, N, F, Ne?

S6.4.13

B ; Boron

Q6.4.14

Which of the following has two unpaired electrons?

a. Mg
b. Si
c. S
d. Both Mg and S
e. Both Si and S.

S6.4.14

Although both (b) and (c) are correct, (e) encompasses both and is the best answer.

Q6.4.15

Which atom would be expected to have a half-filled 6*p* subshell?

S6.4.15

Bi ; Bismuth

Q6.4.16

Which atom would be expected to have a half-filled 4*s* subshell?

S6.4.16

K

Q6.4.17

In one area of Australia, the cattle did not thrive despite the presence of suitable forage. An investigation showed the cause to be the absence of sufficient cobalt in the soil. Cobalt forms cations in two oxidation states, Co^{2+} and Co^{3+}. Write the electron structure of the two cations.

Q6.4.18

Thallium was used as a poison in the Agatha Christie mystery story “The Pale Horse.” Thallium has two possible cationic forms, +1 and +3. The +1 compounds are the more stable. Write the electron structure of the +1 cation of thallium.

S6.4.18

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2 4f^{14} 5d^{10}$

Q6.4.19

Write the electron configurations for the following atoms or ions:

a. B^{3+}
b. O^{-}
c. Cl^{3+}
d. Ca^{2+}
e. Ti

Q6.4.20

Cobalt–60 and iodine–131 are radioactive isotopes commonly used in nuclear medicine. How many protons, neutrons, and electrons are in atoms of these isotopes? Write the complete electron configuration for each isotope.

S6.4.20

Co has 27 protons, 27 electrons, and 33 neutrons: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$.

I has 53 protons, 53 electrons, and 78 neutrons: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^5$.

Q6.4.21

Write a set of quantum numbers for each of the electrons with an n of 3 in a Sc atom.

6.5: Periodic Variations in Element Properties

Q6.5.1

Based on their positions in the periodic table, predict which has the smallest atomic radius: Mg, Sr, Si, Cl, I.

S6.5.1

Cl

Q6.5.2

Based on their positions in the periodic table, predict which has the largest atomic radius: Li, Rb, N, F, I.

Q6.5.3

Based on their positions in the periodic table, predict which has the largest first ionization energy: Mg, Ba, B, O, Te.

S6.5.3

O

Q6.5.4

Based on their positions in the periodic table, predict which has the smallest first ionization energy: Li, Cs, N, F, I.

Q6.5.5

Based on their positions in the periodic table, rank the following atoms in order of increasing first ionization energy: F, Li, N, Rb

S6.5.5

Rb < Li < N < F

Q6.5.6

Based on their positions in the periodic table, rank the following atoms or compounds in order of increasing first ionization energy: Mg, O, S, Si

Q6.5.7

Atoms of which group in the periodic table have a valence shell electron configuration of ns^2np^3?

S6.5.7

15 (5A)

Q6.5.8

Atoms of which group in the periodic table have a valence shell electron configuration of ns^2?

Q6.5.9

Based on their positions in the periodic table, list the following atoms in order of increasing radius: Mg, Ca, Rb, Cs.

S6.5.9

Mg < Ca < Rb < Cs

Q6.5.10

Based on their positions in the periodic table, list the following atoms in order of increasing radius: Sr, Ca, Si, Cl.

Q6.5.11

Based on their positions in the periodic table, list the following ions in order of increasing radius: K^+, Ca^{2+}, Al^{3+}, Si^{4+}.

S6.5.11

$Si^{4+} < Al^{3+} < Ca^{2+} < K^+$

Q6.5.12

List the following ions in order of increasing radius: Li^+, Mg^{2+}, $Br^–$, $Te^{2–}$.

Q6.5.13

Which atom and/or ion is (are) isoelectronic with Br^+: Se^{2+}, Se, $As^–$, Kr, Ga^{3+}, $Cl^–$?

S6.5.13

Se, $As^–$

Q6.5.14

Which of the following atoms and ions is (are) isoelectronic with S^{2+}: Si^{4+}, Cl^{3+}, Ar, As^{3+}, Si, Al^{3+}?

Q6.5.15

Compare both the numbers of protons and electrons present in each to rank the following ions in order of increasing radius: $As^{3–}$, $Br^–$, K^+, Mg^{2+}.

S6.5.15

$Mg^{2+} < K^+ < Br^– < As^{3–}$

Q6.5.16

Of the five elements Al, Cl, I, Na, Rb, which has the most exothermic reaction? (E represents an atom.) What name is given to the energy for the reaction? Hint: note the process depicted does *not* correspond to electron affinity

$$\mathbf{E^+}(g) + \mathbf{e^-} \longrightarrow \mathbf{E}(g)$$

Q6.5.17

Of the five elements Sn, Si, Sb, O, Te, which has the most endothermic reaction? (E represents an atom.) What name is given to the energy for the reaction?

$$\mathbf{E}(g) \longrightarrow \mathbf{E^+}(g) + \mathbf{e^-} \tag{5.E.14}$$

S6.5.17

O, IE_1

Q6.5.18

The ionic radii of the ions S^{2-}, Cl^{-}, and K^{+} are 184, 181, 138 pm respectively. Explain why these ions have different sizes even though they contain the same number of electrons.

Q6.5.19

Which main group atom would be expected to have the lowest second ionization energy?

S6.5.19

Ra

Q6.5.20

Explain why Al is a member of group 13 rather than group 3?

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CHAPTER OVERVIEW

6: Chemical Bonding and Molecular Geometry

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General Chemistry

A chemical bond is an attraction between atoms that allows the formation of chemical substances that contain two or more atoms. The bond is caused by the electrostatic force of attraction between opposite charges, either between electrons and nuclei, or as the result of a dipole attraction. All bonds can be explained by quantum theory, but, in practice, simplification rules allow chemists to predict the strength, directionality, and polarity of bonds. The octet rule and VSEPR theory are two examples. More sophisticated theories are valence bond theory which includes orbital hybridization and resonance, and the linear combination of atomic orbitals molecular orbital method. Electrostatics are used to describe bond polarities and the effects they have on chemical substances.

6.1: Prelude to Chemical Bonding and Molecular Geometry
6.2: Ionic Bonding
6.3: Covalent Bonding
6.4: Lewis Symbols and Structures
6.5: Formal Charges and Resonance
6.6: Strengths of Ionic and Covalent Bonds
6.7: Molecular Structure and Polarity
6.E: Chemical Bonding and Molecular Geometry (Exercises)

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6.1: Prelude to Chemical Bonding and Molecular Geometry

It has long been known that pure carbon occurs in different forms (allotropes) including graphite and diamonds. But it was not until 1985 that a new form of carbon was recognized: buckminsterfullerene, commonly known as a “buckyball.” This molecule was named after the architect and inventor R. Buckminster Fuller (1895–1983), whose signature architectural design was the geodesic dome, characterized by a lattice shell structure supporting a spherical surface. Experimental evidence revealed the formula, C_{60}, and then scientists determined how 60 carbon atoms could form one symmetric, stable molecule. They were guided by bonding theory—the topic of this chapter—which explains how individual atoms connect to form more complex structures.



Figure **6.1.1**: Nicknamed “buckyballs,” buckminsterfullerene molecules (C_{60}) contain only carbon atoms. Here they are shown in a ball-and-stick model (left). These molecules have single and double carbon-carbon bonds arranged to form a geometric framework of hexagons and pentagons, similar to the pattern on a soccer ball (center). This unconventional molecular structure is named after architect R. Buckminster Fuller, whose innovative designs combined simple geometric shapes to create large, strong structures such as this weather radar dome near Tucson, Arizona (right). (credit middle: modification of work by “Petey21”/Wikimedia Commons; credit right: modification of work by Bill Morrow).

Three figures are shown. The left figure is a many-sides spherical ball composed of hexagonal rings which have carbon atoms at each corner. The center picture shows a soccer ball. The right picture shown as water tower with sides shaped like hexagonal rings.

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6.2: Ionic Bonding

Learning Objectives

- Explain the formation of cations, anions, and ionic compounds
- Predict the charge of common metallic and nonmetallic elements, and write their electron configurations

As you have learned, ions are atoms or molecules bearing an electrical charge. A cation (a positive ion) forms when a neutral atom loses one or more electrons from its valence shell, and an anion (a negative ion) forms when a neutral atom gains one or more electrons in its valence shell.

Compounds composed of ions are called ionic compounds (or salts), and their constituent ions are held together by ionic bonds: electrostatic forces of attraction between oppositely charged cations and anions. The properties of ionic compounds shed some light on the nature of ionic bonds. Ionic solids exhibit a crystalline structure and tend to be rigid and brittle; they also tend to have high melting and boiling points, which suggests that ionic bonds are very strong. Ionic solids are also poor conductors of electricity for the same reason—the strength of ionic bonds prevents ions from moving freely in the solid state. Most ionic solids, however, dissolve readily in water. Once dissolved or melted, ionic compounds are excellent conductors of electricity and heat because the ions can move about freely.

Neutral atoms and their associated ions have very different physical and chemical properties. Sodium *atoms* form sodium metal, a soft, silvery-white metal that burns vigorously in air and reacts explosively with water. Chlorine *atoms* form chlorine gas, Cl_2, a yellow-green gas that is extremely corrosive to most metals and very poisonous to animals and plants. The vigorous reaction between the elements sodium and chlorine forms the white, crystalline compound sodium chloride, common table salt, which contains sodium *cations* and chloride *anions* (Figure Figure **6.2.1**). The compound composed of these ions exhibits properties entirely different from the properties of the elements sodium and chlorine. Chlorine is poisonous, but sodium chloride is essential to life; sodium atoms react vigorously with water, but sodium chloride simply dissolves in water.



Figure **6.2.1**: (a) Sodium is a soft metal that must be stored in mineral oil to prevent reaction with air or water. (b) Chlorine is a pale yellow-green gas. (c) When combined, they form white crystals of sodium chloride (table salt). (credit a: modification of work by "Jurii"/Wikimedia Commons)

The Formation of Ionic Compounds

Binary ionic compounds are composed of just two elements: a metal (which forms the cations) and a nonmetal (which forms the anions). For example, NaCl is a binary ionic compound. We can think about the formation of such compounds in terms of the periodic properties of the elements. Many metallic elements have relatively low ionization potentials and lose electrons easily. These elements lie to the left in a period or near the bottom of a group on the periodic table. Nonmetal atoms have relatively high electron affinities and thus readily gain electrons lost by metal atoms, thereby filling their valence shells. Nonmetallic elements are found in the upper-right corner of the periodic table.

As all substances must be electrically neutral, the total number of positive charges on the cations of an ionic compound must equal the total number of negative charges on its anions. The formula of an ionic compound represents the simplest ratio of the numbers of ions necessary to give identical numbers of positive and negative charges. For example, the formula for aluminum oxide, Al_2O_3, indicates that this ionic compound contains two aluminum cations, Al^{3+}, for every three oxide anions, O^{2-} [thus, $(2 \times +3) + (3 \times -2) = 0$].

It is important to note, however, that the formula for an ionic compound does *not* represent the physical arrangement of its ions. It is incorrect to refer to a sodium chloride (NaCl) "molecule" because there is not a single ionic bond, per se, between any specific pair of sodium and chloride ions. The attractive forces between ions are isotropic—the same in all directions—meaning that any particular ion is equally attracted to all of the nearby ions of opposite charge. This results in the ions arranging themselves into a tightly bound, three-dimensional lattice structure. Sodium chloride, for example, consists of a regular arrangement of equal numbers of Na^+ cations and Cl^- anions (Figure Figure **6.2.2**).



Figure **6.2.2**: The atoms in sodium chloride (common table salt) are arranged to (a) maximize opposite charges interacting. The smaller spheres represent sodium ions, the larger ones represent chloride ions. In the expanded view (b), the geometry can be seen more clearly. Note that each ion is "bonded" to all of the surrounding ions—six in this case.

Two diagrams are shown and labeled "a" and "b." Diagram a shows a cube made up of twenty-seven alternating purple and green spheres. The purple spheres are smaller than the green spheres. Diagram b shows the same spheres, but this time, they are spread out and connected in three dimensions by white rods. The purple spheres are labeled "N superscript postive sign" while the green are labeled "C l superscript negative sign."

The strong electrostatic attraction between Na^+ and Cl^- ions holds them tightly together in solid NaCl. It requires 769 kJ of energy to dissociate one mole of solid NaCl into separate gaseous Na^+ and Cl^- ions:

$$\mathrm{NaCl}(s) \longrightarrow \mathrm{Na}^+(g) + \mathrm{Cl}^-(g) \quad \Delta H = 769\ \mathrm{kJ}$$

Electronic Structures of Cations

When forming a cation, an atom of a main group element tends to lose all of its valence electrons, thus assuming the electronic structure of the noble gas that precedes it in the periodic table. For groups 1 (the alkali metals) and 2 (the alkaline earth metals), the group numbers are equal to the numbers of valence shell electrons and, consequently, to the charges of the cations formed from atoms of these elements when all valence shell electrons are removed. For example, calcium is a group 2 element whose neutral atoms have 20 electrons and a ground state electron configuration of $1s^22s^22p^63s^23p^64s^2$. When a Ca atom loses both of its valence electrons, the result is a cation with 18 electrons, a 2+ charge, and an electron configuration of $1s^22s^22p^63s^23p^6$. The Ca^{2+} ion is therefore isoelectronic with the noble gas Ar.

For groups 12–17, the group numbers exceed the number of valence electrons by 10 (accounting for the possibility of full *d* subshells in atoms of elements in the fourth and greater periods). Thus, the charge of a cation formed by the loss of all valence electrons is equal to the group number minus 10. For example, aluminum (in group 13) forms 3+ ions (Al^{3+}).

Exceptions to the expected behavior involve elements toward the bottom of the groups. In addition to the expected ions Tl^{3+}, Sn^{4+}, Pb^{4+}, and Bi^{5+}, a partial loss of these atoms' valence shell electrons can also lead to the formation of Tl^+, Sn^{2+}, Pb^{2+}, and Bi^{3+} ions. The formation of these 1+, 2+, and 3+ cations is ascribed to the inert pair effect, which reflects the relatively low energy of the valence *s*-electron pair for atoms of the heavy elements of groups 13, 14, and 15. Mercury (group 12) also exhibits an unexpected behavior: it forms a diatomic ion, $\mathrm{Hg_2}^{2+}$ (an ion formed from two mercury atoms, with an Hg-Hg bond), in addition to the expected monatomic ion Hg^{2+} (formed from only one mercury atom).

Transition and inner transition metal elements behave differently than main group elements. Most transition metal cations have 2+ or 3+ charges that result from the loss of their outermost *s* electron(s) first, sometimes followed by the loss of one or two *d* electrons from the next-to-outermost shell. For example, iron ($1s^22s^22p^63s^23p^63d^64s^2$) forms the ion Fe^{2+} ($1s^22s^22p^63s^23p^63d^6$) by the loss of the 4*s* electrons and the ion Fe^{3+} ($1s^22s^22p^63s^23p^63d^5$) by the loss of the 4*s* electrons and one of the 3*d* electrons. Although the *d* orbitals of the transition elements are—according to the Aufbau principle—the last to fill when building up electron configurations, the outermost *s* electrons are the first to be lost when these atoms ionize. When the inner transition metals form ions, they usually have a 3+ charge, resulting from the loss of their outermost *s* electrons and a *d* or *f* electron.

✔ Example 6.2.1: Determining the Electronic Structures of Cations

There are at least 14 elements categorized as "essential trace elements" for the human body. They are called "essential" because they are required for healthy bodily functions, "trace" because they are required only in small amounts, and "elements" in spite of the fact that they are really ions. Two of these essential trace elements, chromium and zinc, are required as Cr^{3+} and Zn^{2+}. Write the electron configurations of these cations.

Solution

First, write the electron configuration for the neutral atoms:

- Zn: [Ar]$3d^{10}4s^2$
- Cr: [Ar]$3d^5 4s^1$

Next, remove electrons from the highest energy orbital. For the transition metals, electrons are removed from the *s* orbital first and then from the *d* orbital. For the *p*-block elements, electrons are removed from the *p* orbitals and then from the *s* orbital. Zinc is a member of group 12, so it should have a charge of 2+, and thus loses only the two electrons in its *s* orbital. Chromium is a transition element and should lose its *s* electrons and then its *d* electrons when forming a cation. Thus, we find the following electron configurations of the ions:

- Zn^{2+}: [Ar]$3d^{10}$
- Cr^{3+}: [Ar]$3d^3$

? Exercise 6.2.1

Potassium and magnesium are required in our diet. Write the electron configurations of the ions expected from these elements.

Answer

K^+: [Ar], Mg^{2+}: [Ne]

Electronic Structures of Anions

Most monatomic anions form when a neutral nonmetal atom gains enough electrons to completely fill its outer *s* and *p* orbitals, thereby reaching the electron configuration of the next noble gas. Thus, it is simple to determine the charge on such a negative ion: The charge is equal to the number of electrons that must be gained to fill the *s* and *p* orbitals of the parent atom. Oxygen, for example, has the electron configuration $1s^2 2s^2 2p^4$, whereas the oxygen anion has the electron configuration of the noble gas neon (Ne), $1s^2 2s^2 2p^6$. The two additional electrons required to fill the valence orbitals give the oxide ion the charge of 2– (O^{2-}).

✓ Example 6.2.2: Determining the Electronic Structure of Anions

Selenium and iodine are two essential trace elements that form anions. Write the electron configurations of the anions.

Solution

Se^{2-}: [Ar]$3d^{10}4s^2 4p^6$

I^-: [Kr]$4d^{10}5s^2 5p^6$

? Exercise 6.2.2

Write the electron configurations of a phosphorus atom and its negative ion. Give the charge on the anion.

Answer

P: [Ne]$3s^2 3p^3$

P^{3-}: [Ne]$3s^2 3p^6$

Summary

Atoms gain or lose electrons to form ions with particularly stable electron configurations. The charges of cations formed by the representative metals may be determined readily because, with few exceptions, the electronic structures of these ions have either a

noble gas configuration or a completely filled electron shell. The charges of anions formed by the nonmetals may also be readily determined because these ions form when nonmetal atoms gain enough electrons to fill their valence shells.

Glossary

inert pair effect

tendency of heavy atoms to form ions in which their valence *s* electrons are not lost

ionic bond

strong electrostatic force of attraction between cations and anions in an ionic compound

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6.3: Covalent Bonding

Learning Objectives

- Describe the formation of covalent bonds
- Define electronegativity and assess the polarity of covalent bonds

In ionic compounds, electrons are transferred between atoms of different elements to form ions. But this is not the only way that compounds can be formed. Atoms can also make chemical bonds by sharing electrons between each other. Such bonds are called covalent bonds. Covalent bonds are formed between two atoms when both have similar tendencies to attract electrons to themselves (i.e., when both atoms have identical or fairly similar ionization energies and electron affinities). For example, two hydrogen atoms bond covalently to form an H_2 molecule; each hydrogen atom in the H_2 molecule has two electrons stabilizing it, giving each atom the same number of valence electrons as the noble gas He.

Compounds that contain covalent bonds exhibit different physical properties than ionic compounds. Because the attraction between molecules, which are electrically neutral, is weaker than that between electrically charged ions, covalent compounds generally have much lower melting and boiling points than ionic compounds. In fact, many covalent compounds are liquids or gases at room temperature, and, in their solid states, they are typically much softer than ionic solids. Furthermore, whereas ionic compounds are good conductors of electricity when dissolved in water, most covalent compounds, being electrically neutral, are poor conductors of electricity in any state.

Formation of Covalent Bonds

Nonmetal atoms frequently form covalent bonds with other nonmetal atoms. For example, the hydrogen molecule, H_2, contains a covalent bond between its two hydrogen atoms. Figure **6.3.1** illustrates why this bond is formed. Starting on the far right, we have two separate hydrogen atoms with a particular potential energy, indicated by the red line. Along the *x*-axis is the distance between the two atoms. As the two atoms approach each other (moving left along the *x*-axis), their valence orbitals (1*s*) begin to overlap. The single electrons on each hydrogen atom then interact with both atomic nuclei, occupying the space around both atoms. The strong attraction of each shared electron to both nuclei stabilizes the system, and the potential energy decreases as the bond distance decreases. If the atoms continue to approach each other, the positive charges in the two nuclei begin to repel each other, and the potential energy increases. The bond length is determined by the distance at which the lowest potential energy is achieved.

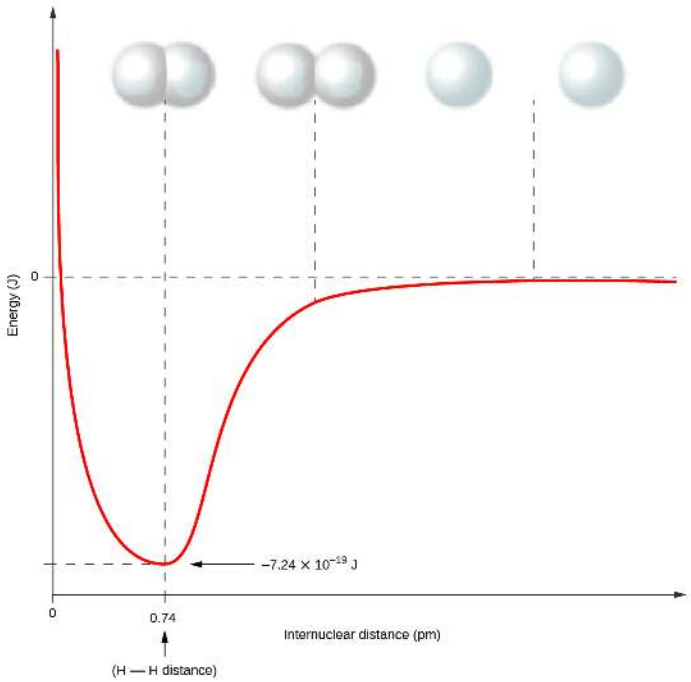


Figure **6.3.1***: The potential energy of two separate hydrogen atoms (right) decreases as they approach each other, and the single electrons on each atom are shared to form a covalent bond. The bond length is the internuclear distance at which the lowest potential energy is achieved.*

It is essential to remember that energy must be added to break chemical bonds (an endothermic process), whereas forming chemical bonds releases energy (an exothermic process). In the case of H_2, the covalent bond is very strong; a large amount of energy, 436 kJ, must be added to break the bonds in one mole of hydrogen molecules and cause the atoms to separate:

$$\mathrm{H_2}(g) \longrightarrow 2\,\mathrm{H}(g) \quad \Delta H = 436\ \mathrm{kJ}$$

Conversely, the same amount of energy is released when one mole of H_2 molecules forms from two moles of H atoms:

$$2\,\mathrm{H}(g) \longrightarrow \mathrm{H_2}(g) \quad \Delta H = -436\ \mathrm{kJ}$$

Pure vs. Polar Covalent Bonds

If the atoms that form a covalent bond are identical, as in H_2, Cl_2, and other diatomic molecules, then the electrons in the bond must be shared equally. We refer to this as a pure covalent bond. Electrons shared in pure covalent bonds have an equal probability of being near each nucleus. In the case of Cl_2, each atom starts off with seven valence electrons, and each Cl shares one electron with the other, forming one covalent bond:

$$\mathrm{Cl} + \mathrm{Cl} \longrightarrow \mathrm{Cl_2}$$

The total number of electrons around each individual atom consists of six nonbonding electrons and two shared (i.e., bonding) electrons for eight total electrons, matching the number of valence electrons in the noble gas argon. Since the bonding atoms are identical, Cl_2 also features a pure covalent bond.

When the atoms linked by a covalent bond are different, the bonding electrons are shared, but no longer equally. Instead, the bonding electrons are more attracted to one atom than the other, giving rise to a shift of electron density toward that atom. This unequal distribution of electrons is known as a polar covalent bond, characterized by a partial positive charge on one atom and a partial negative charge on the other. The atom that attracts the electrons more strongly acquires the partial negative charge and vice versa. For example, the electrons in the H–Cl bond of a hydrogen chloride molecule spend more time near the chlorine atom than near the hydrogen atom. Thus, in an HCl molecule, the chlorine atom carries a partial negative charge and the hydrogen atom has a partial positive charge. Figure **6.3.2** shows the distribution of electrons in the H–Cl bond. Note that the shaded area around Cl is much larger than it is around H. Compare this to Figure **6.3.1**, which shows the even distribution of electrons in the H_2 nonpolar bond.

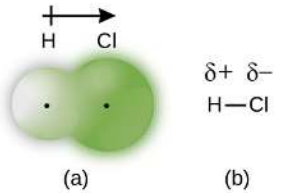


Figure **6.3.2**: (a) The distribution of electron density in the HCl molecule is uneven. The electron density is greater around the chlorine nucleus. The small, black dots indicate the location of the hydrogen and chlorine nuclei in the molecule. (b) Symbols δ+ and δ– indicate the polarity of the H–Cl bond.

We sometimes designate the positive and negative atoms in a polar covalent bond using a lowercase Greek letter "delta," δ, with a plus sign or minus sign to indicate whether the atom has a partial positive charge (δ+) or a partial negative charge (δ–). This symbolism is shown for the H–Cl molecule in Figure **6.3.2***b*.

Electronegativity

Whether a bond is nonpolar or polar covalent is determined by a property of the bonding atoms called electronegativity. Electronegativity is a measure of the tendency of an atom to attract electrons (or electron density) towards itself. It determines how the shared electrons are distributed between the two atoms in a bond. The more strongly an atom attracts the electrons in its bonds, the larger its electronegativity. Electrons in a polar covalent bond are shifted toward the more electronegative atom; thus, the more electronegative atom is the one with the partial negative charge. The greater the difference in electronegativity, the more polarized the electron distribution and the larger the partial charges of the atoms.

Figure **6.3.3** shows the electronegativity values of the elements as proposed by one of the most famous chemists of the twentieth century: Linus Pauling. In general, electronegativity increases from left to right across a period in the periodic table and decreases down a group. Thus, the nonmetals, which lie in the upper right, tend to have the highest electronegativities, with fluorine the most electronegative element of all (EN = 4.0). Metals tend to be less electronegative elements, and the group 1 metals have the lowest electronegativities. Note that noble gases are excluded from this figure because these atoms usually do not share electrons with others atoms since they have a full valence shell. (While noble gas compounds such as XeO_2 do exist, they can only be formed under extreme conditions, and thus they do not fit neatly into the general model of electronegativity.)

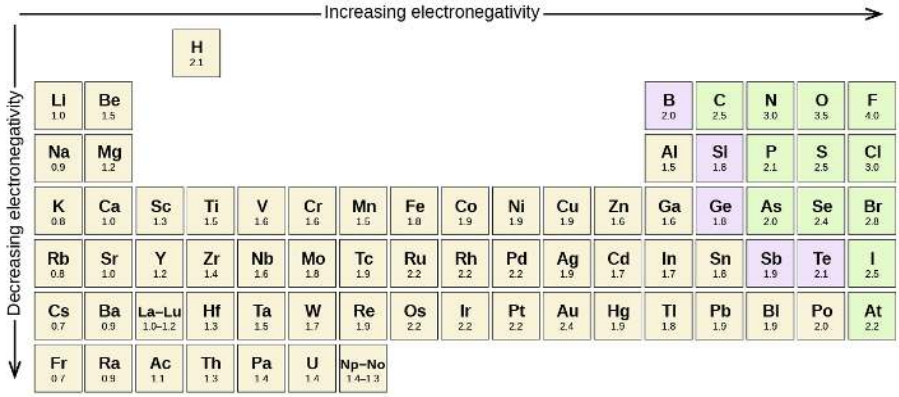


Figure **6.3.3**: The electronegativity values derived by Pauling follow predictable periodic trends with the higher electronegativities toward the upper right of the periodic table.

Linus Pauling

Linus Pauling is the only person to have received two unshared (individual) Nobel Prizes: one for chemistry in 1954 for his work on the nature of chemical bonds and one for peace in 1962 for his opposition to weapons of mass destruction. He developed many of the theories and concepts that are foundational to our current understanding of chemistry, including electronegativity and resonance structures.



Linus Pauling (1901–1994) made many important contributions to the field of chemistry. He was also a prominent activist, publicizing issues related to health and nuclear weapons.

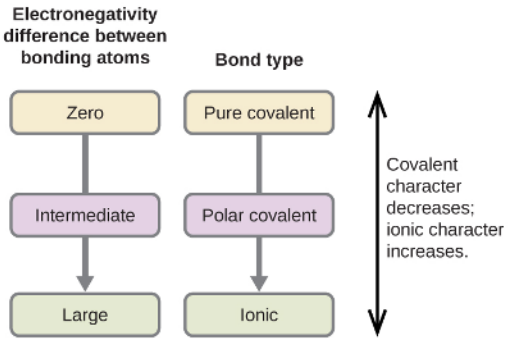
Pauling also contributed to many other fields besides chemistry. His research on sickle cell anemia revealed the cause of the disease—the presence of a genetically inherited abnormal protein in the blood—and paved the way for the field of molecular genetics. His work was also pivotal in curbing the testing of nuclear weapons; he proved that radioactive fallout from nuclear testing posed a public health risk.

Electronegativity versus Electron Affinity

We must be careful not to confuse electronegativity and electron affinity. The electron affinity of an element is a measurable physical quantity, namely, the energy released or absorbed when an isolated gas-phase atom acquires an electron, measured in kJ/mol. Electronegativity, on the other hand, describes how tightly an atom attracts electrons in a bond. It is a dimensionless quantity that is calculated, not measured. Pauling derived the first electronegativity values by comparing the amounts of energy required to break different types of bonds. He chose an arbitrary relative scale ranging from 0 to 4.

Electronegativity and Bond Type

The absolute value of the difference in electronegativity (ΔEN) of two bonded atoms provides a rough measure of the polarity to be expected in the bond and, thus, the bond type. When the difference is very small or zero, the bond is covalent and nonpolar. When it is large, the bond is polar covalent or ionic. The absolute values of the electronegativity differences between the atoms in the bonds H–H, H–Cl, and Na–Cl are 0 (nonpolar), 0.9 (polar covalent), and 2.1 (ionic), respectively. The degree to which electrons are shared between atoms varies from completely equal (pure covalent bonding) to not at all (ionic bonding). Figure **6.3.4** shows the relationship between electronegativity difference and bond type.



Bond Type	Electronegativity Difference
pure covalent	< 0.4
polar covalent	between 0.4 and 1.8
ionic	> 1.8

Figure **6.3.4**: As the electronegativity difference increases between two atoms, the bond becomes more ionic.

A rough approximation of the electronegativity differences associated with covalent, polar covalent, and ionic bonds is shown in Figure **6.3.4**. This table is just a general guide, however, with many exceptions. For example, the H and F atoms in HF have an electronegativity difference of 1.9, and the N and H atoms in NH_3 a difference of 0.9, yet both of these compounds form bonds that are considered polar covalent. Likewise, the Na and Cl atoms in NaCl have an electronegativity difference of 2.1, and the Mn and I atoms in MnI_2 have a difference of 1.0, yet both of these substances form ionic compounds.

The best guide to the covalent or ionic character of a bond is to consider the types of atoms involved and their relative positions in the periodic table. Bonds between two nonmetals are generally covalent; bonding between a metal and a nonmetal is often ionic.

Some compounds contain both covalent and ionic bonds. The atoms in polyatomic ions, such as OH^-, NO_3^-, and NH_4^+, are held together by polar covalent bonds. However, these polyatomic ions form ionic compounds by combining with ions of opposite charge. For example, potassium nitrate, KNO_3, contains the K^+ cation and the polyatomic NO_3^- anion. Thus, bonding in potassium nitrate is ionic, resulting from the electrostatic attraction between the ions K^+ and NO_3^-, as well as covalent between the nitrogen and oxygen atoms in NO_3^-.

Example 6.3.1: Electronegativity and Bond Polarity

Bond polarities play an important role in determining the structure of proteins. Using the electronegativity values in Table A2, arrange the following covalent bonds—all commonly found in amino acids—in order of increasing polarity. Then designate the positive and negative atoms using the symbols δ+ and δ–:

C–H, C–N, C–O, N–H, O–H, S–H

Solution

The polarity of these bonds increases as the absolute value of the electronegativity difference increases. The atom with the δ– designation is the more electronegative of the two. Table 6.3.1 shows these bonds in order of increasing polarity.

Table 6.3.1: Bond Polarity and Electronegativity Difference

Bond	ΔEN	Polarity
C–H	0.4	$\overset{\delta-}{C}-\overset{\delta+}{H}$
S–H	0.4	$\overset{\delta-}{S}-\overset{\delta+}{H}$
C–N	0.5	$\overset{\delta+}{C}-\overset{\delta-}{N}$
N–H	0.9	$\overset{\delta-}{N}-\overset{\delta+}{H}$
C–O	1.0	$\overset{\delta+}{C}-\overset{\delta-}{O}$
O–H	1.4	$\overset{\delta-}{O}-\overset{\delta+}{H}$

Exercise 6.3.1

Silicones are polymeric compounds containing, among others, the following types of covalent bonds: Si–O, Si–C, C–H, and C–C. Using the electronegativity values in Figure 6.3.3, arrange the bonds in order of increasing polarity and designate the positive and negative atoms using the symbols δ+ and δ–.

Answer

Answer to Exercise 7.2.1

Bond	Electronegativity Difference	Polarity
C–C	0.0	nonpolar
C–H	0.4	$\overset{\delta-}{C}-\overset{\delta+}{H}$
Si–C	0.7	$\overset{\delta+}{Si}-\overset{\delta-}{C}$
Si–O	1.7	$\overset{\delta+}{Si}-\overset{\delta-}{O}$

Summary

Covalent bonds form when electrons are shared between atoms and are attracted by the nuclei of both atoms. In pure covalent bonds, the electrons are shared equally. In polar covalent bonds, the electrons are shared unequally, as one atom exerts a stronger force of attraction on the electrons than the other. The ability of an atom to attract a pair of electrons in a chemical bond is called its

electronegativity. The difference in electronegativity between two atoms determines how polar a bond will be. In a diatomic molecule with two identical atoms, there is no difference in electronegativity, so the bond is nonpolar or pure covalent. When the electronegativity difference is very large, as is the case between metals and nonmetals, the bonding is characterized as ionic.

Glossary

bond length
distance between the nuclei of two bonded atoms at which the lowest potential energy is achieved

covalent bond
bond formed when electrons are shared between atoms

electronegativity
tendency of an atom to attract electrons in a bond to itself

polar covalent bond
covalent bond between atoms of different electronegativities; a covalent bond with a positive end and a negative end

pure covalent bond
(also, nonpolar covalent bond) covalent bond between atoms of identical electronegativities

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6.4: Lewis Symbols and Structures

Learning Objectives

- Write Lewis symbols for neutral atoms and ions
- Draw Lewis structures depicting the bonding in simple molecules

Thus far, we have discussed the various types of bonds that form between atoms and/or ions. In all cases, these bonds involve the sharing or transfer of valence shell electrons between atoms. In this section, we will explore the typical method for depicting valence shell electrons and chemical bonds, namely Lewis symbols and Lewis structures.

Lewis Symbols

We use Lewis symbols to describe valence electron configurations of atoms and monatomic ions. A Lewis symbol consists of an elemental symbol surrounded by one dot for each of its valence electrons:



Figure **6.4.1** shows the Lewis symbols for the elements of the third period of the periodic table. Electron dots are typically arranged in four pairs located on the four "sides" of the atomic symbol.

Atoms	Electronic Configuration	Lewis Symbol
sodium	$[Ne]3s^1$	Na•
magnesium	$[Ne]3s^2$	•Mg•
aluminum	$[Ne]3s^23p^1$	•Al•
silicon	$[Ne]3s^23p^2$	•Si•
phosphorus	$[Ne]3s^23p^3$	•P•
sulfur	$[Ne]3s^23p^4$	:S•
chlorine	$[Ne]3s^23p^5$	:Cl•
argon	$[Ne]3s^23p^6$	:Ar:

Figure **6.4.1**: Lewis symbols illustrating the number of valence electrons for each element in the third period of the periodic table.

Lewis symbols can be used to illustrate the formation of cations from atoms, as shown here for sodium and calcium:



Likewise, they can be used to show the formation of anions from atoms, as shown here for chlorine and sulfur:



Figure **6.4.2** demonstrates the use of Lewis symbols to show the transfer of electrons during the formation of ionic compounds.

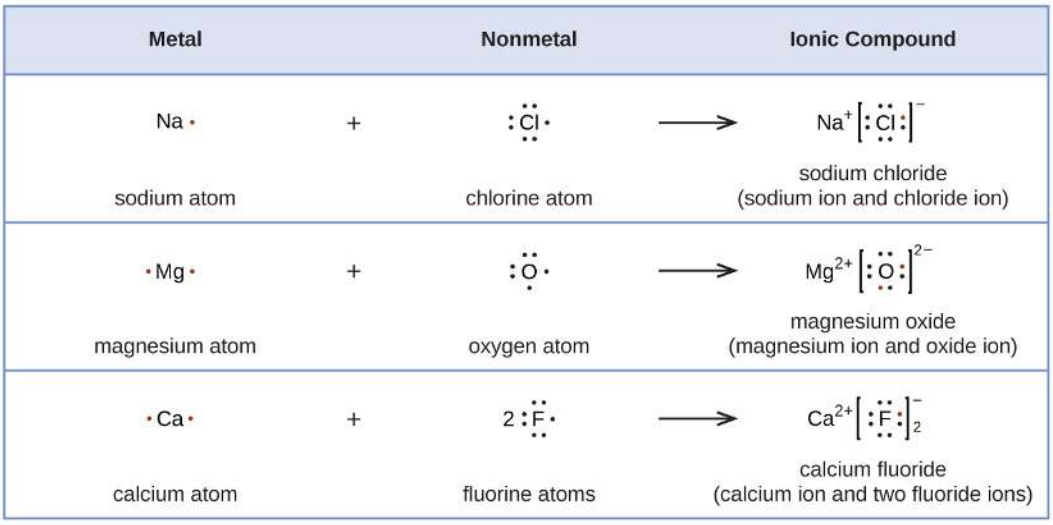
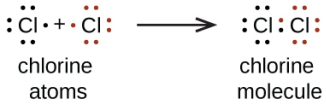


Figure **6.4.2**: Cations are formed when atoms lose electrons, represented by fewer Lewis dots, whereas anions are formed by atoms gaining electrons. The total number of electrons does not change.

Lewis Structures

We also use Lewis symbols to indicate the formation of covalent bonds, which are shown in Lewis structures, drawings that describe the bonding in molecules and polyatomic ions. For example, when two chlorine atoms form a chlorine molecule, they share one pair of electrons:



The Lewis structure indicates that each Cl atom has three pairs of electrons that are not used in bonding (called lone pairs) and one shared pair of electrons (written between the atoms). A dash (or line) is usually used to indicate a shared pair of electrons:

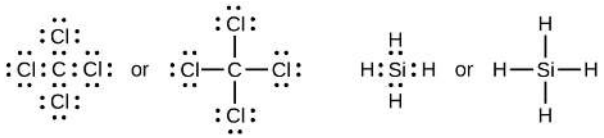


In the Lewis model, a single shared pair of electrons is a single bond. Each Cl atom interacts with eight valence electrons total: the six in the lone pairs and the two in the single bond.

The Octet Rule

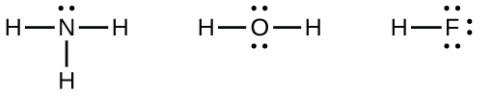
The other halogen molecules (F_2, Br_2, I_2, and At_2) form bonds like those in the chlorine molecule: one single bond between atoms and three lone pairs of electrons per atom. This allows each halogen atom to have a noble gas electron configuration. The tendency of main group atoms to form enough bonds to obtain eight valence electrons is known as the octet rule.

The number of bonds that an atom can form can often be predicted from the number of electrons needed to reach an octet (eight valence electrons); this is especially true of the nonmetals of the second period of the periodic table (C, N, O, and F). For example, each atom of a group 14 element has four electrons in its outermost shell and therefore requires four more electrons to reach an octet. These four electrons can be gained by forming four covalent bonds, as illustrated here for carbon in CCl_4 (carbon tetrachloride) and silicon in SiH_4 (silane). Because hydrogen only needs two electrons to fill its valence shell, it is an exception to the octet rule and only needs to form one bond. The transition elements and inner transition elements also do not follow the octet rule since they have d and f electrons involved in their valence shells.



carbon tetrachloride silane

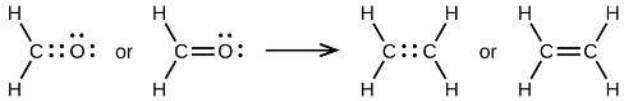
Group 15 elements such as nitrogen have five valence electrons in the atomic Lewis symbol: one lone pair and three unpaired electrons. To obtain an octet, these atoms form three covalent bonds, as in NH_3 (ammonia). Oxygen and other atoms in group 16 obtain an octet by forming two covalent bonds:



ammonia Water hydrogen fluoride

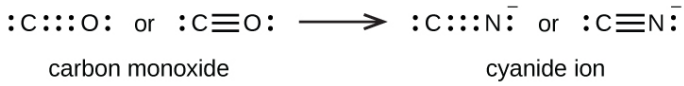
Double and Triple Bonds

As previously mentioned, when a pair of atoms shares one pair of electrons, we call this a single bond. However, a pair of atoms may need to share more than one pair of electrons in order to achieve the requisite octet. A double bond forms when two pairs of electrons are shared between a pair of atoms, as between the carbon and oxygen atoms in CH_2O (formaldehyde) and between the two carbon atoms in C_2H_4 (ethylene):



formaldehyde ethylene

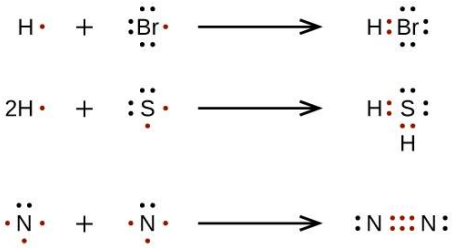
A triple bond forms when three electron pairs are shared by a pair of atoms, as in carbon monoxide (CO) and the cyanide ion (CN^-):



carbon monoxide cyanide ion

Writing Lewis Structures with the Octet Rule

For very simple molecules and molecular ions, we can write the Lewis structures by merely pairing up the unpaired electrons on the constituent atoms. See these examples:



For more complicated molecules and molecular ions, it is helpful to follow the step-by-step procedure outlined here:

1. Determine the total number of valence (outer shell) electrons among all the atoms. For cations, subtract one electron for each positive charge. For anions, add one electron for each negative charge.
2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom. (Generally, the least electronegative element should be placed in the center.) Connect each atom to the central atom with a single bond (one electron pair).

3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen), completing an octet around each atom.
4. Place all remaining electrons on the central atom.
5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

Let us determine the Lewis structures of SiH_4, CHO_2^-, NO^+, and OF_2 as examples in following this procedure:

1. Determine the total number of valence (outer shell) electrons in the molecule or ion.
   - For a molecule, we add the number of valence electrons on each atom in the molecule:

$$\begin{aligned} &SiH_4 && (6.4.1)\\ &\text{Si: 4 valence electrons/atom} \times \text{1 atom} = 4 && (6.4.2)\\ &+\text{H: 1 valence electron/atom} \times \text{4 atoms} = 4 && (6.4.3)\\ &\qquad = \text{8 valence electrons} && (6.4.4)\end{aligned}$$

   - For a *negative ion*, such as CHO_2^-, we add the number of valence electrons on the atoms to the number of negative charges on the ion (one electron is gained for each single negative charge):

$$\begin{aligned} &CHO_2^-\\ &\text{C: 4 valence electrons/atom} \times \text{1 atom} = 4\\ &\text{H: 1 valence electron/atom} \times \text{1 atom} = 1\\ &\text{O: 6 valence electrons/atom} \times \text{2 atoms} = 12\\ &+ \quad \text{1 additional electron} = 1\\ &\qquad = \text{18 valence electrons}\end{aligned}$$

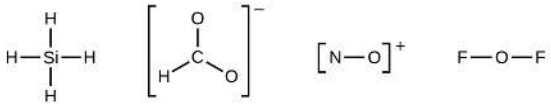
   - For a *positive ion*, such as NO^+, we add the number of valence electrons on the atoms in the ion and then subtract the number of positive charges on the ion (one electron is lost for each single positive charge) from the total number of valence electrons:

$$\begin{aligned} &NO^+\\ &\text{N: 5 valence electrons/atom} \times \text{1 atom} = 5\\ &\text{O: 6 valence electron/atom} \times \text{1 atom} = 6\\ &+ -1 \text{ electron (positive charge)} = -1\\ &\qquad = \text{10 valence electrons}\end{aligned}$$

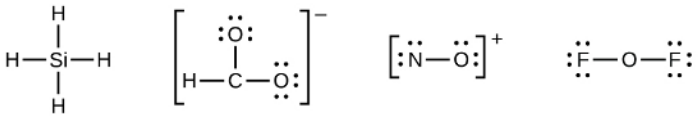
   - Since OF_2 is a neutral molecule, we simply add the number of valence electrons:

$$\begin{aligned} &OF_2\\ &\text{O: 6 valence electrons/atom} \times \text{1 atom} = 6\\ &+ \text{F: 7 valence electrons/atom} \times \text{2 atoms} = 14\\ &\qquad = \text{20 valence electrons}\end{aligned}$$

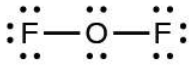
2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom and connecting each atom to the central atom with a single (one electron pair) bond. (Note that we denote ions with brackets around the structure, indicating the charge outside the brackets:)



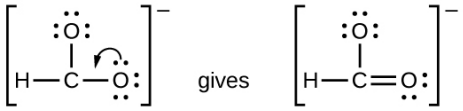
3. When several arrangements of atoms are possible, as for CHO_2^-, we must use experimental evidence to choose the correct one. In general, the less electronegative elements are more likely to be central atoms. In CHO_2^-, the less electronegative carbon atom occupies the central position with the oxygen and hydrogen atoms surrounding it. Other examples include P in $POCl_3$, S in SO_2, and Cl in ClO_4^-. An exception is that hydrogen is almost never a central atom. As the most electronegative element, fluorine also cannot be a central atom.
4. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen) to complete their valence shells with an octet of electrons.
   - There are no remaining electrons on SiH_4, so it is unchanged:



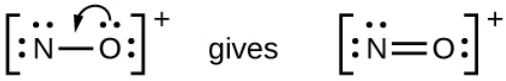
5. Place all remaining electrons on the central atom.
   - For SiH_4, CHO_2^-, and NO^+, there are no remaining electrons; we already placed all of the electrons determined in Step 1.
   - For OF_2, we had 16 electrons remaining in Step 3, and we placed 12, leaving 4 to be placed on the central atom:



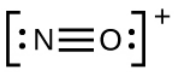
6. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.
   - SiH_4: Si already has an octet, so nothing needs to be done.
   - CHO_2^-: We have distributed the valence electrons as lone pairs on the oxygen atoms, but the carbon atom lacks an octet:



- NO^+: For this ion, we added eight outer electrons, but neither atom has an octet. We cannot add any more electrons since we have already used the total that we found in Step 1, so we must move electrons to form a multiple bond:



- This still does not produce an octet, so we must move another pair, forming a triple bond:



- In OF_2, each atom has an octet as drawn, so nothing changes.

Example 6.4.1: Writing Lewis Structures

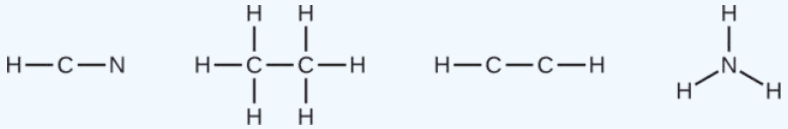
NASA's Cassini-Huygens mission detected a large cloud of toxic hydrogen cyanide (HCN) on Titan, one of Saturn's moons. Titan also contains ethane (H_3CCH_3), acetylene (HCCH), and ammonia (NH_3). What are the Lewis structures of these molecules?

Solution

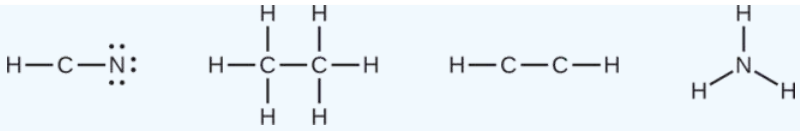
Calculate the number of valence electrons.

- HCN: (1 × 1) + (4 × 1) + (5 × 1) = 10
- H_3CCH_3: (1 × 3) + (2 × 4) + (1 × 3) = 14
- HCCH: (1 × 1) + (2 × 4) + (1 × 1) = 10
- NH_3: (5 × 1) + (3 × 1) = 8

Draw a skeleton and connect the atoms with single bonds. Remember that H is never a central atom:

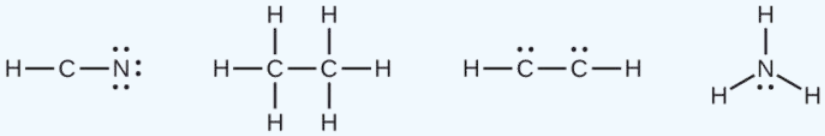


Where needed, distribute electrons to the terminal atoms:



- HCN: six electrons placed on N
- H_3CCH_3: no electrons remain
- HCCH: no terminal atoms capable of accepting electrons
- NH_3: no terminal atoms capable of accepting electrons

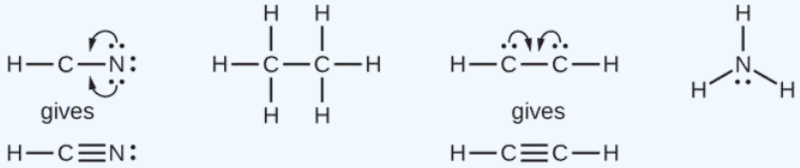
Where needed, place remaining electrons on the central atom:



- HCN: no electrons remain
- H_3CCH_3: no electrons remain
- HCCH: four electrons placed on carbon
- NH_3: two electrons placed on nitrogen

Where needed, rearrange electrons to form multiple bonds in order to obtain an octet on each atom:

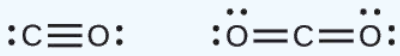
- HCN: form two more C–N bonds
- H_3CCH_3: all atoms have the correct number of electrons
- HCCH: form a triple bond between the two carbon atoms
- NH_3: all atoms have the correct number of electrons



? Exercise 6.4.1

Both carbon monoxide, CO, and carbon dioxide, CO_2, are products of the combustion of fossil fuels. Both of these gases also cause problems: CO is toxic and CO_2 has been implicated in global climate change. What are the Lewis structures of these two molecules?

Answer



Fullerene Chemistry

Carbon soot has been known to man since prehistoric times, but it was not until fairly recently that the molecular structure of the main component of soot was discovered. In 1996, the Nobel Prize in Chemistry was awarded to Richard Smalley, Robert Curl, and Harold Kroto for their work in discovering a new form of carbon, the C_{60} buckminsterfullerene molecule. An entire class of compounds, including spheres and tubes of various shapes, were discovered based on C_{60}. This type of molecule, called a fullerene, consists of a complex network of single- and double-bonded carbon atoms arranged in such a way that each carbon atom obtains a full octet of electrons. Because of their size and shape, fullerenes can encapsulate other molecules, so they have shown potential in various applications from hydrogen storage to targeted drug delivery systems. They also possess unique electronic and optical properties that have been put to good use in solar powered devices and chemical sensors.

Exceptions to the Octet Rule

Many covalent molecules have central atoms that do not have eight electrons in their Lewis structures. These molecules fall into three categories:

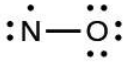
- Odd-electron molecules have an odd number of valence electrons, and therefore have an unpaired electron.
- Electron-deficient molecules have a central atom that has fewer electrons than needed for a noble gas configuration.
- Hypervalent molecules have a central atom that has more electrons than needed for a noble gas configuration.

Odd-electron Molecules

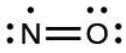
We call molecules that contain an odd number of electrons free radicals. Nitric oxide, NO, is an example of an odd-electron molecule; it is produced in internal combustion engines when oxygen and nitrogen react at high temperatures.

To draw the Lewis structure for an odd-electron molecule like NO, we follow the same five steps we would for other molecules, but with a few minor changes:

1. *Determine the total number of valence (outer shell) electrons*. The sum of the valence electrons is 5 (from N) + 6 (from O) = 11. The odd number immediately tells us that we have a free radical, so we know that not every atom can have eight electrons in its valence shell.
2. *Draw a skeleton structure of the molecule*. We can easily draw a skeleton with an N–O single bond: N–O
3. *Distribute the remaining electrons as lone pairs on the terminal atoms*. In this case, there is no central atom, so we distribute the electrons around both atoms. We give eight electrons to the more electronegative atom in these situations; thus oxygen has the filled valence shell:

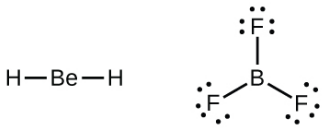


4. *Place all remaining electrons on the central atom*. Since there are no remaining electrons, this step does not apply.
5. *Rearrange the electrons to make multiple bonds with the central atom in order to obtain octets wherever possible.* We know that an odd-electron molecule cannot have an octet for every atom, but we want to get each atom as close to an octet as possible. In this case, nitrogen has only five electrons around it. To move closer to an octet for nitrogen, we take one of the lone pairs from oxygen and use it to form a NO double bond. (We cannot take another lone pair of electrons on oxygen and form a triple bond because nitrogen would then have nine electrons:)

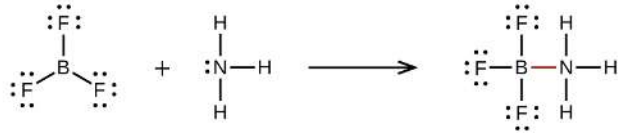


Electron-deficient Molecules

We will also encounter a few molecules that contain central atoms that do not have a filled valence shell. Generally, these are molecules with central atoms from groups 2 and 13 and outer atoms that are hydrogen or other atoms that do not form multiple bonds. For example, in the Lewis structures of beryllium dihydride, BeH_2, and boron trifluoride, BF_3, the beryllium and boron atoms each have only four and six electrons, respectively. It is possible to draw a structure with a double bond between a boron atom and a fluorine atom in BF_3, satisfying the octet rule, but experimental evidence indicates the bond lengths are closer to that expected for B–F single bonds. This suggests the best Lewis structure has three B–F single bonds and an electron deficient boron. The reactivity of the compound is also consistent with an electron deficient boron. However, the B–F bonds are slightly shorter than what is actually expected for B–F single bonds, indicating that some double bond character is found in the actual molecule.



An atom like the boron atom in BF_3, which does not have eight electrons, is very reactive. It readily combines with a molecule containing an atom with a lone pair of electrons. For example, NH_3 reacts with BF_3 because the lone pair on nitrogen can be shared with the boron atom:



Hypervalent Molecules

Elements in the second period of the periodic table ($n = 2$) can accommodate only eight electrons in their valence shell orbitals because they have only four valence orbitals (one 2*s* and three 2*p* orbitals). Elements in the third and higher periods ($n \geq 3$) have more than four valence orbitals and can share more than four pairs of electrons with other atoms because they have empty *d* orbitals in the same shell. Molecules formed from these elements are sometimes called hypervalent molecules.Table **6.4.5** shows the Lewis structures for two hypervalent molecules, PCl_5 and SF_6.

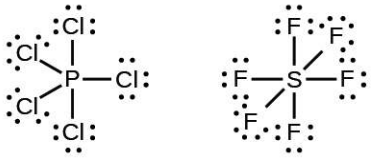
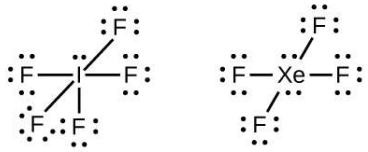


Table **6.4.5**: *In PCl_5, the central atom phosphorus shares five pairs of electrons. In SF_6, sulfur shares six pairs of electrons.*

In some hypervalent molecules, such as IF_5 and XeF_4, some of the electrons in the outer shell of the central atom are lone pairs:



When we write the Lewis structures for these molecules, we find that we have electrons left over after filling the valence shells of the outer atoms with eight electrons. These additional electrons must be assigned to the central atom.

Example 6.4.2: Octet Rule Violations

Xenon is a noble gas, but it forms a number of stable compounds. We examined $\mathbf{XeF_4}$ earlier. What are the Lewis structures of $\mathbf{XeF_2}$ and $\mathbf{XeF_6}$?

Solution

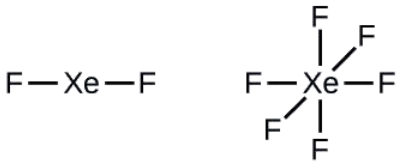
We can draw the Lewis structure of any covalent molecule by following the six steps discussed earlier. In this case, we can condense the last few steps, since not all of them apply.

Step 1: Calculate the number of valence electrons:

$\mathbf{XeF_2}$: $8 + (2 \times 7) = 22$

$\mathbf{XeF_6}$: $8 + (6 \times 7) = 50$

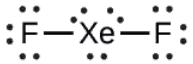
Step 2: Draw a skeleton joining the atoms by single bonds. **Xenon will be the central atom because fluorine cannot be a central atom:**



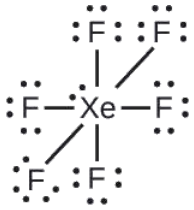
Step 3: Distribute the remaining electrons.

XeF_2: We place three lone pairs of electrons around each F atom, accounting for 12 electrons and giving each F atom 8 electrons. Thus, six electrons (three lone pairs) remain. These lone pairs must be placed on the Xe atom. This is acceptable because Xe atoms

have empty valence shell *d* orbitals and can accommodate more than eight electrons. The Lewis structure of XeF_2 shows two bonding pairs and three lone pairs of electrons around the Xe atom:



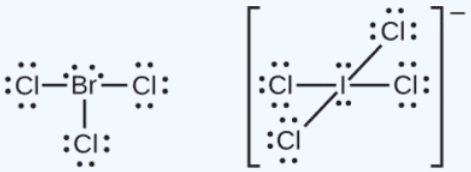
XeF_6: We place three lone pairs of electrons around each F atom, accounting for 36 electrons. Two electrons remain, and this lone pair is placed on the Xe atom:



? Exercise 6.4.2: interhalogens

The halogens form a class of compounds called the interhalogens, in which halogen atoms covalently bond to each other. Write the Lewis structures for the interhalogens $\mathbf{BrCl_3}$ and $\mathbf{ICl_4^-}$.

Answer



Summary

Valence electronic structures can be visualized by drawing Lewis symbols (for atoms and monatomic ions) and Lewis structures (for molecules and polyatomic ions). Lone pairs, unpaired electrons, and single, double, or triple bonds are used to indicate where the valence electrons are located around each atom in a Lewis structure. Most structures—especially those containing second row elements—obey the octet rule, in which every atom (except H) is surrounded by eight electrons. Exceptions to the octet rule occur for odd-electron molecules (free radicals), electron-deficient molecules, and hypervalent molecules.

Glossary

double bond
covalent bond in which two pairs of electrons are shared between two atoms

free radical
molecule that contains an odd number of electrons

hypervalent molecule
molecule containing at least one main group element that has more than eight electrons in its valence shell

Lewis structure
diagram showing lone pairs and bonding pairs of electrons in a molecule or an ion

Lewis symbol
symbol for an element or monatomic ion that uses a dot to represent each valence electron in the element or ion

lone pair

two (a pair of) valence electrons that are not used to form a covalent bond

octet rule

guideline that states main group atoms will form structures in which eight valence electrons interact with each nucleus, counting bonding electrons as interacting with both atoms connected by the bond

single bond

bond in which a single pair of electrons is shared between two atoms

triple bond

bond in which three pairs of electrons are shared between two atoms

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6.5: Formal Charges and Resonance

Learning Objectives

- Compute formal charges for atoms in any Lewis structure
- Use formal charges to identify the most reasonable Lewis structure for a given molecule
- Explain the concept of resonance and draw Lewis structures representing resonance forms for a given molecule

Previously, we discussed how to write Lewis structures for molecules and polyatomic ions. In some cases, however, there is seemingly more than one valid structure for a molecule. We can use the concept of formal charges to help us predict the most appropriate Lewis structure when more than one is reasonable.

Calculating Formal Charge

The formal charge of an atom in a molecule is the *hypothetical* charge the atom would have if we could redistribute the electrons in the bonds evenly between the atoms. Another way of saying this is that formal charge results when we take the number of valence electrons of a neutral atom, subtract the nonbonding electrons, and then subtract the number of bonds connected to that atom in the Lewis structure.

Thus, we calculate formal charge as follows:

Misplaced '#'

We can double-check formal charge calculations by determining the sum of the formal charges for the whole structure. The sum of the formal charges of all atoms in a molecule must be zero; the sum of the formal charges in an ion should equal the charge of the ion.

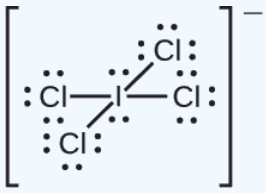
We must remember that the formal charge calculated for an atom is not the *actual* charge of the atom in the molecule. Formal charge is only a useful bookkeeping procedure; it does not indicate the presence of actual charges.

Example 6.5.1: Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen ion $\mathrm{ICl_4^-}$.

Solution

We divide the bonding electron pairs equally for all I–Cl bonds:



We assign lone pairs of electrons to their atoms. Each Cl atom now has seven electrons assigned to it, and the I atom has eight.

Subtract this number from the number of valence electrons for the neutral atom:

- I: 7 – 8 = –1
- Cl: 7 – 7 = 0

The sum of the formal charges of all the atoms equals –1, which is identical to the charge of the ion (–1).

Exercise 6.5.1

Calculate the formal charge for each atom in the carbon monoxide molecule:



Answer

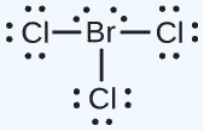
C −1, O +1

Example 6.5.2: Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen molecule $\mathbf{BrCl_3}$.

Solution

Assign one of the electrons in each Br–Cl bond to the Br atom and one to the Cl atom in that bond:



Assign the lone pairs to their atom. Now each Cl atom has seven electrons and the Br atom has seven electrons.

Subtract this number from the number of valence electrons for the neutral atom. This gives the formal charge:

- Br: 7 – 7 = 0
- Cl: 7 – 7 = 0

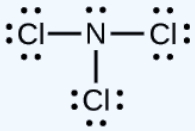
All atoms in $\mathbf{BrCl_3}$ have a formal charge of zero, and the sum of the formal charges totals zero, as it must in a neutral molecule.

Exercise 6.5.2

Determine the formal charge for each atom in $\mathbf{NCl_3}$.

Answer

N: 0; all three Cl atoms: 0



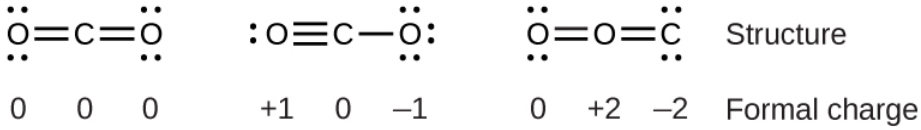
Using Formal Charge to Predict Molecular Structure

The arrangement of atoms in a molecule or ion is called its molecular structure. In many cases, following the steps for writing Lewis structures may lead to more than one possible molecular structure—different multiple bond and lone-pair electron placements or different arrangements of atoms, for instance. A few guidelines involving formal charge can be helpful in deciding which of the possible structures is most likely for a particular molecule or ion.

Predicting Molecular Structure Guidelines

1. A molecular structure in which all formal charges are zero is preferable to one in which some formal charges are not zero.
2. If the Lewis structure must have nonzero formal charges, the arrangement with the smallest nonzero formal charges is preferable.
3. Lewis structures are preferable when adjacent formal charges are zero or of the opposite sign.
4. When we must choose among several Lewis structures with similar distributions of formal charges, the structure with the negative formal charges on the more electronegative atoms is preferable.

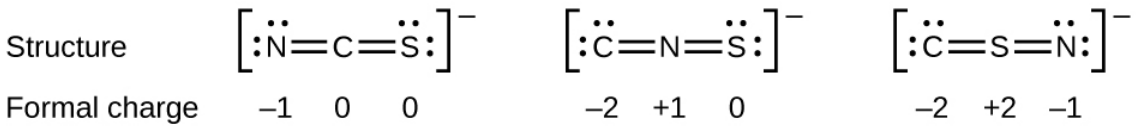
To see how these guidelines apply, let us consider some possible structures for carbon dioxide, CO_2. We know from our previous discussion that the less electronegative atom typically occupies the central position, but formal charges allow us to understand *why* this occurs. We can draw three possibilities for the structure: carbon in the center and double bonds, carbon in the center with a single and triple bond, and oxygen in the center with double bonds:



Three Lewis structures are shown. The left and right structures show a carbon atom double bonded to two oxygen atoms, each of which has two lone pairs of electrons. The center structure shows a carbon atom that is triple bonded to an oxygen atom with one lone pair of electrons and single bonded to an oxygen atom with three lone pairs of electrons. The third structure shows an oxygen atom double bonded to another oxygen atom with to lone pairs of electrons. The first oxygen atom is also double bonded to a carbon atom with two lone pairs of electrons.

Comparing the three formal charges, we can definitively identify the structure on the left as preferable because it has only formal charges of zero (Guideline 1).

As another example, the thiocyanate ion, an ion formed from a carbon atom, a nitrogen atom, and a sulfur atom, could have three different molecular structures: CNS^-, NCS^-, or CSN^-. The formal charges present in each of these molecular structures can help us pick the most likely arrangement of atoms. Possible Lewis structures and the formal charges for each of the three possible structures for the thiocyanate ion are shown here:

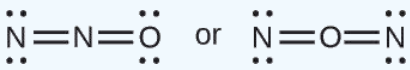


Two rows of structures and numbers are shown. The top row is labeled, “Structure” and depicts three Lewis structures and the bottom row is labeled, “Formal charge.” The left structure shows a carbon atom double bonded to a nitrogen atom with two lone electron pairs on one side and double bonded to a sulfur atom with two lone electron pairs on the other. The structure is surrounded by brackets and has a superscripted negative sign. Below this structure are the numbers negative one, zero, and zero. The middle structure shows a carbon atom with two lone pairs of electrons double bonded to a nitrogen atom that is double bonded to a sulfur atom with two lone electron pairs. The structure is surrounded by brackets and has a superscripted negative sign. Below this structure are the numbers negative two, positive one, and zero. The right structure shows a carbon atom with two lone electron pairs double bonded to a sulfur atom that is double bonded to a nitrogen atom with two lone electron pairs. The structure is surrounded by brackets and has a superscripted negative sign. Below this structure are the numbers negative two, positive two, and one.

Note that the sum of the formal charges in each case is equal to the charge of the ion (–1). However, the first arrangement of atoms is preferred because it has the lowest number of atoms with nonzero formal charges (Guideline 2). Also, it places the least electronegative atom in the center, and the negative charge on the more electronegative element (Guideline 4).

Example 6.5.3: Using Formal Charge to Determine Molecular Structure

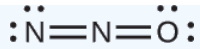
Nitrous oxide, N_2O, commonly known as laughing gas, is used as an anesthetic in minor surgeries, such as the routine extraction of wisdom teeth. Which is the likely structure for nitrous oxide?



Solution Determining formal charge yields the following:



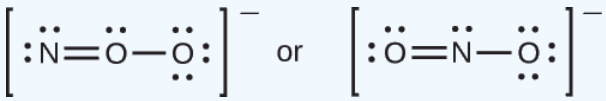
The structure with a terminal oxygen atom best satisfies the criteria for the most stable distribution of formal charge:



The number of atoms with formal charges are minimized (Guideline 2), and there is no formal charge larger than one (Guideline 2). This is again consistent with the preference for having the less electronegative atom in the central position.

? Exercise 6.5.3

Which is the most likely molecular structure for the nitrite (NO_2^-) ion?



Answer

ONO^-

Resonance

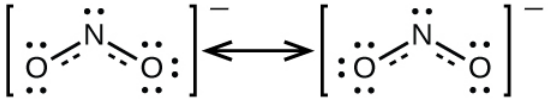
You may have noticed that the nitrite anion in Example **6.5.3** can have two possible structures with the atoms in the same positions. The electrons involved in the N–O double bond, however, are in different positions:



Two Lewis structures are shown. The left structure shows an oxygen atom with three lone pairs of electrons single bonded to a nitrogen atom with one lone pair of electrons that is double bonded to an oxygen with two lone pairs of electrons. Brackets surround this structure, and there is a superscripted negative sign. The right structure shows an oxygen atom with two lone pairs of electrons double bonded to a nitrogen atom with one lone pair of electrons that is single bonded to an oxygen atom with three lone pairs of electrons. Brackets surround this structure, and there is a superscripted negative sign.

If nitrite ions do indeed contain a single and a double bond, we would expect for the two bond lengths to be different. A double bond between two atoms is shorter (and stronger) than a single bond between the same two atoms. Experiments show, however, that both N–O bonds in NO_2^- have the same strength and length, and are identical in all other properties.

It is not possible to write a single Lewis structure for NO_2^- in which nitrogen has an octet and both bonds are equivalent. Instead, we use the concept of resonance: if two or more Lewis structures with the same arrangement of atoms can be written for a molecule or ion, the actual distribution of electrons is an *average* of that shown by the various Lewis structures. The actual distribution of electrons in each of the nitrogen-oxygen bonds in NO_2^- is the average of a double bond and a single bond. We call the individual Lewis structures resonance forms. The actual electronic structure of the molecule (the average of the resonance forms) is called a resonance hybrid of the individual resonance forms. A double-headed arrow between Lewis structures indicates that they are resonance forms. Thus, the electronic structure of the NO_2^- ion is shown as:

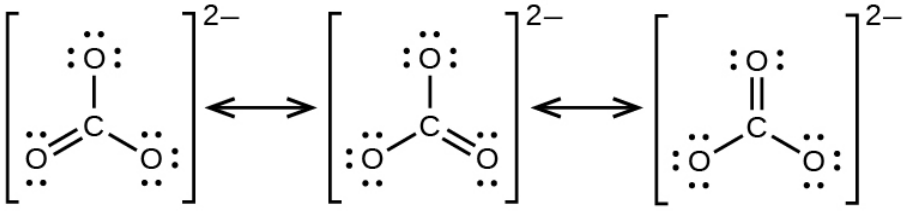


Two Lewis structures are shown with a double headed arrow drawn between them. The left structure shows an oxygen atom with two lone pairs of electrons double bonded to a nitrogen atom with one lone pair of electrons that is single bonded to an oxygen atom with three lone pairs of electrons. Brackets surround this structure, and there is a superscripted negative sign. The right structure shows an oxygen atom with three lone pairs of electrons single bonded to a nitrogen atom with one lone pair of electrons that is double bonded to an oxygen atom with two lone pairs of electrons. Brackets surround this structure, and there is a superscripted negative sign.

We should remember that a molecule described as a resonance hybrid *never* possesses an electronic structure described by either resonance form. It does not fluctuate between resonance forms; rather, the actual electronic structure is *always* the average of that

shown by all resonance forms. George Wheland, one of the pioneers of resonance theory, used a historical analogy to describe the relationship between resonance forms and resonance hybrids. A medieval traveler, having never before seen a rhinoceros, described it as a hybrid of a dragon and a unicorn because it had many properties in common with both. Just as a rhinoceros is neither a dragon sometimes nor a unicorn at other times, a resonance hybrid is neither of its resonance forms at any given time. Like a rhinoceros, it is a real entity that experimental evidence has shown to exist. It has some characteristics in common with its resonance forms, but the resonance forms themselves are convenient, imaginary images (like the unicorn and the dragon).

The carbonate anion, CO_3^{2-}, provides a second example of resonance:



Three Lewis structures are shown with double headed arrows in between. Each structure is surrounded by brackets, and each has a superscripted two negative sign. The left structure depicts a carbon atom bonded to three oxygen atoms. It is single bonded to two of these oxygen atoms, each of which has three lone pairs of electrons, and double bonded to the third, which has two lone pairs of electrons. The double bond is located between the lower left oxygen atom and the carbon atom. The central and right structures are the same as the first, but the position of the double bonded oxygen has moved to the lower right oxygen in the central structure and to the top oxygen in the right structure.

One oxygen atom must have a double bond to carbon to complete the octet on the central atom. All oxygen atoms, however, are equivalent, and the double bond could form from any one of the three atoms. This gives rise to three resonance forms of the carbonate ion. Because we can write three identical resonance structures, we know that the actual arrangement of electrons in the carbonate ion is the average of the three structures. Again, experiments show that all three C–O bonds are exactly the same.

Summary

In a Lewis structure, formal charges can be assigned to each atom by treating each bond as if one-half of the electrons are assigned to each atom. These hypothetical formal charges are a guide to determining the most appropriate Lewis structure. A structure in which the formal charges are as close to zero as possible is preferred. Resonance occurs in cases where two or more Lewis structures with identical arrangements of atoms but different distributions of electrons can be written. The actual distribution of electrons (the resonance hybrid) is an average of the distribution indicated by the individual Lewis structures (the resonance forms).

Key Equations

- Misplaced '#'

Glossary

formal charge

charge that would result on an atom by taking the number of valence electrons on the neutral atom and subtracting the nonbonding electrons and the number of bonds (one-half of the bonding electrons)

molecular structure

arrangement of atoms in a molecule or ion

resonance

situation in which one Lewis structure is insufficient to describe the bonding in a molecule and the average of multiple structures is observed

resonance forms

two or more Lewis structures that have the same arrangement of atoms but different arrangements of electrons

resonance hybrid

average of the resonance forms shown by the individual Lewis structures

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6.6: Strengths of Ionic and Covalent Bonds

Learning Objectives

- Describe the energetics of covalent and ionic bond formation and breakage
- Use the Born-Haber cycle to compute lattice energies for ionic compounds
- Use average covalent bond energies to estimate enthalpies of reaction

A bond's strength describes how strongly each atom is joined to another atom, and therefore how much energy is required to break the bond between the two atoms. In this section, you will learn about the bond strength of covalent bonds, and then compare that to the strength of ionic bonds, which is related to the lattice energy of a compound.

Bond Strength: Covalent Bonds

Stable molecules exist because covalent bonds hold the atoms together. We measure the strength of a covalent bond by the energy required to break it, that is, the energy necessary to separate the bonded atoms. Separating any pair of bonded atoms requires energy; *the stronger a bond, the greater the energy required to break it.* The energy required to break a specific covalent bond in one mole of gaseous molecules is called the bond energy or the bond dissociation energy. The bond energy for a diatomic molecule, D_{X-Y}, is defined as the standard enthalpy change for the endothermic reaction:

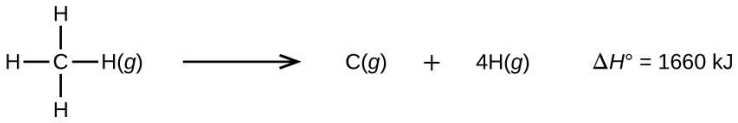
$$XY_{(g)} \longrightarrow X_{(g)} + Y_{(g)} \quad D_{X-Y} = \Delta H° \tag{6.6.1}$$

For example, the bond energy of the pure covalent H–H bond, Δ_{H-H}, is 436 kJ per mole of H–H bonds broken:

$$H_{2(g)} \longrightarrow 2H_{(g)} \quad D_{H-H} = \Delta H° = 436kJ \tag{6.6.2}$$

> *Breaking a bond **always** require energy to be added to the molecule. Correspondingly, making a bond **always** releases energy.*

Molecules with three or more atoms have two or more bonds. The sum of all bond energies in such a molecule is equal to the standard enthalpy change for the endothermic reaction that breaks all the bonds in the molecule. For example, the sum of the four C–H bond energies in CH_4, 1660 kJ, is equal to the standard enthalpy change of the reaction:



A reaction is shown with Lewis structures. The first structure shows a carbon atom single bonded to four hydrogen atoms with the symbol, "(g)" written next to it. A right-facing arrow points to the letter "C" and the symbol "(g)," which is followed by a plus sign. Next is the number 4, the letter "H" and the symbol, "(g)." To the right of this equation is another equation: capital delta H superscript degree symbol equals 1660 k J.

The average C–H bond energy, D_{C-H}, is 1660/4 = 415 kJ/mol because there are four moles of C–H bonds broken per mole of the reaction. Although the four C–H bonds are equivalent in the original molecule, they do not each require the same energy to break; once the first bond is broken (which requires 439 kJ/mol), the remaining bonds are easier to break. The 415 kJ/mol value is the average, not the exact value required to break any one bond.

The strength of a bond between two atoms increases as the number of electron pairs in the bond increases. Generally, as the bond strength increases, the bond length decreases. Thus, we find that triple bonds are stronger and shorter than double bonds between the same two atoms; likewise, double bonds are stronger and shorter than single bonds between the same two atoms. Average bond energies for some common bonds appear in Table **6.6.2**, and a comparison of bond lengths and bond strengths for some common bonds appears in Table **6.6.2**. When one atom bonds to various atoms in a group, the bond strength typically decreases as we move down the group. For example, C–F is 439 kJ/mol, C–Cl is 330 kJ/mol, and C–Br is 275 kJ/mol.

Table **6.6.1**: Bond Energies (kJ/mol)

Bond	Bond Energy	Bond	Bond Energy	Bond	Bond Energy
H–H	436	C–S	260	F–Cl	255
H–C	415	C–Cl	330	F–Br	235
H–N	390	C–Br	275	Si–Si	230
H–O	464	C–I	240	Si–P	215
H–F	569	N–N	160	Si–S	225
H–Si	395	N = N	418	Si–Cl	359
H–P	320	N ≡ N	946	Si–Br	290
H–S	340	N–O	200	Si–I	215
H–Cl	432	N–F	270	P–P	215
H–Br	370	N–P	210	P–S	230
H–I	295	N–Cl	200	P–Cl	330
C–C	345	N–Br	245	P–Br	270
C = C	611	O–O	140	P–I	215
C ≡ C	837	O = O	498	S–S	215
C–N	290	O–F	160	S–Cl	250
C = N	615	O–Si	370	S–Br	215
C ≡ N	891	O–P	350	Cl–Cl	243
C–O	350	O–Cl	205	Cl–Br	220
C = O	741	O–I	200	Cl–I	210
C ≡ O	1080	F–F	160	Br–Br	190
C–F	439	F–Si	540	Br–I	180
C–Si	360	F–P	489	I–I	150
C–P	265	F–S	285		

Table **6.6.2**: Average Bond Lengths and Bond Energies for Some Common Bonds

Bond	Bond Length (Å)	Bond Energy (kJ/mol)
C–C	1.54	345
C = C	1.34	611
C ≡ C	1.20	837
C–N	1.43	290
C = N	1.38	615
C ≡ N	1.16	891
C–O	1.43	350
C = O	1.23	741
C ≡ O	1.13	1080

We can use bond energies to calculate approximate enthalpy changes for reactions where enthalpies of formation are not available. Calculations of this type will also tell us whether a reaction is exothermic or endothermic.

- An **exothermic reaction** (ΔH negative, heat produced) results when the bonds in the products are stronger than the bonds in the reactants.
- An **endothermic reaction** (ΔH positive, heat absorbed) results when the bonds in the products are weaker than those in the reactants.

The enthalpy change, ΔH, for a chemical reaction is approximately equal to the sum of the energy required to break all bonds in the reactants (energy "in", positive sign) plus the energy released when all bonds are formed in the products (energy "out," negative sign). This can be expressed mathematically in the following way:

$$\Delta H = \sum D_{\text{bonds broken}} - \sum D_{\text{bonds formed}} \tag{6.6.3}$$

In this expression, the symbol Σ means "the sum of" and D represents the bond energy in kilojoules per mole, which is always a positive number. The bond energy is obtained from a table and will depend on whether the particular bond is a single, double, or triple bond. Thus, in calculating enthalpies in this manner, it is important that we consider the bonding in all reactants and products. Because D values are typically averages for one type of bond in many different molecules, this calculation provides a rough estimate, not an exact value, for the enthalpy of reaction.

Consider the following reaction:

$$\mathrm{H_{2(g)} + Cl_{2(g)} \longrightarrow 2\,HCl_{(g)}} \tag{6.6.4}$$

or

$$\mathrm{H{-}H_{(g)} + Cl{-}Cl_{(g)} \longrightarrow 2\,H{-}Cl_{(g)}} \tag{6.6.5}$$

To form two moles of HCl, one mole of H–H bonds and one mole of Cl–Cl bonds must be broken. The energy required to break these bonds is the sum of the bond energy of the H–H bond (436 kJ/mol) and the Cl–Cl bond (243 kJ/mol). During the reaction, two moles of H–Cl bonds are formed (bond energy = 432 kJ/mol), releasing 2 × 432 kJ; or 864 kJ. Because the bonds in the products are stronger than those in the reactants, the reaction releases more energy than it consumes:

$$\begin{aligned}\Delta H &= \sum \mathrm{D_{bonds\ broken}} - \sum \mathrm{D_{bonds\ formed}} \\ &= [\mathrm{D_{H-H}} + \mathrm{D_{Cl-Cl}}] - 2\mathrm{D_{H-Cl}} \\ &= [436 + 243] - 2(432) = -185\ \mathrm{kJ}\end{aligned}$$

This excess energy is released as heat, so the reaction is exothermic. Table T2 gives a value for the standard molar enthalpy of formation of HCl(g), ΔH_f°, of –92.307 kJ/mol. Twice that value is –184.6 kJ, which agrees well with the answer obtained earlier for the formation of two moles of HCl.

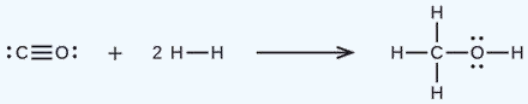
Example 6.6.1: Using Bond Energies to Approximate Enthalpy Changes

Methanol, CH_3OH, may be an excellent alternative fuel. The high-temperature reaction of steam and carbon produces a mixture of the gases carbon monoxide, CO, and hydrogen, H_2, from which methanol can be produced. Using the bond energies in Table **6.6.2**, calculate the approximate enthalpy change, ΔH, for the reaction here:

$$CO_{(g)} + 2H2_{(g)} \longrightarrow CH_3OH_{(g)}$$

Solution

First, we need to write the Lewis structures of the reactants and the products:



A set of Lewis diagrams show a chemical reaction. The first structure shows a carbon atom with a lone pair of electrons triple bonded to an oxygen with a lone pair of electrons. To the right of this structure is a plus sign, then the number 2 followed by a hydrogen atom single bonded to a hydrogen atom. To the right of this structure is a right-facing arrow followed by a hydrogen atom single bonded to a carbon atom that is single bonded to two hydrogen atoms and an oxygen atom with two lone pairs of electrons. The oxygen atom is also single bonded to a hydrogen atom.

From this, we see that ΔH for this reaction involves the energy required to break a C–O triple bond and two H–H single bonds, as well as the energy produced by the formation of three C–H single bonds, a C–O single bond, and an O–H single bond. We can express this as follows (via Equation 6.6.3):

$$\Delta H = \sum D_{bonds\ broken} - \sum D_{bonds\ formed}$$
$$\Delta H = [\mathrm{D_{C\equiv O} + 2(D_{H-H})}] - [\mathrm{3(D_{C-H}) + D_{C-O} + D_{O-H}}]$$

Using the bond energy values in Table **6.6.2**, we obtain:

$$\begin{aligned}\Delta H &= [1080 + 2(436)] - [3(415) + 350 + 464] \\ &= -107\ k\,\mathrm{J}\end{aligned}$$

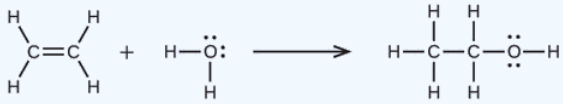
We can compare this value to the value calculated based on ΔH_f° data from Appendix G:

$$\begin{aligned}\Delta H &= [\Delta H_f^\circ \mathrm{CH_3OH}(g)] - [\Delta H_f^\circ \mathrm{CO}(g) + 2 \times \Delta H_f^\circ \mathrm{H_2}] \\ &= [-201.0] - [-110.52 + 2 \times 0] \\ &= -90.5\ \mathrm{kJ}\end{aligned}$$

Note that there is a fairly significant gap between the values calculated using the two different methods. This occurs because D values are the *average* of different bond strengths; therefore, they often give only rough agreement with other data.

Exercise 6.6.1

Ethyl alcohol, CH_3CH_2OH, was one of the first organic chemicals deliberately synthesized by humans. It has many uses in industry, and it is the alcohol contained in alcoholic beverages. It can be obtained by the fermentation of sugar or synthesized by the hydration of ethylene in the following reaction:



A set of Lewis structures show a chemical reaction. The first structure shows two carbon atoms that are double bonded together and are each single bonded to two hydrogen atoms. This structure is followed by a plus sign, then an oxygen atom with two lone pairs of electrons single bonded to two hydrogen atoms. A right-facing arrow leads to a carbon atom single bonded to three hydrogen atoms and a second carbon atom. The second carbon atom is single bonded to two hydrogen atoms and an oxygen atom with two lone pairs of electrons. The oxygen atom is single bonded to a hydrogen atom as well.

Using the bond energies in Table **6.6.2**, calculate an approximate enthalpy change, Δ*H*, for this reaction.

Answer

–35 kJ

Ionic Bond Strength and Lattice Energy

An ionic compound is stable because of the electrostatic attraction between its positive and negative ions. The lattice energy of a compound is a measure of the strength of this attraction. The lattice energy ($\Delta H_{lattice}$) of an ionic compound is defined as the energy required to separate one mole of the solid into its component gaseous ions. For the ionic solid MX, the lattice energy is the enthalpy change of the process:

$$MX_{(s)} \longrightarrow Mn^{+}_{(g)} + X^{n-}_{(g)} \quad \Delta H_{lattice} \tag{6.6.6}$$

Note that we are using the convention where the ionic solid is separated into ions, so our lattice energies will be endothermic (positive values). Some texts use the equivalent but opposite convention, defining lattice energy as the energy released when separate ions combine to form a lattice and giving negative (exothermic) values. Thus, if you are looking up lattice energies in another reference, be certain to check which definition is being used. In both cases, a larger magnitude for lattice energy indicates a more stable ionic compound. For sodium chloride, $\Delta H_{\text{lattice}}$ = 769 kJ. Thus, it requires 769 kJ to separate one mole of solid NaCl into gaseous Na^+ and Cl^- ions. When one mole each of gaseous Na^+ and Cl^- ions form solid NaCl, 769 kJ of heat is released.

The lattice energy $\Delta H_{lattice}$ of an ionic crystal can be expressed by the following equation (derived from Coulomb's law, governing the forces between electric charges):

$$\Delta H_{lattice} = \frac{C(Z^+)(Z^-)}{R_o} \tag{6.6.7}$$

in which

- **C** is a constant that depends on the type of crystal structure;
- Z^+ and Z^- are the charges on the ions; and
- R_o is the interionic distance (the sum of the radii of the positive and negative ions).

Thus, the lattice energy of an ionic crystal increases rapidly as the charges of the ions increase and the sizes of the ions decrease. When all other parameters are kept constant, doubling the charge of both the cation and anion quadruples the lattice energy. For example, the lattice energy of LiF (Z^+ and Z^- = 1) is 1023 kJ/mol, whereas that of MgO (Z^+ and Z^- = 2) is 3900 kJ/mol (R_o is nearly the same—about 200 pm for both compounds).

Different interatomic distances produce different lattice energies. For example, we can compare the lattice energy of MgF_2 (2957 kJ/mol) to that of MgI_2 (2327 kJ/mol) to observe the effect on lattice energy of the smaller ionic size of F^- as compared to I^-.

Example 6.6.2: Lattice Energy Comparisons

The precious gem ruby is aluminum oxide, Al_2O_3, containing traces of Cr^{3+}. The compound Al_2Se_3 is used in the fabrication of some semiconductor devices. Which has the larger lattice energy, Al_2O_3 or Al_2Se_3?

Solution

In these two ionic compounds, the charges Z^+ and Z^- are the same, so the difference in lattice energy will mainly depend upon R_o. The O^{2-} ion is smaller than the Se^{2-} ion. Thus, Al_2O_3 would have a shorter interionic distance than Al_2Se_3, and Al_2O_3 would have the larger lattice energy.

? Exercise 6.6.2

Zinc oxide, ZnO, is a very effective sunscreen. How would the lattice energy of ZnO compare to that of NaCl?

Answer

ZnO would have the larger lattice energy because the Z values of both the cation and the anion in ZnO are greater, and the interionic distance of ZnO is smaller than that of NaCl.

The Born-Haber Cycle

It is not possible to measure lattice energies directly. However, the lattice energy can be calculated using the equation given in the previous section or by using a thermochemical cycle. The Born-Haber cycle is an application of Hess's law that breaks down the formation of an ionic solid into a series of individual steps:

- ΔH_f°, the standard enthalpy of formation of the compound
- IE, the ionization energy of the metal
- EA, the electron affinity of the nonmetal
- ΔH_s°, the enthalpy of sublimation of the metal
- D, the bond dissociation energy of the nonmetal
- $\Delta H_{lattice}$, the lattice energy of the compound

Figure 6.6.1 diagrams the Born-Haber cycle for the formation of solid cesium fluoride.

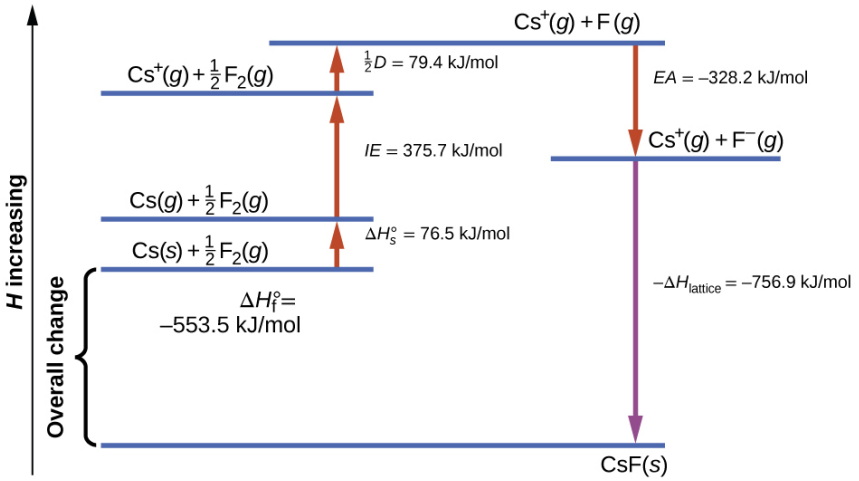


Figure **6.6.1**: The Born-Haber cycle shows the relative energies of each step involved in the formation of an ionic solid from the necessary elements in their reference states.

A diagram is shown. An upward facing arrow is drawn to the far left of the chart and is labeled “H increasing.” A horizontal line is drawn at the bottom of the chart. A downward-facing, vertical arrow to the left side of this line is labeled, “Overall change.” Beside this arrow is another label, “capital delta H subscript f, equals negative 553.5 k J per mol, (Enthalpy of formation).” Three horizontal lines, one above the other, and all above the bottom line, are labeled, from bottom to top, as: “C s (s), plus sign, one half F subscript 2, (g),” “C s (g), plus sign, one half F subscript 2, (g),” and “C s, superscript positive sign, (g), plus sign, one half F subscript 2, (g).” Each of these lines is connected by an upward-facing vertical arrow. Each arrow is labeled, “capital delta H subscript 1, equals 76.5 k J per mol, (Enthalpy of sublimation),” “capital delta H subscript 2, equals 375.7 k J per mol, (ionization energy),” and “capital delta H subscript 3 equals 79.4 k J / mol (one half dissociation energy).” Another horizontal line is drawn in the center top portion of the diagram and is labeled “C s, superscript positive sign, (g), plus sign, F, (g).” There is one more horizontal line drawn to the right of the overall diagram and located halfway down the image. An arrow connects the top line to this line and is labeled, “capital delta H equals negative 328.2 k J / mol (electron affinity).” The line is labeled, “C s superscript positive sign (g) plus F superscript negative sign (g).” The arrow connecting this line to the bottom line is labeled, “negative capital delta H subscript lattice equals negative 756.9 k J / mol.” The arrow points to a label on the bottom line which reads, “C s F (s).”

We begin with the elements in their most common states, Cs(s) and $F_2(g)$. The ΔH_s° represents the conversion of solid cesium into a gas, and then the ionization energy converts the gaseous cesium atoms into cations. In the next step, we account for the energy required to break the F–F bond to produce fluorine atoms. Converting one mole of fluorine atoms into fluoride ions is an exothermic process, so this step gives off energy (the electron affinity) and is shown as decreasing along the y-axis. We now have one mole of Cs cations and one mole of F anions. These ions combine to produce solid cesium fluoride. The enthalpy change in this step is the negative of the lattice energy, so it is also an exothermic quantity. The total energy involved in this conversion is equal to the experimentally determined enthalpy of formation, ΔH_f°, of the compound from its elements. In this case, the overall change is exothermic.

Hess’s law can also be used to show the relationship between the enthalpies of the individual steps and the enthalpy of formation. Table **6.6.3** shows this for cesium fluoride, CsF.

Table **6.6.3**: Enthalpies of Select Transitions

Enthalpy of sublimation of Cs(s)	$\mathrm{Cs}(s) \longrightarrow \mathrm{Cs}(g) \quad \Delta H = \Delta H_s^\circ = 77\ \mathrm{kJ/mol}$
One-half of the bond energy of F_2	$\frac{1}{2}\mathrm{F_2}(g) \longrightarrow \mathrm{F}(g) \quad \Delta H = \frac{1}{2}D = 79\ \mathrm{kJ/mol}$
Ionization energy of Cs(g)	$\mathrm{Cs}(g) \longrightarrow \mathrm{Cs^+}(g) + \mathrm{e^-} \quad \Delta H = IE = 376\ k\mathrm{J/mol}$
Negative of the electron affinity of F	$\mathrm{F}(g) + \mathrm{e^-} \longrightarrow \mathrm{F^-}(g) \quad \Delta H = -EA = -328\ k\mathrm{J/mol}$
Negative of the lattice energy of CsF(s)	$\mathrm{Cs^+}(g) + \mathrm{F^-}(g) \longrightarrow \mathrm{CsF}(s) \quad \Delta H = -\Delta H_{\text{lattice}} = ?$
Enthalpy of formation of CsF(s), add steps 1–5	$\Delta H = \Delta H_f^\circ = \Delta H_s^\circ + \frac{1}{2}D + IE + (-EA) + (-\Delta H_{\text{lattice}})$ $\mathrm{Cs}(s) + \frac{1}{2}\mathrm{F_2}(g) \longrightarrow \mathrm{CsF}(s) = -554\ k\mathrm{J/mol}$

Thus, the lattice energy can be calculated from other values. For cesium chloride, using this data, the lattice energy is:

$$\Delta H_{\text{lattice}} = (411 + 109 + 122 + 496 + 368)\ \text{kJ} = 770\ \text{kJ}$$

The Born-Haber cycle may also be used to calculate any one of the other quantities in the equation for lattice energy, provided that the remainder is known. For example, if the relevant enthalpy of sublimation ΔH_s°, ionization energy (IE), bond dissociation enthalpy (D), lattice energy $\Delta H_{\text{lattice}}$, and standard enthalpy of formation ΔH_f° are known, the Born-Haber cycle can be used to determine the electron affinity of an atom.

Lattice energies calculated for ionic compounds are typically much larger than bond dissociation energies measured for covalent bonds. Whereas lattice energies typically fall in the range of 600–4000 kJ/mol (some even higher), covalent bond dissociation energies are typically between 150–400 kJ/mol for single bonds. Keep in mind, however, that these are not directly comparable values. For ionic compounds, lattice energies are associated with many interactions, as cations and anions pack together in an extended lattice. For covalent bonds, the bond dissociation energy is associated with the interaction of just two atoms.

Summary

The strength of a covalent bond is measured by its bond dissociation energy, that is, the amount of energy required to break that particular bond in a mole of molecules. Multiple bonds are stronger than single bonds between the same atoms. The enthalpy of a reaction can be estimated based on the energy input required to break bonds and the energy released when new bonds are formed. For ionic bonds, the lattice energy is the energy required to separate one mole of a compound into its gas phase ions. Lattice energy increases for ions with higher charges and shorter distances between ions. Lattice energies are often calculated using the Born-Haber cycle, a thermochemical cycle including all of the energetic steps involved in converting elements into an ionic compound.

Key Equations

- Bond energy for a diatomic molecule: $\text{XY}(g) \longrightarrow \text{X}(g) + \text{Y}(g) \quad D_{\text{X–Y}} = \Delta H^\circ$
- Enthalpy change: $\Delta H = \Sigma D_{\text{bonds broken}} - \Sigma D_{\text{bonds formed}}$
- Lattice energy for a solid MX: $\text{MX}(s) \longrightarrow \text{M}^{n+}(g) + \text{X}^{n-}(g) \quad \Delta H_{\text{lattice}}$
- Lattice energy for an ionic crystal: $\Delta H_{\text{lattice}} = \dfrac{C(Z^+)(Z^-)}{R_o}$

Footnotes

1. This question is taken from the Chemistry Advanced Placement Examination and is used with the permission of the Educational Testing Service.

Glossary

bond energy
(also, bond dissociation energy) energy required to break a covalent bond in a gaseous substance

Born-Haber cycle
thermochemical cycle relating the various energetic steps involved in the formation of an ionic solid from the relevant elements

lattice energy ($\Delta H_{\text{lattice}}$)
energy required to separate one mole of an ionic solid into its component gaseous ions

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6.7: Molecular Structure and Polarity

Learning Objectives

- Predict the structures of small molecules using valence shell electron pair repulsion (VSEPR) theory
- Explain the concepts of polar covalent bonds and molecular polarity
- Assess the polarity of a molecule based on its bonding and structure

Thus far, we have used two-dimensional Lewis structures to represent molecules. However, molecular structure is actually three-dimensional, and it is important to be able to describe molecular bonds in terms of their distances, angles, and relative arrangements in space (Figure **6.7.1**). A bond angle is the angle between any two bonds that include a common atom, usually measured in degrees. A bond distance (or bond length) is the distance between the nuclei of two bonded atoms along the straight line joining the nuclei. Bond distances are measured in Ångstroms (1 Å = 10^{-10} m) or picometers (1 pm = 10^{-12} m, 100 pm = 1 Å).

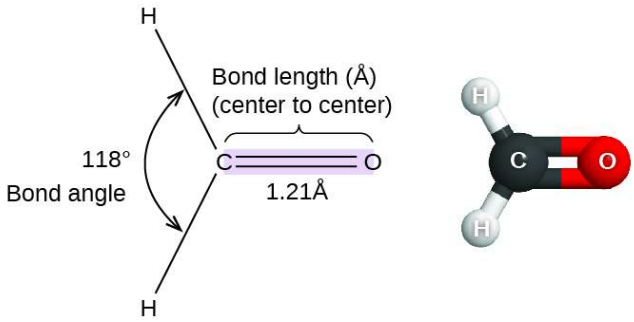


Figure **6.7.1**: Bond distances (lengths) and angles are shown for the formaldehyde molecule, H_2CO.

A pair of images are shown. The left image shows a carbon atom with three atoms bonded in a triangular arrangement around it. There are two hydrogen atoms bonded on the left side of the carbon and the angle between them is labeled, “118 degrees” and, “Bond angle.” The carbon is also double bonded to an oxygen atom. The double bond is shaded and there is a bracket which labels the bond, “Bond length (angstrom), (center to center),” and, “1.21 angstrom.” The right image shows a ball-and-stick model of the same elements. The hydrogen atoms are white, the carbon atom is black, and the oxygen atom is red."

VSEPR Theory

Valence shell electron-pair repulsion theory (VSEPR theory) enables us to predict the molecular structure, including approximate bond angles around a central atom, of a molecule from an examination of the number of bonds and lone electron pairs in its Lewis structure. The VSEPR model assumes that electron pairs in the valence shell of a central atom will adopt an arrangement that minimizes repulsions between these electron pairs by maximizing the distance between them. The electrons in the valence shell of a central atom form either bonding pairs of electrons, located primarily between bonded atoms, or lone pairs. The electrostatic repulsion of these electrons is reduced when the various regions of high electron density assume positions as far from each other as possible.

VSEPR theory predicts the arrangement of electron pairs around each central atom and, usually, the correct arrangement of atoms in a molecule. We should understand, however, that the theory only considers electron-pair repulsions. Other interactions, such as nuclear-nuclear repulsions and nuclear-electron attractions, are also involved in the final arrangement that atoms adopt in a particular molecular structure.

As a simple example of VSEPR theory, let us predict the structure of a gaseous BeF_2 molecule. The Lewis structure of BeF_2 (Figure **6.7.2**) shows only two electron pairs around the central beryllium atom. With two bonds and no lone pairs of electrons on the central atom, the bonds are as far apart as possible, and the electrostatic repulsion between these regions of high electron density is reduced to a minimum when they are on opposite sides of the central atom. The bond angle is 180° (Figure **6.7.2**).

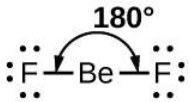


Figure **6.7.2**: The BeF_2 molecule adopts a linear structure in which the two bonds are as far apart as possible, on opposite sides of the Be atom.

A Lewis structure is shown. A fluorine atom with three lone pairs of electrons is single bonded to a beryllium atom which is single bonded to a fluorine atom with three lone pairs of electrons. The angle of the bonds between the two fluorine atoms and the beryllium atom is labeled, “180 degrees.”

Figure **6.7.3** illustrates this and other electron-pair geometries that minimize the repulsions among regions of high electron density (bonds and/or lone pairs). Two regions of electron density around a central atom in a molecule form a linear geometry; three regions form a trigonal planar geometry; four regions form a tetrahedral geometry; five regions form a trigonal bipyramidal geometry; and six regions form an octahedral geometry.

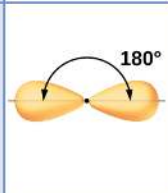
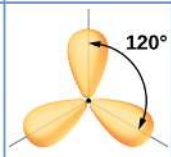
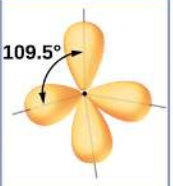
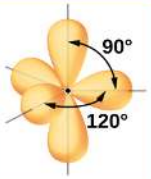
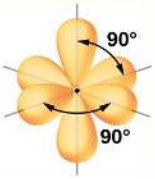
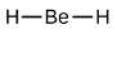
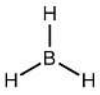
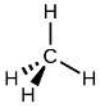
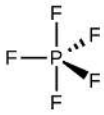
Number of regions	Two regions of high electron density (bonds and/or unshared pairs)	Three regions of high electron density (bonds and/or unshared pairs)	Four regions of high electron density (bonds and/or unshared pairs)	Five regions of high electron density (bonds and/or unshared pairs)	Six regions of high electron density (bonds and/or unshared pairs)
Spatial arrangement					
Line-dash-wedge notation					
Electron pair geometry	Linear; 180° angle	Trigonal planar; all angles 120°	Tetrahedral; all angles 109.5°	Trigonal bipyramidal; angles of 90° or 120° An attached atom may be equatorial (in the plane of the triangle) or axial (above or below the plane of the triangle).	Octahedral; all angles 90° or 180°

Figure **6.7.3**: The basic electron-pair geometries predicted by VSEPR theory maximize the space around any region of electron density (bonds or lone pairs).

A table with four rows and six columns is shown. The header column contains the phrases, “Number of regions,” “Spatial arrangement,” “Wedge/dash Notation,” and “Electron pair Geometry.” The first row reads: “Two regions of high electron density (bonds and/or unshared pairs)”, “Three regions of high electron density (bonds and/or unshared pairs),” “Four regions of high electron density (bonds and/or unshared pairs),” “Five regions of high electron density (bonds and/or unshared pairs),” and “Six regions of high electron density (bonds and/or unshared pairs).” The second row shows diagrams of orbitals. The first image shows two oval-shaped orbs with an arrow indicating an angle of 180 degrees. The second image shows three oval-shaped orbs with an arrow indicating an angle of 120 degrees. The third image shows four oval-shaped orbs with an arrow indicating an angle of 109.5 degrees. The fourth image shows five oval-shaped orbs with an arrow indicating an angle of 90 and 120 degrees. The fifth image shows six oval-shaped orbs with an arrow indicating an angle of 90 degrees. The third row contains Lewis structures. The first structure shows a beryllium atom single bonded to two hydrogen atoms. The second structure shows a boron atom single bonded to three hydrogen atoms. The third structure shows a carbon atom single bonded to four hydrogen atoms. The fourth structure shows a phosphorus atom single bonded to five fluorine atoms. The fifth structure shows a sulfur atom single bonded to six fluorine atoms. The fourth row contains the phrases “Linear; 180 degree angle,” Trigonal Planar; all angles 120 degrees,” “Tetrahedral; all angles 109.5 degrees,” “Trigonal bipyramidal; angles of 90 degrees and 120 degrees. An attached atom may be equatorial, (in the plane of the triangle), or axial, (above the plane of the triangle),” and “Octahedral; 90 degrees or 180 degrees.”

Electron-pair Geometry versus Molecular Structure

It is important to note that electron-pair geometry around a central atom is *not* the same thing as its molecular structure. The electron-pair geometries shown in Figure **6.7.3** describe all regions where electrons are located, bonds as well as lone pairs. Molecular structure describes the location of the *atoms*, not the electrons.

We differentiate between these two situations by naming the geometry that includes *all* electron pairs the electron-pair geometry. The structure that includes only the placement of the atoms in the molecule is called the molecular structure. The electron-pair geometries will be the same as the molecular structures when there are no lone electron pairs around the central atom, but they will be different when there are lone pairs present on the central atom.

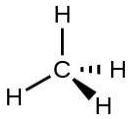


Figure **6.7.4**: The molecular structure of the methane molecule, CH_4, is shown with a tetrahedral arrangement of the hydrogen atoms. VSEPR structures like this one are often drawn using the wedge and dash notation, in which solid lines represent bonds in the plane of the page, solid wedges represent bonds coming up out of the plane, and dashed lines represent bonds going down into the plane.

A Lewis structure shows a carbon atom single bonded to four hydrogen atoms. This structure uses wedges and dashes to give it a three dimensional appearance.

For example, the methane molecule, CH_4, which is the major component of natural gas, has four bonding pairs of electrons around the central carbon atom; the electron-pair geometry is tetrahedral, as is the molecular structure (Figure **6.7.4**). On the other hand, the ammonia molecule, NH_3, also has four electron pairs associated with the nitrogen atom, and thus has a tetrahedral electron-pair geometry. One of these regions, however, is a lone pair, which is not included in the molecular structure, and this lone pair influences the shape of the molecule (Figure **6.7.5**).

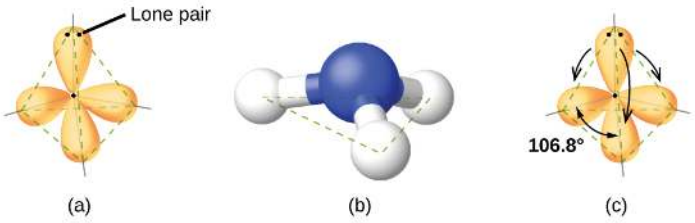


Figure **6.7.5**: (a) The electron-pair geometry for the ammonia molecule is tetrahedral with one lone pair and three single bonds. (b) The trigonal pyramidal molecular structure is determined from the electron-pair geometry. (c) The actual bond angles deviate slightly from the idealized angles because the lone pair takes up a larger region of space than do the single bonds, causing the HNH angle to be slightly smaller than 109.5°.

Three images are shown and labeled, “a,” “b,” and “c.” Image a shows a nitrogen atom single bonded to three hydrogen atoms. There are four oval-shaped orbs that surround each hydrogen and one facing away from the rest of the molecule. These orbs are located in a tetrahedral arrangement. Image b shows a ball-and-stick model of the nitrogen single bonded to the three hydrogen atoms. Image c is the same as image a, but there are four curved, double headed arrows that circle the molecule and are labeled, “106.8 degrees.”

Small distortions from the ideal angles in Figure **6.7.5** can result from differences in repulsion between various regions of electron density. VSEPR theory predicts these distortions by establishing an order of repulsions and an order of the amount of space occupied by different kinds of electron pairs. The order of electron-pair repulsions from greatest to least repulsion is:

lone pair-lone pair > lone pair-bonding pair > bonding pair-bonding pair

This order of repulsions determines the amount of space occupied by different regions of electrons. A lone pair of electrons occupies a larger region of space than the electrons in a triple bond; in turn, electrons in a triple bond occupy more space than those in a double bond, and so on. The order of sizes from largest to smallest is:

lone pair > triple bond > double bond > single bond

Consider formaldehyde, H_2CO, which is used as a preservative for biological and anatomical specimens. This molecule has regions of high electron density that consist of two single bonds and one double bond. The basic geometry is trigonal planar with 120° bond angles, but we see that the double bond causes slightly larger angles (121°), and the angle between the single bonds is slightly smaller (118°).

In the ammonia molecule, the three hydrogen atoms attached to the central nitrogen are not arranged in a flat, trigonal planar molecular structure, but rather in a three-dimensional trigonal pyramid (Figure **6.7.6**) with the nitrogen atom at the apex and the three hydrogen atoms forming the base. The ideal bond angles in a trigonal pyramid are based on the tetrahedral electron pair geometry. Again, there are slight deviations from the ideal because lone pairs occupy larger regions of space than do bonding electrons. The H–N–H bond angles in NH_3 are slightly smaller than the 109.5° angle in a regular tetrahedron (Figure **6.7.6**) because the lone pair-bonding pair repulsion is greater than the bonding pair-bonding pair repulsion. The ideal molecular structures are predicted based on the electron-pair geometries for various combinations of lone pairs and bonding pairs.

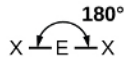
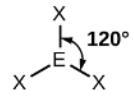
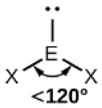
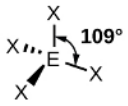
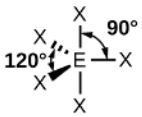
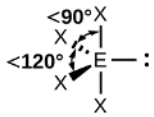
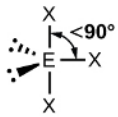
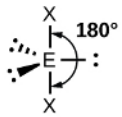
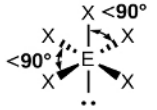
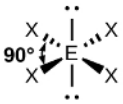
Number of electron pairs	Electron pair geometries: 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	 Linear				
3	 Trigonal planar	 Bent or angular			
4	 Tetrahedral	 Trigonal pyramid	 Bent or angular		
5	 Trigonal bipyramid	 Sawhorse or seesaw	 T-shape	 Linear	
6	 Octahedral	 Square pyramid	 Square planar	 T-shape	 Linear

Figure **6.7.6**: The molecular structures are identical to the electron-pair geometries when there are no lone pairs present (first column). For a particular number of electron pairs (row), the molecular structures for one or more lone pairs are determined based on modifications of the corresponding electron-pair geometry.

A table is shown that is comprised of six rows and six columns. The header row reads: “Number of Electron Pairs,” “Electron pair geometries; 0 lone pair,” “1 lone pair,” “2 lone pairs,” “3 lone pairs,” and “4 lone pairs.” The first column contains the numbers 2, 3, 4, 5, and 6. The first space in the second column contains a structure in which the letter E is single bonded to the letter X on each side. The angle of the bonds is labeled with a curved, double headed arrow and the value, “180 degrees.” The structure is labeled, “Linear.” The second space in the second column contains a structure in which the letter E is single bonded to the letter X on three sides. The angle between the bonds is labeled with a curved, double headed arrow and the value, “120 degrees.” The structure is labeled, “Trigonal planar.” The third space in the second column contains a structure in which the letter E is single bonded to the letter X four times. The angle between the bonds is labeled with a curved, double headed arrow and the value, “109 degrees.” The structure is labeled, “Tetrahedral.” The fourth space in the second column contains a structure in which the letter E is single bonded to the letter X on five sides. The angle between the bonds is labeled with a curved, double headed arrow and the values “90 and 120 degrees.” The structure is labeled, “Trigonal bipyramid.” The fifth space in the second column contains a structure in which the letter E is single bonded to the letter X on six sides. The angle between the bonds is labeled with a curved, double headed arrow and the value, “90 degrees.” The structure is labeled, “Octahedral.” The first space in the third column is empty while the second contains a structure in which the letter E is single bonded to the letter X on each side and has a lone pair of electrons. The angle between the bonds is labeled with a curved, double headed arrow and the value, “less than 120 degrees.” The structure is labeled, “Bent or angular.” The third space in the third column contains a structure in which the letter E is single bonded to the letter X three times and to a lone pair of electrons. It is labeled with a curved, double headed arrow and the value, “less than 109 degrees.” The structure is labeled, “Trigonal pyramid.” The fourth space in the third column contains a structure in which the letter E is single bonded to the letter X on four sides and has a lone pair of electrons. The bond angle is labeled with a curved, double headed arrow and the values, “less than 90 and less than 120 degrees.” The structure is labeled, “Sawhorse or seesaw.” The fifth space in the third column contains a structure in which the letter E is single bonded to the letter X on five sides and has a lone pair of electrons. The bond angle is labeled with a curved, double headed arrow and the value, “less than 90 degrees.” The structure is labeled, “Square pyramidal.” The first and second spaces in the fourth column are empty while the third contains a structure in which the letter E is single bonded to the letter X on each side and has two lone pairs of electrons. The bond angle is labeled with a curved, double headed arrow and the value, “less than less than 109 degrees.” The structure is labeled, “Bent or angular.” The fourth space in the fourth column contains a structure in which the letter E is single bonded to the letter X three times and to two lone pairs of electrons. The bond angle is labeled with a curved, double headed arrow and the value, “less than 90 degrees.” The structure is labeled, “T - shape.” The fifth space in the fourth column contains a structure in which the letter E is single bonded to the letter X on four sides and has two lone pairs of electrons. The bond angle is labeled with a curved, double headed arrow and the value “90 degrees.” The structure is labeled, “Square planar.” The first, second and third spaces in the fifth column are empty while the fourth contains a structure in which the letter E is single bonded to the letter X on each side and has three lone pairs of electrons. The bond angle is labeled with a curved, double headed arrow and the value, “180 degrees.” The structure is labeled, “Linear.” The fifth space in the fifth column contains a structure in which the letter E is single bonded to the letter X three times and to three lone pairs of electrons. The bond angle is labeled with a curved, double headed arrow and the value, “less than 90 degrees.” The structure is labeled, “T - shape.” The first, second, third, and fourth spaces in the sixth column are empty while the fifth contains a structure in which the letter E is single bonded to the letter X on each side and has four lone pairs of electrons. The bond angle is labeled with a curved, double headed arrow and the value “180 degrees.” The structure is labeled, “Linear.” All the structures use wedges and dashes to give them three dimensional appearances.

According to VSEPR theory, the terminal atom locations (Xs in Figure **6.7.7**) are equivalent within the linear, trigonal planar, and tetrahedral electron-pair geometries (the first three rows of the table). It does not matter which X is replaced with a lone pair because the molecules can be rotated to convert positions. For trigonal bipyramidal electron-pair geometries, however, there are two distinct X positions (Figure **6.7.7**a): an axial position (if we hold a model of a trigonal bipyramid by the two axial positions, we have an axis around which we can rotate the model) and an equatorial position (three positions form an equator around the middle of the molecule). The axial position is surrounded by bond angles of 90°, whereas the equatorial position has more space available because of the 120° bond angles. In a trigonal bipyramidal electron-pair geometry, lone pairs always occupy equatorial positions because these more spacious positions can more easily accommodate the larger lone pairs.

Theoretically, we can come up with three possible arrangements for the three bonds and two lone pairs for the ClF_3 molecule (Figure **6.7.7**). The stable structure is the one that puts the lone pairs in equatorial locations, giving a T-shaped molecular structure.

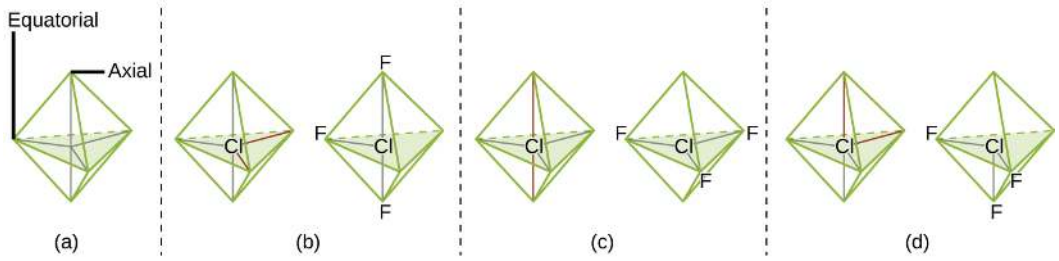


Figure **6.7.7**: (a) In a trigonal bipyramid, the two axial positions are located directly across from one another, whereas the three equatorial positions are located in a triangular arrangement. (b–d) The two lone pairs (red lines) in ClF_3 have several possible arrangements, but the T-shaped molecular structure (b) is the one actually observed, consistent with the larger lone pairs both occupying equatorial positions.

Four sets of images are shown and labeled, “a,” “b,” “c,” and “d.” Each image is separated by a dashed vertical line. Image a shows a six-faced, bi-pyramidal structure where the central vertical axis is labeled, “Axial,” and the horizontal plane is labeled, “Equatorial.” Image b shows a pair of diagrams in the same shape as image a, but in these diagrams, the left has a chlorine atom in the center while the right has a chlorine atom in the center, two fluorine atoms on the upper and lower ends, and one fluorine in the left horizontal position. Image c shows a pair of diagrams in the same shape as image a, but in these diagrams, the left has a chlorine atom in the center while the right has a chlorine atom in the center and three fluorine atoms in each horizontal position. Image d shows a pair of diagrams in the same shape as image a, but in these diagrams, the left has a chlorine atom in the center while the right has a chlorine atom in the center, two fluorine atoms in the horizontal positions, and one in the axial bottom position.

When a central atom has two lone electron pairs and four bonding regions, we have an octahedral electron-pair geometry. The two lone pairs are on opposite sides of the octahedron (180° apart), giving a square planar molecular structure that minimizes lone pair-lone pair repulsions.

Predicting Electron Pair Geometry and Molecular Structure

The following procedure uses VSEPR theory to determine the electron pair geometries and the molecular structures:

1. Write the Lewis structure of the molecule or polyatomic ion.
2. Count the number of regions of electron density (lone pairs and bonds) around the central atom. A single, double, or triple bond counts as one region of electron density.
3. Identify the electron-pair geometry based on the number of regions of electron density: linear, trigonal planar, tetrahedral, trigonal bipyramidal, or octahedral (Figure **6.7.7**, first column).
4. Use the number of lone pairs to determine the molecular structure (Figure **6.7.7**). If more than one arrangement of lone pairs and chemical bonds is possible, choose the one that will minimize repulsions, remembering that lone pairs occupy more space than multiple bonds, which occupy more space than single bonds. In trigonal bipyramidal arrangements, repulsion is minimized when every lone pair is in an equatorial position. In an octahedral arrangement with two lone pairs, repulsion is minimized when the lone pairs are on opposite sides of the central atom.

The following examples illustrate the use of VSEPR theory to predict the molecular structure of molecules or ions that have no lone pairs of electrons. In this case, the molecular structure is identical to the electron pair geometry.

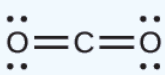
Example 6.7.1: Predicting Electron-pair Geometry and Molecular Structure

Predict the electron-pair geometry and molecular structure for each of the following:

a. carbon dioxide, CO_2, a molecule produced by the combustion of fossil fuels
b. boron trichloride, BCl_3, an important industrial chemical

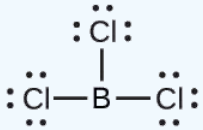
Solution

(a) We write the Lewis structure of CO_2 as:

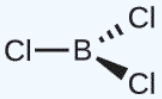


This shows us two regions of high electron density around the carbon atom—each double bond counts as one region, and there are no lone pairs on the carbon atom. Using VSEPR theory, we predict that the two regions of electron density arrange themselves on opposite sides of the central atom with a bond angle of 180°. The electron-pair geometry and molecular structure are identical, and CO_2 molecules are linear.

(b) We write the Lewis structure of BCl_3 as:



Thus we see that BCl_3 contains three bonds, and there are no lone pairs of electrons on boron. The arrangement of three regions of high electron density gives a trigonal planar electron-pair geometry. The B–Cl bonds lie in a plane with 120° angles between them. BCl_3 also has a trigonal planar molecular structure.



The electron-pair geometry and molecular structure of BCl_3 are both trigonal planar. Note that the VSEPR geometry indicates the correct bond angles (120°), unlike the Lewis structure shown above.

? Exercise 6.7.1

Carbonate, CO_3^{2-}, is a common polyatomic ion found in various materials from eggshells to antacids. What are the electron-pair geometry and molecular structure of this polyatomic ion?

Answer

The electron-pair geometry is trigonal planar and the molecular structure is trigonal planar. Due to resonance, all three C–O bonds are identical. Whether they are single, double, or an average of the two, each bond counts as one region of electron density.

✓ Example 6.7.2: Predicting Electron-pair Geometry and Molecular Structure

Two of the top 50 chemicals produced in the United States, ammonium nitrate and ammonium sulfate, both used as fertilizers, contain the ammonium ion. Predict the electron-pair geometry and molecular structure of the NH_4^+ cation.

Solution

We write the Lewis structure of NH_4^+ as:

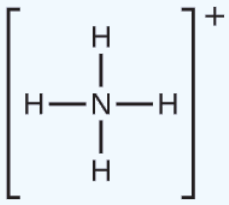


Figure 6.7.7).

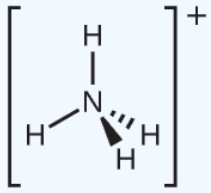


Figure 6.7.8: *The ammonium ion displays a tetrahedral electron-pair geometry as well as a tetrahedral molecular structure.*

? Exercise 6.7.2

Identify a molecule with trigonal bipyramidal molecular structure.

Answer

Any molecule with five electron pairs around the central atoms including no lone pairs will be trigonal bipyramidal. $\mathbf{PF_5}$ is a common example

The next several examples illustrate the effect of lone pairs of electrons on molecular structure.

✓ Example 6.7.3: Lone Pairs on the Central Atom

Predict the electron-pair geometry and molecular structure of a water molecule.

Solution

The Lewis structure of H_2O indicates that there are four regions of high electron density around the oxygen atom: two lone pairs and two chemical bonds:

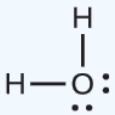


Figure 6.7.9. Thus, the electron-pair geometry is tetrahedral and the molecular structure is bent with an angle slightly less than 109.5°. In fact, the bond angle is 104.5°.

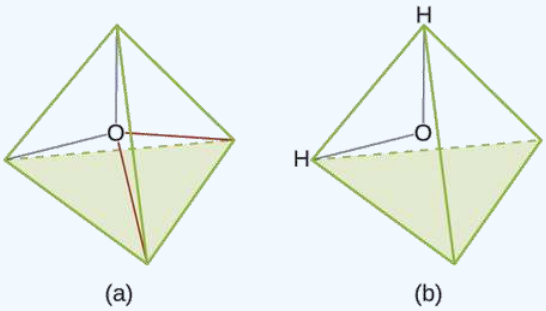


Figure 6.7.9: (a) H_2O has four regions of electron density around the central atom, so it has a tetrahedral electron-pair geometry. (b) Two of the electron regions are lone pairs, so the molecular structure is bent.

? Exercise 6.7.3

The hydronium ion, H_3O^+, forms when acids are dissolved in water. Predict the electron-pair geometry and molecular structure of this cation.

Answer

electron pair geometry: tetrahedral; molecular structure: trigonal pyramidal

Example 6.7.4: SF_4 Sulfur tetrafluoride,

Predicting Electron-pair Geometry and Molecular Structure: SF_4, is extremely valuable for the preparation of fluorine-containing compounds used as herbicides (i.e., SF_4 is used as a fluorinating agent). Predict the electron-pair geometry and molecular structure of a SF_4 molecule.

Solution

The Lewis structure of SF_4 indicates five regions of electron density around the sulfur atom: one lone pair and four bonding pairs:

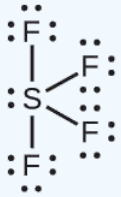


Figure 6.7.10).

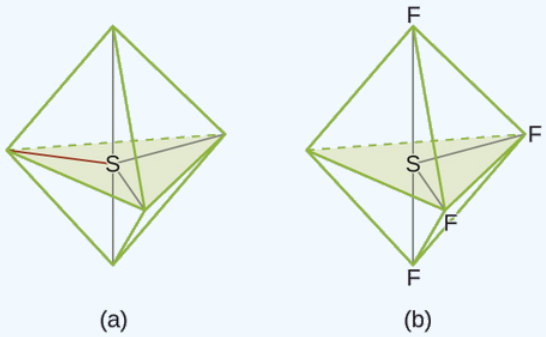


Figure 6.7.10: (a) SF_4 has a trigonal bipyramidal arrangement of the five regions of electron density. (b) One of the regions is a lone pair, which results in a seesaw-shaped molecular structure.

Exercise 6.7.4

Predict the electron pair geometry and molecular structure for molecules of XeF_2.

Answer

The electron-pair geometry is trigonal bipyramidal. The molecular structure is linear.

Example 6.7.4: XeF_4

Of all the noble gases, xenon is the most reactive, frequently reacting with elements such as oxygen and fluorine. Predict the electron-pair geometry and molecular structure of the XeF_4 molecule.

Solution

The Lewis structure of XeF_4 indicates six regions of high electron density around the xenon atom: two lone pairs and four bonds:

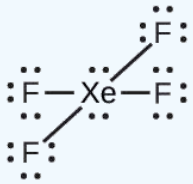


Figure 6.7.11: The five atoms are all in the same plane and have a square planar molecular structure.

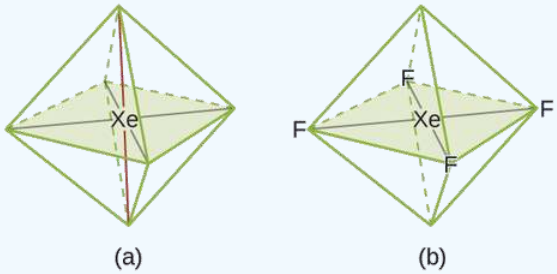


Figure **6.7.11**: (a) XeF_4 adopts an octahedral arrangement with two lone pairs (red lines) and four bonds in the electron-pair geometry. (b) The molecular structure is square planar with the lone pairs directly across from one another.

? Exercise 6.7.4

In a certain molecule, the central atom has three lone pairs and two bonds. What will the electron pair geometry and molecular structure be?

Answer

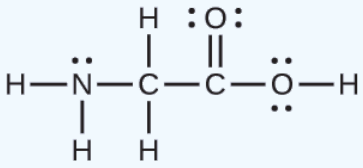
electron pair geometry: trigonal bipyramidal; molecular structure: linear

Molecular Structure for Multicenter Molecules

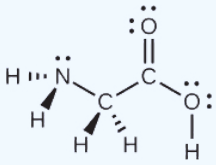
When a molecule or polyatomic ion has only one central atom, the molecular structure completely describes the shape of the molecule. Larger molecules do not have a single central atom, but are connected by a chain of interior atoms that each possess a "local" geometry. The way these local structures are oriented with respect to each other also influences the molecular shape, but such considerations are largely beyond the scope of this introductory discussion. For our purposes, we will only focus on determining the local structures.

✓ Example 6.7.5: Predicting Structure in Multicenter Molecules

The Lewis structure for the simplest amino acid, glycine, $H_2NCH_2CO_2H$, is shown here. Predict the local geometry for the nitrogen atom, the two carbon atoms, and the oxygen atom with a hydrogen atom attached:



Solution



Consider each central atom independently. The electron-pair geometries:

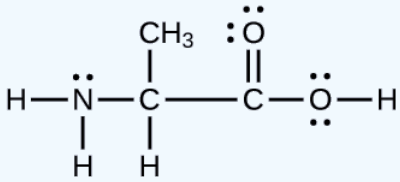
- nitrogen—four regions of electron density; tetrahedral
- carbon ($\underline{C}H_2$)—four regions of electron density; tetrahedral
- carbon ($\underline{C}O_2$)—three regions of electron density; trigonal planar
- oxygen ($\underline{O}H$)—four regions of electron density; tetrahedral

The local structures:

- nitrogen—three bonds, one lone pair; trigonal pyramidal
- carbon ($\underline{C}H_2$)—four bonds, no lone pairs; tetrahedral
- carbon ($\underline{C}O_2$)—three bonds (double bond counts as one bond), no lone pairs; trigonal planar
- oxygen ($\underline{O}H$)—two bonds, two lone pairs; bent (109°)

? Exercise 6.7.5

Another amino acid is alanine, which has the Lewis structure shown here. Predict the electron-pair geometry and local structure of the nitrogen atom, the three carbon atoms, and the oxygen atom with hydrogen attached:



Answer

electron-pair geometries: nitrogen—tetrahedral; carbon ($\underline{C}H$)—tetrahedral; carbon ($\underline{C}H_3$)—tetrahedral; carbon ($\underline{C}O_2$)—trigonal planar; oxygen ($\underline{O}H$)—tetrahedral; local structures: nitrogen—trigonal pyramidal; carbon ($\underline{C}H$)—tetrahedral; carbon ($\underline{C}H_3$)—tetrahedral; carbon ($\underline{C}O_2$)—trigonal planar; oxygen ($\underline{O}H$)—bent (109°)

✓ Example 6.7.6: Molecular Simulation

Using this molecular shape simulator allows us to control whether bond angles and/or lone pairs are displayed by checking or unchecking the boxes under “Options” on the right. We can also use the “Name” checkboxes at bottom-left to display or hide the electron pair geometry (called “electron geometry” in the simulator) and/or molecular structure (called “molecular shape” in the simulator).

Build the molecule HCN in the simulator based on the following Lewis structure:

$$\mathbf{H–C\equiv N}$$

Click on each bond type or lone pair at right to add that group to the central atom. Once you have the complete molecule, rotate it to examine the predicted molecular structure. What molecular structure is this?

Solution

The molecular structure is linear.

? Exercise 6.7.6

Build a more complex molecule in the simulator. Identify the electron-group geometry, molecular structure, and bond angles. Then try to find a chemical formula that would match the structure you have drawn.

Answer

Answers will vary. For example, an atom with four single bonds, a double bond, and a lone pair has an octahedral electron-group geometry and a square pyramidal molecular structure. $XeOF_4$ is a molecule that adopts this structure.

Molecular Polarity and Dipole Moment

As discussed previously, polar covalent bonds connect two atoms with differing electronegativities, leaving one atom with a partial positive charge (δ+) and the other atom with a partial negative charge (δ–), as the electrons are pulled toward the more electronegative atom. This separation of charge gives rise to a bond dipole moment. The magnitude of a bond dipole moment is represented by the Greek letter mu (μ) and is given by

$$\mu = Qr \tag{6.7.1}$$

where

- Q is the magnitude of the partial charges (determined by the electronegativity difference) and
- r is the distance between the charges:

This bond moment can be represented as a vector, a quantity having both direction and magnitude (Figure **6.7.12**). Dipole vectors are shown as arrows pointing along the bond from the less electronegative atom toward the more electronegative atom. A small plus sign is drawn on the less electronegative end to indicate the partially positive end of the bond. The length of the arrow is proportional to the magnitude of the electronegativity difference between the two atoms.

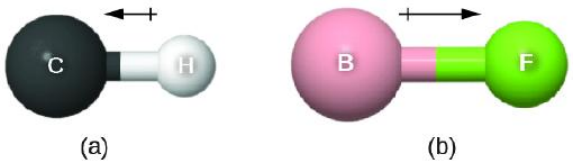


Figure **6.7.12**: (a) There is a small difference in electronegativity between C and H, represented as a short vector. (b) The electronegativity difference between B and F is much larger, so the vector representing the bond moment is much longer.

A whole molecule may also have a separation of charge, depending on its molecular structure and the polarity of each of its bonds. If such a charge separation exists, the molecule is said to be a polar molecule (or dipole); otherwise the molecule is said to be nonpolar. The dipole moment measures the extent of net charge separation in the molecule as a whole. We determine the dipole moment by adding the bond moments in three-dimensional space, taking into account the molecular structure.

For diatomic molecules, there is only one bond, so its bond dipole moment determines the molecular polarity. Homonuclear diatomic molecules such as Br_2 and N_2 have no difference in electronegativity, so their dipole moment is zero. For heteronuclear molecules such as CO, there is a small dipole moment. For HF, there is a larger dipole moment because there is a larger difference in electronegativity.

When a molecule contains more than one bond, the geometry must be taken into account. If the bonds in a molecule are arranged such that their bond moments cancel (vector sum equals zero), then the molecule is nonpolar. This is the situation in CO_2 (Figure **6.7.13***A*). Each of the bonds is polar, but the molecule as a whole is nonpolar. From the Lewis structure, and using VSEPR theory, we determine that the CO_2 molecule is linear with polar C=O bonds on opposite sides of the carbon atom. The bond moments cancel because they are pointed in opposite directions. In the case of the water molecule (Figure **6.7.13***B*), the Lewis structure again shows that there are two bonds to a central atom, and the electronegativity difference again shows that each of these bonds has a nonzero bond moment. In this case, however, the molecular structure is bent because of the lone pairs on O, and the two bond moments do not cancel. Therefore, water does have a net dipole moment and is a polar molecule (dipole).

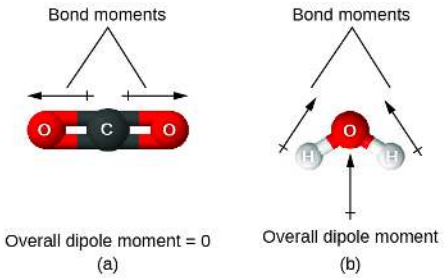
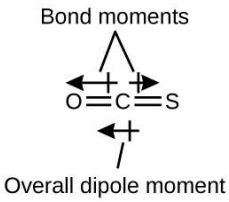


Figure **6.7.13**: The overall dipole moment of a molecule depends on the individual bond dipole moments and how they are arranged. (a) Each CO bond has a bond dipole moment, but they point in opposite directions so that the net CO_2 molecule is nonpolar. (b) In contrast, water is polar because the OH bond moments do not cancel out.

The OCS molecule has a structure similar to CO_2, but a sulfur atom has replaced one of the oxygen atoms. To determine if this molecule is polar, we draw the molecular structure. VSEPR theory predicts a linear molecule:

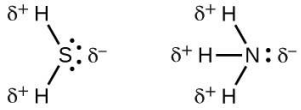


The C–O bond is considerably polar. Although C and S have very similar electronegativity values, S is slightly more electronegative than C, and so the C-S bond is just slightly polar. Because oxygen is more electronegative than sulfur, the oxygen end of the molecule is the negative end.

Chloromethane, CH_3Cl, is another example of a polar molecule. Although the polar C–Cl and C–H bonds are arranged in a tetrahedral geometry, the C–Cl bonds have a larger bond moment than the C–H bond, and the bond moments do not completely cancel each other. All of the dipoles have a upward component in the orientation shown, since carbon is more electronegative than hydrogen and less electronegative than chlorine:



When we examine the highly symmetrical molecules BF_3 (trigonal planar), CH_4 (tetrahedral), PF_5 (trigonal bipyramidal), and SF_6 (octahedral), in which all the polar bonds are identical, the molecules are nonpolar. The bonds in these molecules are arranged such that their dipoles cancel. However, just because a molecule contains identical bonds does not mean that the dipoles will always cancel. Many molecules that have identical bonds and lone pairs on the central atoms have bond dipoles that do not cancel. Examples include H_2S and NH_3. A hydrogen atom is at the positive end and a nitrogen or sulfur atom is at the negative end of the polar bonds in these molecules:



To summarize, to be polar, a molecule must:

1. Contain at least one polar covalent bond.
2. Have a molecular structure such that the sum of the vectors of each bond dipole moment does not cancel.

Properties of Polar Molecules

Polar molecules tend to align when placed in an electric field with the positive end of the molecule oriented toward the negative plate and the negative end toward the positive plate (Figure **6.7.14**). We can use an electrically charged object to attract polar molecules, but nonpolar molecules are not attracted. Also, polar solvents are better at dissolving polar substances, and nonpolar solvents are better at dissolving nonpolar substances.

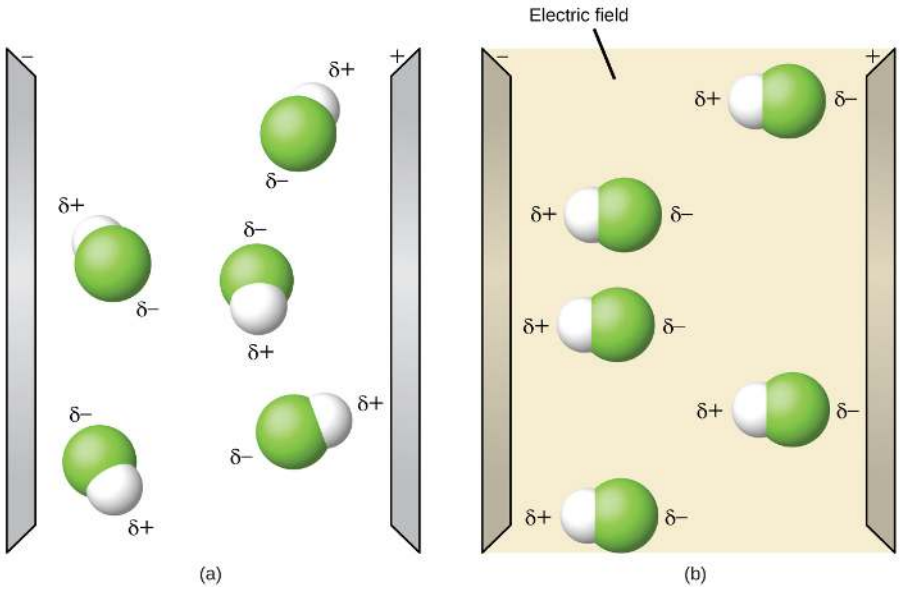


Figure **6.7.14**: (a) Molecules are always randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction.

✔ Example 6.7.7: Polarity Simulations

Open the molecule polarity simulation and select the "Three Atoms" tab at the top. This should display a molecule ABC with three electronegativity adjustors. You can display or hide the bond moments, molecular dipoles, and partial charges at the right. Turning on the Electric Field will show whether the molecule moves when exposed to a field, similar to Figure **6.7.14**.

Use the electronegativity controls to determine how the molecular dipole will look for the starting bent molecule if:

a. A and C are very electronegative and B is in the middle of the range.
b. A is very electronegative, and B and C are not.

Solution

a. Molecular dipole moment points immediately between A and C.
b. Molecular dipole moment points along the A–B bond, toward A.

? Exercise 6.7.7

Determine the partial charges that will give the largest possible bond dipoles.

Answer

The largest bond moments will occur with the largest partial charges. The two solutions above represent how unevenly the electrons are shared in the bond. The bond moments will be maximized when the electronegativity difference is greatest. The controls for A and C should be set to one extreme, and B should be set to the opposite extreme. Although the magnitude of the bond moment will not change based on whether B is the most electronegative or the least, the direction of the bond moment will.

Summary

VSEPR theory predicts the three-dimensional arrangement of atoms in a molecule. It states that valence electrons will assume an electron-pair geometry that minimizes repulsions between areas of high electron density (bonds and/or lone pairs). Molecular structure, which refers only to the placement of atoms in a molecule and not the electrons, is equivalent to electron-pair geometry only when there are no lone electron pairs around the central atom. A dipole moment measures a separation of charge. For one

bond, the bond dipole moment is determined by the difference in electronegativity between the two atoms. For a molecule, the overall dipole moment is determined by both the individual bond moments and how these dipoles are arranged in the molecular structure. Polar molecules (those with an appreciable dipole moment) interact with electric fields, whereas nonpolar molecules do not.

Glossary

axial position
location in a trigonal bipyramidal geometry in which there is another atom at a 180° angle and the equatorial positions are at a 90° angle

bond angle
angle between any two covalent bonds that share a common atom

bond distance
(also, bond length) distance between the nuclei of two bonded atoms

bond dipole moment
separation of charge in a bond that depends on the difference in electronegativity and the bond distance represented by partial charges or a vector

dipole moment
property of a molecule that describes the separation of charge determined by the sum of the individual bond moments based on the molecular structure

electron-pair geometry
arrangement around a central atom of all regions of electron density (bonds, lone pairs, or unpaired electrons)

equatorial position
one of the three positions in a trigonal bipyramidal geometry with 120° angles between them; the axial positions are located at a 90° angle

linear
shape in which two outside groups are placed on opposite sides of a central atom

molecular structure
structure that includes only the placement of the atoms in the molecule

octahedral
shape in which six outside groups are placed around a central atom such that a three-dimensional shape is generated with four groups forming a square and the other two forming the apex of two pyramids, one above and one below the square plane

polar molecule
(also, dipole) molecule with an overall dipole moment

tetrahedral
shape in which four outside groups are placed around a central atom such that a three-dimensional shape is generated with four corners and 109.5° angles between each pair and the central atom

trigonal bipyramidal
shape in which five outside groups are placed around a central atom such that three form a flat triangle with 120° angles between each pair and the central atom, and the other two form the apex of two pyramids, one above and one below the triangular plane

trigonal planar

shape in which three outside groups are placed in a flat triangle around a central atom with 120° angles between each pair and the central atom

valence shell electron-pair repulsion theory (VSEPR)

theory used to predict the bond angles in a molecule based on positioning regions of high electron density as far apart as possible to minimize electrostatic repulsion

vector

quantity having magnitude and direction

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6.E: Chemical Bonding and Molecular Geometry (Exercises)

7.1: Ionic Bonding

Q7.1.1

Does a cation gain protons to form a positive charge or does it lose electrons?

S7.1.1

The protons in the nucleus do not change during normal chemical reactions. Only the outer electrons move. Positive charges form when electrons are lost.

Q7.1.2

Iron(III) sulfate [$Fe_2(SO_4)_3$] is composed of Fe^{3+} and SO_4^{2-} ions. Explain why a sample of iron(III) sulfate is uncharged.

Q7.1.3

Which of the following atoms would be expected to form negative ions in binary ionic compounds and which would be expected to form positive ions: P, I, Mg, Cl, In, Cs, O, Pb, Co?

S7.1.3

P, I, Cl, and O would form anions because they are nonmetals. Mg, In, Cs, Pb, and Co would form cations because they are metals.

Q7.1.4

Which of the following atoms would be expected to form negative ions in binary ionic compounds and which would be expected to form positive ions: Br, Ca, Na, N, F, Al, Sn, S, Cd?

Q7.1.5

Predict the charge on the monatomic ions formed from the following atoms in binary ionic compounds:

a. P
b. Mg
c. Al
d. O
e. Cl
f. Cs

S7.1.5

P^{3-}; Mg^{2+}; Al^{3+}; O^{2-}; Cl^{-}; Cs^{+}

Q7.1.6

Predict the charge on the monatomic ions formed from the following atoms in binary ionic compounds:

1. I
2. Sr
3. K
4. N
5. S
6. In

S7.1.6

1. I^{-}
2. Sr^{2+}
3. K^{+}
4. N^{3-}

5. S^{2-}
6. In^{3+}

Q7.1.7

Write the electron configuration for each of the following ions:

1. As^{3-}
2. I^{-}
3. Be^{2+}
4. Cd^{2+}
5. O^{2-}
6. Ga^{3+}
7. Li^{+}
8. (h) N^{3-}
9. (i) Sn^{2+}
10. (j) Co^{2+}
11. (k) Fe^{2+}
12. (l) As^{3+}

S7.1.7

$[Ar]4s^2 3d^{10} 4p^6$; $[Kr]4d^{10} 5s^2 5p^6$ $1s^2$ $[Kr]4d^{10}$; $[He]2s^2 2p^6$; $[Ar]3d^{10}$; $1s^2$ (h) $[He]2s^2 2p^6$ (i) $[Kr]4d^{10} 5s^2$ (j) $[Ar]3d^7$ (k) $[Ar]3d^6$, (l) $[Ar]3d^{10} 4s^2$

Q7.1.8

Write the electron configuration for the monatomic ions formed from the following elements (which form the greatest concentration of monatomic ions in seawater):

1. Cl
2. Na
3. Mg
4. Ca
5. K
6. Br
7. Sr
8. (h) F

Q7.1.9

Write out the full electron configuration for each of the following atoms and for the monatomic ion found in binary ionic compounds containing the element:

a. Al
b. Br
c. Sr
d. Li
e. As
f. S

S7.1.9

$1s^2 2s^2 2p^6 3s^2 3p^1$; Al^{3+}: $1s^2 2s^2 2p^6$; $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$; $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$; $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$;

Sr^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$; $1s^2 2s^1$;

Li^{+}: $1s^2$; $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$; $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$; $1s^2 2s^2 2p^6 3s^2 3p^4$; $1s^2 2s^2 2p^6 3s^2 3p^6$

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Q7.1.10

From the labels of several commercial products, prepare a list of six ionic compounds in the products. For each compound, write the formula. (You may need to look up some formulas in a suitable reference.)

7.3: Covalent Bonding

Why is it incorrect to speak of a molecule of solid NaCl?

NaCl consists of discrete ions arranged in a crystal lattice, not covalently bonded molecules.

What information can you use to predict whether a bond between two atoms is covalent or ionic?

Predict which of the following compounds are ionic and which are covalent, based on the location of their constituent atoms in the periodic table:

1. Cl_2CO
2. MnO
3. NCl_3
4. $CoBr_2$
5. K_2S
6. CO
7. CaF_2
8. (h) HI
9. (i) CaO
10. (j) IBr
11. (k) CO_2

ionic: (b), (d), (e), (g), and (i); covalent: (a), (c), (f), (h), (j), and (k)

Explain the difference between a nonpolar covalent bond, a polar covalent bond, and an ionic bond.

From its position in the periodic table, determine which atom in each pair is more electronegative:

1. Br or Cl
2. N or O
3. S or O
4. P or S
5. Si or N
6. Ba or P
7. N or K

Cl; O; O; S; N; P; N

From its position in the periodic table, determine which atom in each pair is more electronegative:

1. N or P
2. N or Ge
3. S or F
4. Cl or S
5. H or C
6. Se or P
7. C or Si

From their positions in the periodic table, arrange the atoms in each of the following series in order of increasing electronegativity:

1. C, F, H, N, O
2. Br, Cl, F, H, I
3. F, H, O, P, S
4. Al, H, Na, O, P

5. Ba, H, N, O, As

H, C, N, O, F; H, I, Br, Cl, F; H, P, S, O, F; Na, Al, H, P, O; Ba, H, As, N, O

From their positions in the periodic table, arrange the atoms in each of the following series in order of increasing electronegativity:

1. As, H, N, P, Sb
2. Cl, H, P, S, Si
3. Br, Cl, Ge, H, Sr
4. Ca, H, K, N, Si
5. Cl, Cs, Ge, H, Sr

Which atoms can bond to sulfur so as to produce a positive partial charge on the sulfur atom?

N, O, F, and Cl

Which is the most polar bond?

1. C–C
2. C–H
3. N–H
4. O–H
5. Se–H

Identify the more polar bond in each of the following pairs of bonds:

1. HF or HCl
2. NO or CO
3. SH or OH
4. PCl or SCl
5. CH or NH
6. SO or PO
7. CN or NN

HF; CO; OH; PCl; NH; PO; CN

Which of the following molecules or ions contain polar bonds?

1. O_3
2. S_8
3. $\mathbf{O_2^{2-}}$
4. $\mathbf{NO_3^-}$
5. CO_2
6. H_2S
7. $\mathbf{BH_4^-}$

7.4: Lewis Symbols and Structures

Q7.4.1

Write the Lewis symbols for each of the following ions:

a. As^{3-}
b. I^-
c. Be^{2+}
d. O^{2-}
e. Ga^{3+}
f. Li^+
g. N^{3-}

S7.4.1

eight electrons:



eight electrons:



no electrons

Be^{2+};

eight electrons:



no electrons

Ga^{3+};

no electrons

Li^{+};

eight electrons:



Q7.4.2

Many monatomic ions are found in seawater, including the ions formed from the following list of elements. Write the Lewis symbols for the monatomic ions formed from the following elements:

a. Cl
b. Na
c. Mg
d. Ca
e. K
f. Br
g. Sr
h. F

Q7.4.3

Write the Lewis symbols of the ions in each of the following ionic compounds and the Lewis symbols of the atom from which they are formed:

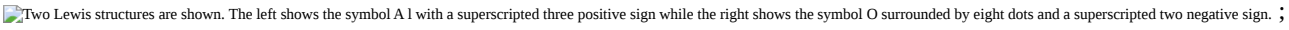
1. MgS
2. Al_2O_3
3. $GaCl_3$
4. K_2O
5. Li_3N
6. KF

(a)

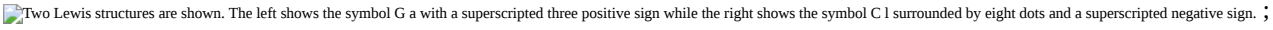
https://chem.libretexts.org/@go/page/242840



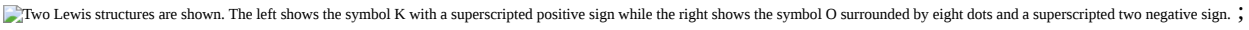
(b)



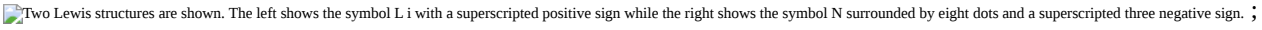
(c)



(d)



(e)

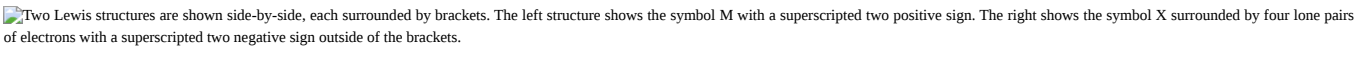


(f)

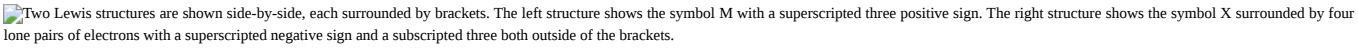


In the Lewis structures listed here, M and X represent various elements in the third period of the periodic table. Write the formula of each compound using the chemical symbols of each element:

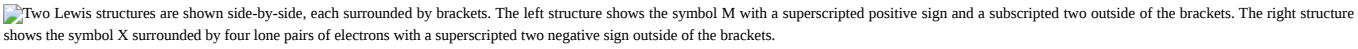
(a)



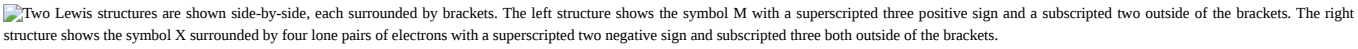
(b)



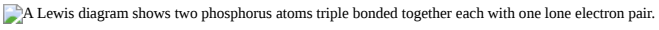
(c)



(d)



Write the Lewis structure for the diatomic molecule P_2, an unstable form of phosphorus found in high-temperature phosphorus vapor.



Write Lewis structures for the following:

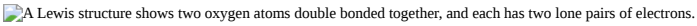
a. H_2
b. HBr
c. PCl_3
d. SF_2
e. H_2CCH_2
f. HNNH
g. H_2CNH
h. (h) NO^-
i. (i) N_2
j. (j) CO
k. (k) CN^-

Write Lewis structures for the following:

a. O_2
b. H_2CO

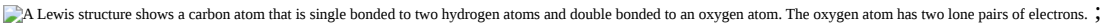
c. AsF_3
d. ClNO
e. $SiCl_4$
f. H_3O^+
g. NH_4^+
h. (h) BF_4^-
i. (i) HCCH
j. (j) ClCN
k. (k) C_2^{2+}

(a)

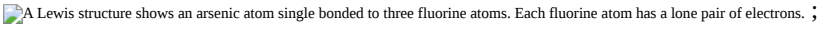

A Lewis structure shows two oxygen atoms double bonded together, and each has two lone pairs of electrons.

In this case, the Lewis structure is inadequate to depict the fact that experimental studies have shown two unpaired electrons in each oxygen molecule.

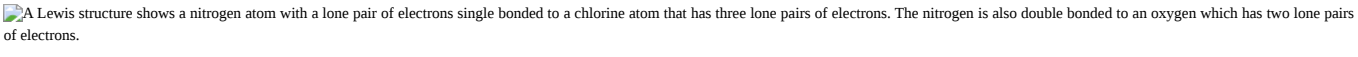
(b)


A Lewis structure shows a carbon atom that is single bonded to two hydrogen atoms and double bonded to an oxygen atom. The oxygen atom has two lone pairs of electrons. ;

(c)

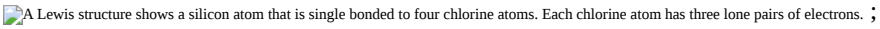

A Lewis structure shows an arsenic atom single bonded to three fluorine atoms. Each fluorine atom has a lone pair of electrons. ;

(d)

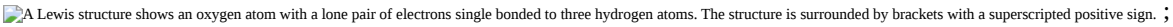

A Lewis structure shows a nitrogen atom with a lone pair of electrons single bonded to a chlorine atom that has three lone pairs of electrons. The nitrogen is also double bonded to an oxygen which has two lone pairs of electrons.

;

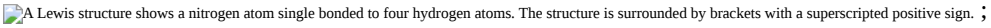
(e)


A Lewis structure shows a silicon atom that is single bonded to four chlorine atoms. Each chlorine atom has three lone pairs of electrons. ;

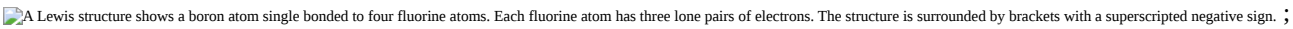
(f)


A Lewis structure shows an oxygen atom with a lone pair of electrons single bonded to three hydrogen atoms. The structure is surrounded by brackets with a superscripted positive sign. ;

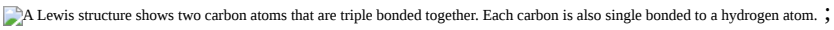
(g)


A Lewis structure shows a nitrogen atom single bonded to four hydrogen atoms. The structure is surrounded by brackets with a superscripted positive sign. ;

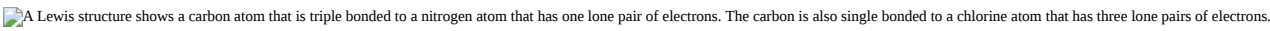
(h)


A Lewis structure shows a boron atom single bonded to four fluorine atoms. Each fluorine atom has three lone pairs of electrons. The structure is surrounded by brackets with a superscripted negative sign. ;

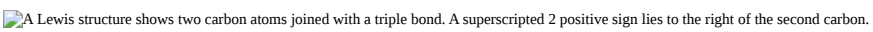
(i)


A Lewis structure shows two carbon atoms that are triple bonded together. Each carbon is also single bonded to a hydrogen atom. ;

(j)


A Lewis structure shows a carbon atom that is triple bonded to a nitrogen atom that has one lone pair of electrons. The carbon is also single bonded to a chlorine atom that has three lone pairs of electrons. ;

(k)


A Lewis structure shows two carbon atoms joined with a triple bond. A superscripted 2 positive sign lies to the right of the second carbon.

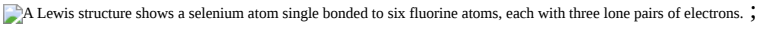
Write Lewis structures for the following:

1. ClF_3
2. PCl_5
3. BF_3
4. PF_6^-

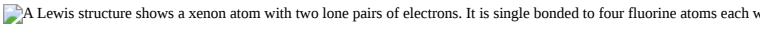
Write Lewis structures for the following:

1. SeF_6
2. XeF_4
3. $\mathbf{SeCl_3^+}$
4. Cl_2BBCl_2 (contains a B–B bond)

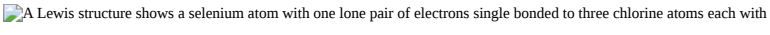
SeF_6:


A Lewis structure shows a selenium atom single bonded to six fluorine atoms, each with three lone pairs of electrons. ;

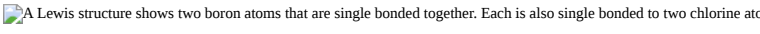
XeF_4:


A Lewis structure shows a xenon atom with two lone pairs of electrons. It is single bonded to four fluorine atoms each with three lone pairs of electrons. ;

$\mathbf{SeCl_3^+}$:


A Lewis structure shows a selenium atom with one lone pair of electrons single bonded to three chlorine atoms each with three lone pairs of electrons. The whole structure is surrounded by brackets. ;

Cl_2BBCl_2:


A Lewis structure shows two boron atoms that are single bonded together. Each is also single bonded to two chlorine atoms that both have three lone pairs of electrons.

Write Lewis structures for:

1. $\mathbf{PO_4^{3-}}$
2. $\mathbf{ICl_4^-}$
3. $\mathbf{SO_3^{2-}}$
4. HONO

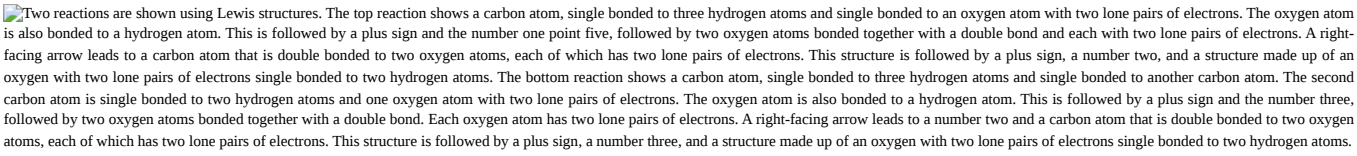
Correct the following statement: “The bonds in solid $PbCl_2$ are ionic; the bond in a HCl molecule is covalent. Thus, all of the valence electrons in $PbCl_2$ are located on the Cl^- ions, and all of the valence electrons in a HCl molecule are shared between the H and Cl atoms.”

Two valence electrons per Pb atom are transferred to Cl atoms; the resulting Pb^{2+} ion has a $6s^2$ valence shell configuration. Two of the valence electrons in the HCl molecule are shared, and the other six are located on the Cl atom as lone pairs of electrons.

Write Lewis structures for the following molecules or ions:

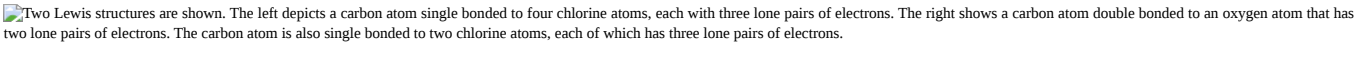
1. SbH_3
2. XeF_2
3. Se_8 (a cyclic molecule with a ring of eight Se atoms)

Methanol, H_3COH, is used as the fuel in some race cars. Ethanol, C_2H_5OH, is used extensively as motor fuel in Brazil. Both methanol and ethanol produce CO_2 and H_2O when they burn. Write the chemical equations for these combustion reactions using Lewis structures instead of chemical formulas.


Two reactions are shown using Lewis structures. The top reaction shows a carbon atom, single bonded to three hydrogen atoms and single bonded to an oxygen atom with two lone pairs of electrons. The oxygen atom is also bonded to a hydrogen atom. This is followed by a plus sign and the number one point five, followed by two oxygen atoms bonded together with a double bond and each with two lone pairs of electrons. A right-facing arrow leads to a carbon atom that is double bonded to two oxygen atoms, each of which has two lone pairs of electrons. This structure is followed by a plus sign, a number two, and a structure made up of an oxygen with two lone pairs of electrons single bonded to two hydrogen atoms. The bottom reaction shows a carbon atom, single bonded to three hydrogen atoms and single bonded to another carbon atom. The second carbon atom is single bonded to two hydrogen atoms and one oxygen atom with two lone pairs of electrons. The oxygen atom is also bonded to a hydrogen atom. This is followed by a plus sign and the number three, followed by two oxygen atoms bonded together with a double bond. Each oxygen atom has two lone pairs of electrons. A right-facing arrow leads to a number two and a carbon atom that is double bonded to two oxygen atoms, each of which has two lone pairs of electrons. This structure is followed by a plus sign, a number three, and a structure made up of an oxygen with two lone pairs of electrons single bonded to two hydrogen atoms.

Many planets in our solar system contain organic chemicals including methane (CH_4) and traces of ethylene (C_2H_4), ethane (C_2H_6), propyne (H_3CCCH), and diacetylene (HCCCCH). Write the Lewis structures for each of these molecules.

Carbon tetrachloride was formerly used in fire extinguishers for electrical fires. It is no longer used for this purpose because of the formation of the toxic gas phosgene, Cl_2CO. Write the Lewis structures for carbon tetrachloride and phosgene.


Two Lewis structures are shown. The left depicts a carbon atom single bonded to four chlorine atoms, each with three lone pairs of electrons. The right shows a carbon atom double bonded to an oxygen atom that has two lone pairs of electrons. The carbon atom is also single bonded to two chlorine atoms, each of which has three lone pairs of electrons.

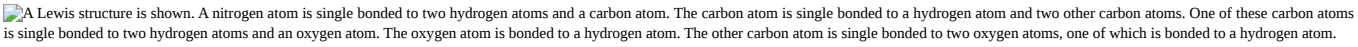
Identify the atoms that correspond to each of the following electron configurations. Then, write the Lewis symbol for the common ion formed from each atom:

1. $1s^2 2s^2 2p^5$
2. $1s^2 2s^2 2p^6 3s^2$

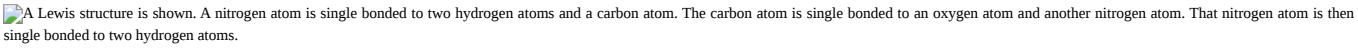
3. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$
4. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^4$
5. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^1$

The arrangement of atoms in several biologically important molecules is given here. Complete the Lewis structures of these molecules by adding multiple bonds and lone pairs. Do not add any more atoms.

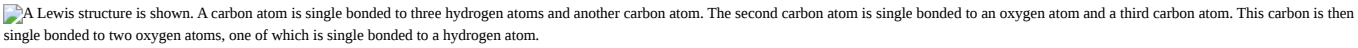
the amino acid serine:


A Lewis structure is shown. A nitrogen atom is single bonded to two hydrogen atoms and a carbon atom. The carbon atom is single bonded to a hydrogen atom and two other carbon atoms. One of these carbon atoms is single bonded to two hydrogen atoms and an oxygen atom. The oxygen atom is bonded to a hydrogen atom. The other carbon atom is single bonded to two oxygen atoms, one of which is bonded to a hydrogen atom.

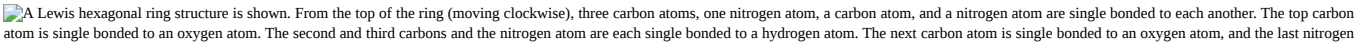
urea:


A Lewis structure is shown. A nitrogen atom is single bonded to two hydrogen atoms and a carbon atom. The carbon atom is single bonded to an oxygen atom and another nitrogen atom. That nitrogen atom is then single bonded to two hydrogen atoms.

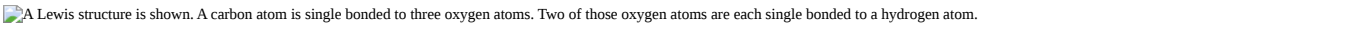
pyruvic acid:


A Lewis structure is shown. A carbon atom is single bonded to three hydrogen atoms and another carbon atom. The second carbon atom is single bonded to an oxygen atom and a third carbon atom. This carbon is then single bonded to two oxygen atoms, one of which is single bonded to a hydrogen atom.

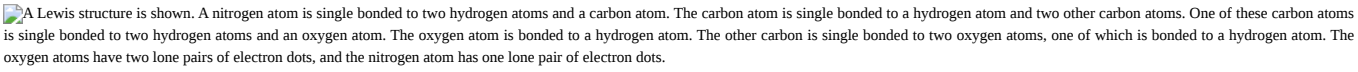
uracil:


A Lewis hexagonal ring structure is shown. From the top of the ring (moving clockwise), three carbon atoms, one nitrogen atom, a carbon atom, and a nitrogen atom are single bonded to each another. The top carbon atom is single bonded to an oxygen atom. The second and third carbons and the nitrogen atom are each single bonded to a hydrogen atom. The next carbon atom is single bonded to an oxygen atom, and the last nitrogen atom is single bonded to a hydrogen atom.

carbonic acid:

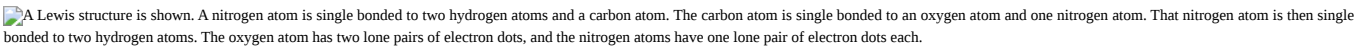

A Lewis structure is shown. A carbon atom is single bonded to three oxygen atoms. Two of those oxygen atoms are each single bonded to a hydrogen atom.

(a)


A Lewis structure is shown. A nitrogen atom is single bonded to two hydrogen atoms and a carbon atom. The carbon atom is single bonded to a hydrogen atom and two other carbon atoms. One of these carbon atoms is single bonded to two hydrogen atoms and an oxygen atom. The oxygen atom is bonded to a hydrogen atom. The other carbon is single bonded to two oxygen atoms, one of which is bonded to a hydrogen atom. The oxygen atoms have two lone pairs of electron dots, and the nitrogen atom has one lone pair of electron dots.

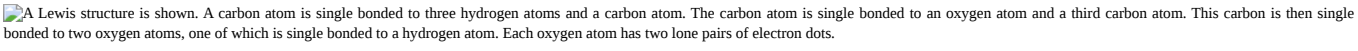
;

(b)


A Lewis structure is shown. A nitrogen atom is single bonded to two hydrogen atoms and a carbon atom. The carbon atom is single bonded to an oxygen atom and one nitrogen atom. That nitrogen atom is then single bonded to two hydrogen atoms. The oxygen atom has two lone pairs of electron dots, and the nitrogen atoms have one lone pair of electron dots each.

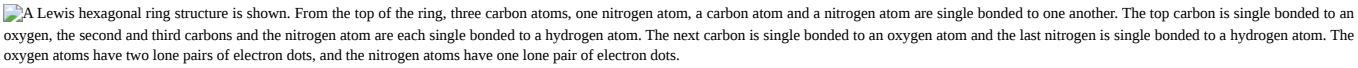
;

(c)


A Lewis structure is shown. A carbon atom is single bonded to three hydrogen atoms and a carbon atom. The carbon atom is single bonded to an oxygen atom and a third carbon atom. This carbon is then single bonded to two oxygen atoms, one of which is single bonded to a hydrogen atom. Each oxygen atom has two lone pairs of electron dots.

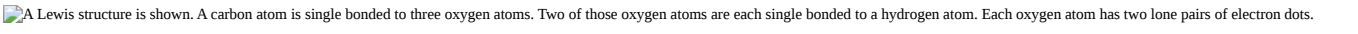
;

(d)


A Lewis hexagonal ring structure is shown. From the top of the ring, three carbon atoms, one nitrogen atom, a carbon atom and a nitrogen atom are single bonded to one another. The top carbon is single bonded to an oxygen, the second and third carbons and the nitrogen atom are each single bonded to a hydrogen atom. The next carbon is single bonded to an oxygen atom and the last nitrogen is single bonded to a hydrogen atom. The oxygen atoms have two lone pairs of electron dots, and the nitrogen atoms have one lone pair of electron dots.

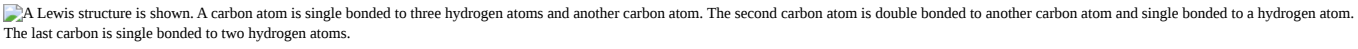
;

(e)


A Lewis structure is shown. A carbon atom is single bonded to three oxygen atoms. Two of those oxygen atoms are each single bonded to a hydrogen atom. Each oxygen atom has two lone pairs of electron dots.

A compound with a molar mass of about 28 g/mol contains 85.7% carbon and 14.3% hydrogen by mass. Write the Lewis structure for a molecule of the compound.

A compound with a molar mass of about 42 g/mol contains 85.7% carbon and 14.3% hydrogen by mass. Write the Lewis structure for a molecule of the compound.


A Lewis structure is shown. A carbon atom is single bonded to three hydrogen atoms and another carbon atom. The second carbon atom is double bonded to another carbon atom and single bonded to a hydrogen atom. The last carbon is single bonded to two hydrogen atoms.

Two arrangements of atoms are possible for a compound with a molar mass of about 45 g/mol that contains 52.2% C, 13.1% H, and 34.7% O by mass. Write the Lewis structures for the two molecules.

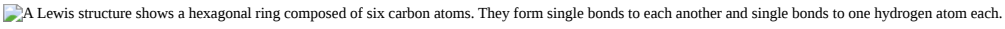
How are single, double, and triple bonds similar? How do they differ?

Each bond includes a sharing of electrons between atoms. Two electrons are shared in a single bond; four electrons are shared in a double bond; and six electrons are shared in a triple bond.

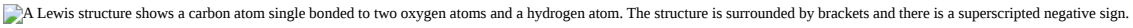
7.5: Formal Charges and Resonance

Write resonance forms that describe the distribution of electrons in each of these molecules or ions.

1. selenium dioxide, OSeO
2. nitrate ion, $\mathbf{NO_3^-}$
3. nitric acid, HNO_3 (N is bonded to an OH group and two O atoms)
4. benzene, C_6H_6:

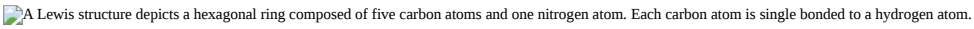

A Lewis structure shows a hexagonal ring composed of six carbon atoms. They form single bonds to each another and single bonds to one hydrogen atom each.

the formate ion:

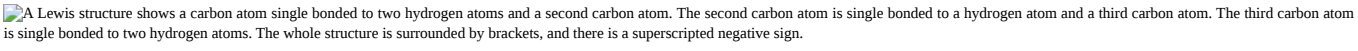

A Lewis structure shows a carbon atom single bonded to two oxygen atoms and a hydrogen atom. The structure is surrounded by brackets and there is a superscripted negative sign.

Write resonance forms that describe the distribution of electrons in each of these molecules or ions.

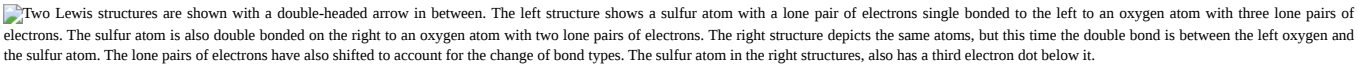
1. sulfur dioxide, SO_2
2. carbonate ion, $\mathbf{CO_3^{2-}}$
3. hydrogen carbonate ion, $\mathbf{HCO_3^-}$ (C is bonded to an OH group and two O atoms)
4. pyridine:


A Lewis structure depicts a hexagonal ring composed of five carbon atoms and one nitrogen atom. Each carbon atom is single bonded to a hydrogen atom.

the allyl ion:

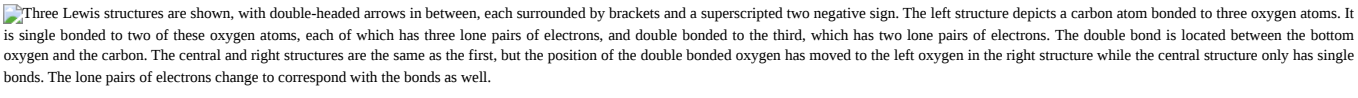

A Lewis structure shows a carbon atom single bonded to two hydrogen atoms and a second carbon atom. The second carbon atom is single bonded to a hydrogen atom and a third carbon atom. The third carbon atom is single bonded to two hydrogen atoms. The whole structure is surrounded by brackets, and there is a superscripted negative sign.

(a)


Two Lewis structures are shown with a double-headed arrow in between. The left structure shows a sulfur atom with a lone pair of electrons single bonded to the left to an oxygen atom with three lone pairs of electrons. The sulfur atom is also double bonded on the right to an oxygen atom with two lone pairs of electrons. The right structure depicts the same atoms, but this time the double bond is between the left oxygen and the sulfur atom. The lone pairs of electrons have also shifted to account for the change of bond types. The sulfur atom in the right structures, also has a third electron dot below it.

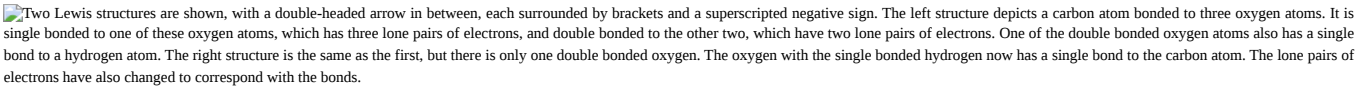
;

(b)


Three Lewis structures are shown, with double-headed arrows in between, each surrounded by brackets and a superscripted two negative sign. The left structure depicts a carbon atom bonded to three oxygen atoms. It is single bonded to two of these oxygen atoms, each of which has three lone pairs of electrons, and double bonded to the third, which has two lone pairs of electrons. The double bond is located between the bottom oxygen and the carbon. The central and right structures are the same as the first, but the position of the double bonded oxygen has moved to the left oxygen in the right structure while the central structure only has single bonds. The lone pairs of electrons change to correspond with the bonds as well.

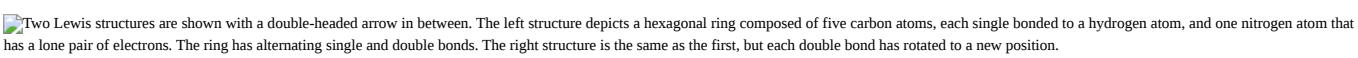
;

(c)


Two Lewis structures are shown, with a double-headed arrow in between, each surrounded by brackets and a superscripted negative sign. The left structure depicts a carbon atom bonded to three oxygen atoms. It is single bonded to one of these oxygen atoms, which has three lone pairs of electrons, and double bonded to the other two, which have two lone pairs of electrons. One of the double bonded oxygen atoms also has a single bond to a hydrogen atom. The right structure is the same as the first, but there is only one double bonded oxygen. The oxygen with the single bonded hydrogen now has a single bond to the carbon atom. The lone pairs of electrons have also changed to correspond with the bonds.

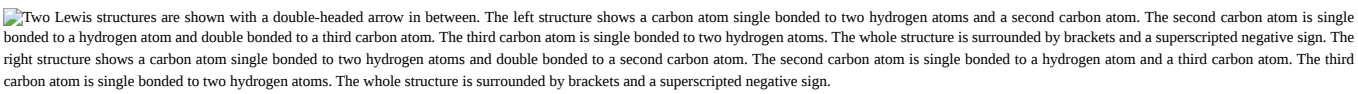
;

(d)


Two Lewis structures are shown with a double-headed arrow in between. The left structure depicts a hexagonal ring composed of five carbon atoms, each single bonded to a hydrogen atom, and one nitrogen atom that has a lone pair of electrons. The ring has alternating single and double bonds. The right structure is the same as the first, but each double bond has rotated to a new position.

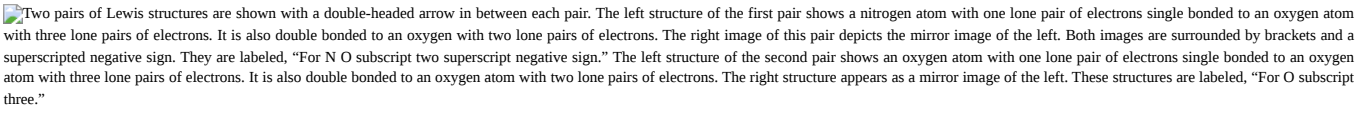
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(e)

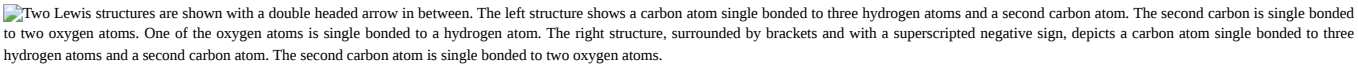

Two Lewis structures are shown with a double-headed arrow in between. The left structure shows a carbon atom single bonded to two hydrogen atoms and a second carbon atom. The second carbon atom is single bonded to a hydrogen atom and double bonded to a third carbon atom. The third carbon atom is single bonded to two hydrogen atoms. The whole structure is surrounded by brackets and a superscripted negative sign. The right structure shows a carbon atom single bonded to two hydrogen atoms and double bonded to a second carbon atom. The second carbon atom is single bonded to a hydrogen atom and a third carbon atom. The third carbon atom is single bonded to two hydrogen atoms. The whole structure is surrounded by brackets and a superscripted negative sign.

Write the resonance forms of ozone, O_3, the component of the upper atmosphere that protects the Earth from ultraviolet radiation.

Sodium nitrite, which has been used to preserve bacon and other meats, is an ionic compound. Write the resonance forms of the nitrite ion, NO_2^-.


Two pairs of Lewis structures are shown with a double-headed arrow in between each pair. The left structure of the first pair shows a nitrogen atom with one lone pair of electrons single bonded to an oxygen atom with three lone pairs of electrons. It is also double bonded to an oxygen with two lone pairs of electrons. The right image of this pair depicts the mirror image of the left. Both images are surrounded by brackets and a superscripted negative sign. They are labeled, “For N O subscript two superscript negative sign.” The left structure of the second pair shows an oxygen atom with one lone pair of electrons single bonded to an oxygen atom with three lone pairs of electrons. It is also double bonded to an oxygen atom with two lone pairs of electrons. The right structure appears as a mirror image of the left. These structures are labeled, “For O subscript three.”

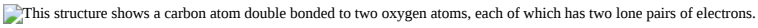
In terms of the bonds present, explain why acetic acid, CH_3CO_2H, contains two distinct types of carbon-oxygen bonds, whereas the acetate ion, formed by loss of a hydrogen ion from acetic acid, only contains one type of carbon-oxygen bond. The skeleton structures of these species are shown:


Two Lewis structures are shown with a double headed arrow in between. The left structure shows a carbon atom single bonded to three hydrogen atoms and a second carbon atom. The second carbon is single bonded to two oxygen atoms. One of the oxygen atoms is single bonded to a hydrogen atom. The right structure, surrounded by brackets and with a superscripted negative sign, depicts a carbon atom single bonded to three hydrogen atoms and a second carbon atom. The second carbon atom is single bonded to two oxygen atoms.

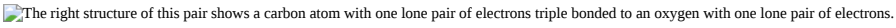
Write the Lewis structures for the following, and include resonance structures where appropriate. Indicate which has the strongest carbon-oxygen bond.

1. CO_2
2. CO

(a)


This structure shows a carbon atom double bonded to two oxygen atoms, each of which has two lone pairs of electrons.

(b)


The right structure of this pair shows a carbon atom with one lone pair of electrons triple bonded to an oxygen with one lone pair of electrons.

CO has the strongest carbon-oxygen bond because there is a triple bond joining C and O. CO_2 has double bonds.

Toothpastes containing sodium hydrogen carbonate (sodium bicarbonate) and hydrogen peroxide are widely used. Write Lewis structures for the hydrogen carbonate ion and hydrogen peroxide molecule, with resonance forms where appropriate.

Determine the formal charge of each element in the following:

1. HCl
2. CF_4
3. PCl_3
4. PF_5

H: 0, Cl: 0; C: 0, F: 0; P: 0, Cl 0; P: 0, F: 0

Determine the formal charge of each element in the following:

1. H_3O^+
2. SO_4^{2-}
3. NH_3
4. O_2^{2-}
5. H_2O_2

Calculate the formal charge of chlorine in the molecules Cl_2, $BeCl_2$, and ClF_5.

Cl in Cl_2: 0; Cl in $BeCl_2$: 0; Cl in ClF_5: 0

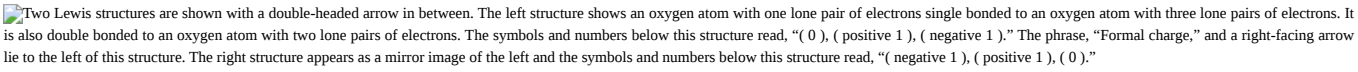
Calculate the formal charge of each element in the following compounds and ions:

1. F_2CO
2. NO^-
3. BF_4^-
4. $SnCl_3^-$
5. H_2CCH_2
6. ClF_3

7. SeF_6
8. (h) PO_4^{3-}

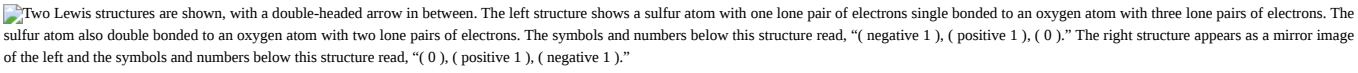
Draw all possible resonance structures for each of these compounds. Determine the formal charge on each atom in each of the resonance structures:

1. O_3
2. SO_2
3. NO_2^-
4. NO_3^-


Two Lewis structures are shown with a double-headed arrow in between. The left structure shows an oxygen atom with one lone pair of electrons single bonded to an oxygen atom with three lone pairs of electrons. It is also double bonded to an oxygen atom with two lone pairs of electrons. The symbols and numbers below this structure read, “(0), (positive 1), (negative 1).” The phrase, “Formal charge,” and a right-facing arrow lie to the left of this structure. The right structure appears as a mirror image of the left and the symbols and numbers below this structure read, “(negative 1), (positive 1), (0).”

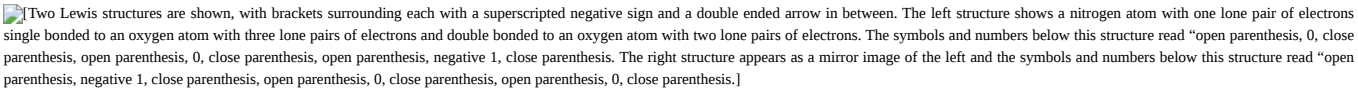
;

(b)


Two Lewis structures are shown, with a double-headed arrow in between. The left structure shows a sulfur atom with one lone pair of electrons single bonded to an oxygen atom with three lone pairs of electrons. The sulfur atom also double bonded to an oxygen atom with two lone pairs of electrons. The symbols and numbers below this structure read, “(negative 1), (positive 1), (0).” The right structure appears as a mirror image of the left and the symbols and numbers below this structure read, “(0), (positive 1), (negative 1).”

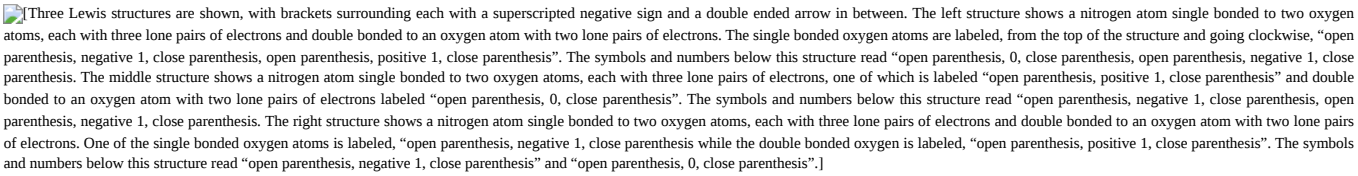
;

(c)


[Two Lewis structures are shown, with brackets surrounding each with a superscripted negative sign and a double ended arrow in between. The left structure shows a nitrogen atom with one lone pair of electrons single bonded to an oxygen atom with three lone pairs of electrons and double bonded to an oxygen atom with two lone pairs of electrons. The symbols and numbers below this structure read “open parenthesis, 0, close parenthesis, open parenthesis, 0, close parenthesis, open parenthesis, negative 1, close parenthesis. The right structure appears as a mirror image of the left and the symbols and numbers below this structure read “open parenthesis, negative 1, close parenthesis, open parenthesis, 0, close parenthesis, open parenthesis, 0, close parenthesis.]

;

(d)


[Three Lewis structures are shown, with brackets surrounding each with a superscripted negative sign and a double ended arrow in between. The left structure shows a nitrogen atom single bonded to two oxygen atoms, each with three lone pairs of electrons and double bonded to an oxygen atom with two lone pairs of electrons. The single bonded oxygen atoms are labeled, from the top of the structure and going clockwise, “open parenthesis, negative 1, close parenthesis, open parenthesis, positive 1, close parenthesis”. The symbols and numbers below this structure read “open parenthesis, 0, close parenthesis, open parenthesis, negative 1, close parenthesis. The middle structure shows a nitrogen atom single bonded to two oxygen atoms, each with three lone pairs of electrons, one of which is labeled “open parenthesis, positive 1, close parenthesis” and double bonded to an oxygen atom with two lone pairs of electrons labeled “open parenthesis, 0, close parenthesis”. The symbols and numbers below this structure read “open parenthesis, negative 1, close parenthesis, open parenthesis, negative 1, close parenthesis. The right structure shows a nitrogen atom single bonded to two oxygen atoms, each with three lone pairs of electrons and double bonded to an oxygen atom with two lone pairs of electrons. One of the single bonded oxygen atoms is labeled, “open parenthesis, negative 1, close parenthesis while the double bonded oxygen is labeled, “open parenthesis, positive 1, close parenthesis”. The symbols and numbers below this structure read “open parenthesis, negative 1, close parenthesis” and “open parenthesis, 0, close parenthesis”.]

Based on formal charge considerations, which of the following would likely be the correct arrangement of atoms in nitrosyl chloride: ClNO or ClON?

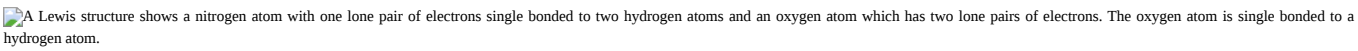
Based on formal charge considerations, which of the following would likely be the correct arrangement of atoms in hypochlorous acid: HOCl or OClH?

HOCl

Based on formal charge considerations, which of the following would likely be the correct arrangement of atoms in sulfur dioxide: OSO or SOO?

Draw the structure of hydroxylamine, H_3NO, and assign formal charges; look up the structure. Is the actual structure consistent with the formal charges?

The structure that gives zero formal charges is consistent with the actual structure:

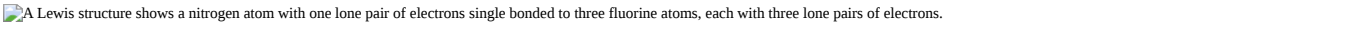

A Lewis structure shows a nitrogen atom with one lone pair of electrons single bonded to two hydrogen atoms and an oxygen atom which has two lone pairs of electrons. The oxygen atom is single bonded to a hydrogen atom.

Iodine forms a series of fluorides (listed here). Write Lewis structures for each of the four compounds and determine the formal charge of the iodine atom in each molecule:

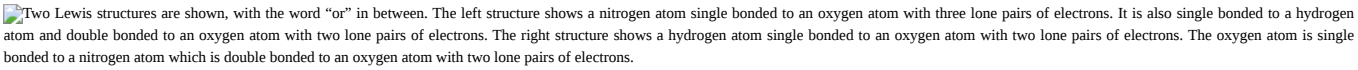
1. IF
2. IF_3
3. IF_5
4. IF_7

Write the Lewis structure and chemical formula of the compound with a molar mass of about 70 g/mol that contains 19.7% nitrogen and 80.3% fluorine by mass, and determine the formal charge of the atoms in this compound.

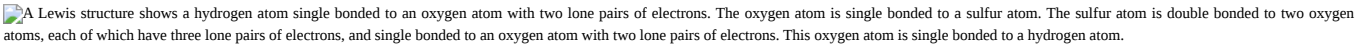
NF_3;


A Lewis structure shows a nitrogen atom with one lone pair of electrons single bonded to three fluorine atoms, each with three lone pairs of electrons.

Which of the following structures would we expect for nitrous acid? Determine the formal charges:


Two Lewis structures are shown, with the word “or” in between. The left structure shows a nitrogen atom single bonded to an oxygen atom with three lone pairs of electrons. It is also single bonded to a hydrogen atom and double bonded to an oxygen atom with two lone pairs of electrons. The right structure shows a hydrogen atom single bonded to an oxygen atom with two lone pairs of electrons. The oxygen atom is single bonded to a nitrogen atom which is double bonded to an oxygen atom with two lone pairs of electrons.

Sulfuric acid is the industrial chemical produced in greatest quantity worldwide. About 90 billion pounds are produced each year in the United States alone. Write the Lewis structure for sulfuric acid, H_2SO_4, which has two oxygen atoms and two OH groups bonded to the sulfur.


A Lewis structure shows a hydrogen atom single bonded to an oxygen atom with two lone pairs of electrons. The oxygen atom is single bonded to a sulfur atom. The sulfur atom is double bonded to two oxygen atoms, each of which have three lone pairs of electrons, and single bonded to an oxygen atom with two lone pairs of electrons. This oxygen atom is single bonded to a hydrogen atom.

7.6: Strengths of Ionic and Covalent Bonds

Which bond in each of the following pairs of bonds is the strongest?

1. C–C or $\mathbf{C=C}$
2. C–N or $\mathbf{C\equiv N}$
3. $\mathbf{C\equiv O}$ or $\mathbf{C=O}$
4. H–F or H–Cl
5. C–H or O–H
6. C–N or C–O

Using the bond energies in Table, determine the approximate enthalpy change for each of the following reactions:

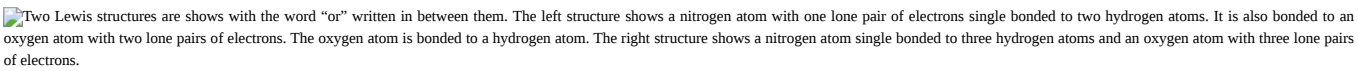
1. $\mathbf{H_2}(g) + \mathbf{Br_2}(g) \longrightarrow \mathbf{2\,HBr}(g)$
2. $\mathbf{CH_4}(g) + \mathbf{I_2}(g) \longrightarrow \mathbf{CH_3I}(g) + \mathbf{HI}(g)$
3. (c) $\mathbf{C_2H_4}(g) + \mathbf{3\,O_2}(g) \longrightarrow \mathbf{2\,CO_2}(g) + \mathbf{2\,H_2O}(g)$

1. −114 kJ;
2. 30 kJ;
3. (c) −1055 kJ

Using the bond energies in Table, determine the approximate enthalpy change for each of the following reactions:

1. $\mathbf{Cl_2}(g) + \mathbf{3\,F_2}(g) \longrightarrow \mathbf{2\,ClF_3}(g)$
2. $\mathbf{H_2C=CH_2}(g) + \mathbf{H_2}(g) \longrightarrow \mathbf{H_3CCH_3}(g)$
3. (c) $\mathbf{2\,C_2H_6}(g) + \mathbf{7\,O_2}(g) \longrightarrow \mathbf{4\,CO_2}(g) + \mathbf{6\,H_2O}(g)$

When a molecule can form two different structures, the structure with the stronger bonds is usually the more stable form. Use bond energies to predict the correct structure of the hydroxylamine molecule:


Two Lewis structures are shows with the word “or” written in between them. The left structure shows a nitrogen atom with one lone pair of electrons single bonded to two hydrogen atoms. It is also bonded to an oxygen atom with two lone pairs of electrons. The oxygen atom is bonded to a hydrogen atom. The right structure shows a nitrogen atom single bonded to three hydrogen atoms and an oxygen atom with three lone pairs of electrons.

The greater bond energy is in the figure on the left. It is the more stable form.

How does the bond energy of HCldiffer from the standard enthalpy of formation of HCl(g)?

Using the standard enthalpy of formation data in Appendix G, show how the standard enthalpy of formation of HCl(g) can be used to determine the bond energy.

$$\begin{aligned} \mathbf{HCl}(g) &\longrightarrow \frac{1}{2}\mathbf{H_2}(g) + \frac{1}{2}\mathbf{Cl_2}(g) \quad & \Delta H_1^\circ = -\Delta H_{f[\mathbf{HCl}(g)]}^\circ \\ \frac{1}{2}\mathbf{H_2}(g) &\longrightarrow \mathbf{H}(g) & \Delta H_2^\circ = \Delta H_{f[\mathbf{H}(g)]}^\circ \end{aligned}$$

$$\frac{\frac{1}{2}\mathrm{Cl_2}(g) \longrightarrow \mathrm{Cl}(g) \qquad \Delta H_3^\circ = \Delta H_{f[\mathrm{Cl}(g)]}^\circ}{\mathrm{HCl}(g) \longrightarrow \mathrm{H}(g) + \mathrm{Cl}(g) \qquad \Delta H_{298}^\circ = \Delta H_1^\circ + \Delta H_2^\circ + \Delta H_3^\circ}$$

$$D_{\mathrm{HCl}} = \Delta H_{298}^\circ = \Delta H_{f[\mathrm{HCl}(g)]}^\circ + \Delta H_{f[\mathrm{H}(g)]}^\circ + \Delta H_{f[\mathrm{Cl}(g)]}^\circ \tag{6.E.1}$$

$$= -(-92.307\ \mathrm{kJ}) + 217.97\ \mathrm{kJ} + 121.3\ \mathrm{kJ} \tag{6.E.2}$$

$$= 431.6\ \mathrm{kJ} \tag{6.E.3}$$

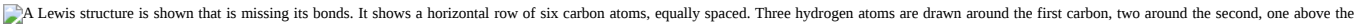
Using the standard enthalpy of formation data in Appendix G, calculate the bond energy of the carbon-sulfur double bond in CS_2.

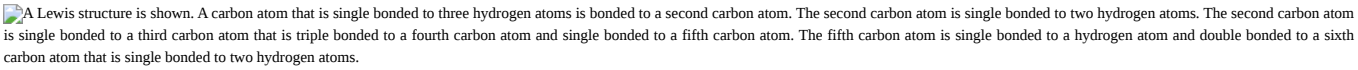
Using the standard enthalpy of formation data in Appendix G, determine which bond is stronger: the S–F bond in $SF_4(g)$ or in $SF_6(g)$?

The S–F bond in SF_4 is stronger.

Using the standard enthalpy of formation data in Appendix G, determine which bond is stronger: the P–Cl bond in $PCl_3(g)$ or in $PCl_5(g)$?

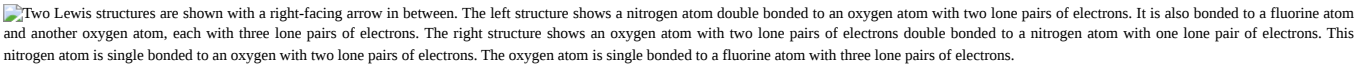
Complete the following Lewis structure by adding bonds (not atoms), and then indicate the longest bond:


A Lewis structure is shown that is missing its bonds. It shows a horizontal row of six carbon atoms, equally spaced. Three hydrogen atoms are drawn around the first carbon, two around the second, one above the fifth, and two by the sixth.


A Lewis structure is shown. A carbon atom that is single bonded to three hydrogen atoms is bonded to a second carbon atom. The second carbon atom is single bonded to two hydrogen atoms. The second carbon atom is single bonded to a third carbon atom that is triple bonded to a fourth carbon atom and single bonded to a fifth carbon atom. The fifth carbon atom is single bonded to a hydrogen atom and double bonded to a sixth carbon atom that is single bonded to two hydrogen atoms.

The C–C single bonds are longest.

Use the bond energy to calculate an approximate value of ΔH for the following reaction. Which is the more stable form of FNO_2?


Two Lewis structures are shown with a right-facing arrow in between. The left structure shows a nitrogen atom double bonded to an oxygen atom with two lone pairs of electrons. It is also bonded to a fluorine atom and another oxygen atom, each with three lone pairs of electrons. The right structure shows an oxygen atom with two lone pairs of electrons double bonded to a nitrogen atom with one lone pair of electrons. This nitrogen atom is single bonded to an oxygen with two lone pairs of electrons. The oxygen atom is single bonded to a fluorine atom with three lone pairs of electrons.

Use principles of atomic structure to answer each of the following:[1]

1. The radius of the Ca atom is 197 pm; the radius of the Ca^{2+} ion is 99 pm. Account for the difference.
2. The lattice energy of CaO(*s*) is –3460 kJ/mol; the lattice energy of K_2O is –2240 kJ/mol. Account for the difference.
3. (c) Given these ionization values, explain the difference between Ca and K with regard to their first and second ionization energies.

Element	First Ionization Energy (kJ/mol)	Second Ionization Energy (kJ/mol)
K	419	3050
Ca	590	1140

The first ionization energy of Mg is 738 kJ/mol and that of Al is 578 kJ/mol. Account for this difference.

When two electrons are removed from the valence shell, the Ca radius loses the outermost energy level and reverts to the lower n = 3 level, which is much smaller in radius. The +2 charge on calcium pulls the oxygen much closer compared with K, thereby increasing the lattice energy relative to a less charged ion. (c) Removal of the 4*s* electron in Ca requires more energy than removal of the 4*s* electron in K because of the stronger attraction of the nucleus and the extra energy required to break the pairing of the electrons. The second ionization energy for K requires that an electron be removed from a lower energy level, where the attraction is much stronger from the nucleus for the electron. In addition, energy is required to unpair two electrons in a full orbital. For Ca, the second ionization potential requires removing only a lone electron in the exposed outer energy level. In Al, the removed electron is relatively unprotected and unpaired in a *p* orbital. The higher energy for Mg mainly reflects the unpairing of the 2*s* electron.

The lattice energy of LiF is 1023 kJ/mol, and the Li–F distance is 200.8 pm. NaF crystallizes in the same structure as LiF but with a Na–F distance of 231 pm. Which of the following values most closely approximates the lattice energy of NaF: 510, 890, 1023, 1175, or 4090 kJ/mol? Explain your choice.

For which of the following substances is the least energy required to convert one mole of the solid into separate ions?

1. MgO
2. SrO
3. (c) KF
4. CsF
5. MgF_2

(d)

The reaction of a metal, M, with a halogen, X_2, proceeds by an exothermic reaction as indicated by this equation: $\mathbf{M}(s) + \mathbf{X_2}(g) \longrightarrow \mathbf{MX_2}(s)$. For each of the following, indicate which option will make the reaction more exothermic. Explain your answers.

1. a large radius vs. a small radius for M^{+2}
2. a high ionization energy vs. a low ionization energy for M
3. (c) an increasing bond energy for the halogen
4. a decreasing electron affinity for the halogen
5. an increasing size of the anion formed by the halogen

The lattice energy of LiF is 1023 kJ/mol, and the Li–F distance is 201 pm. MgO crystallizes in the same structure as LiF but with a Mg–O distance of 205 pm. Which of the following values most closely approximates the lattice energy of MgO: 256 kJ/mol, 512 kJ/mol, 1023 kJ/mol, 2046 kJ/mol, or 4008 kJ/mol? Explain your choice.

4008 kJ/mol; both ions in MgO have twice the charge of the ions in LiF; the bond length is very similar and both have the same structure; a quadrupling of the energy is expected based on the equation for lattice energy

Which compound in each of the following pairs has the larger lattice energy? Note: Mg^{2+} and Li^+ have similar radii; O^{2-} and F^- have similar radii. Explain your choices.

1. MgO or MgSe
2. LiF or MgO
3. (c) Li_2O or LiCl
4. Li_2Se or MgO

Which compound in each of the following pairs has the larger lattice energy? Note: Ba^{2+} and

K^+ have similar radii; S^{2-} and Cl^- have similar radii. Explain your choices.

1. K_2O or Na_2O
2. K_2S or BaS
3. (c) KCl or BaS
4. BaS or $BaCl_2$

Na_2O; Na^+ has a smaller radius than K^+; BaS; Ba has a larger charge than K; (c) BaS; Ba and S have larger charges; BaS; S has a larger charge

Which of the following compounds requires the most energy to convert one mole of the solid into separate ions?

1. MgO
2. SrO
3. (c) KF
4. CsF
5. MgF_2

Which of the following compounds requires the most energy to convert one mole of the solid into separate ions?

1. K_2S
2. K_2O
3. (c) CaS
4. Cs_2S
5. CaO

(e)

The lattice energy of KF is 794 kJ/mol, and the interionic distance is 269 pm. The Na–F

distance in NaF, which has the same structure as KF, is 231 pm. Which of the following values is the closest approximation of the lattice energy of NaF: 682 kJ/mol, 794 kJ/mol, 924 kJ/mol, 1588 kJ/mol, or 3175 kJ/mol? Explain your answer.

7.7: Molecular Structure and Polarity

Explain why the HOH molecule is bent, whereas the HBeH molecule is linear.

The placement of the two sets of unpaired electrons in water forces the bonds to assume a tetrahedral arrangement, and the resulting HOH molecule is bent. The HBeH molecule (in which Be has only two electrons to bond with the two electrons from the hydrogens) must have the electron pairs as far from one another as possible and is therefore linear.

What feature of a Lewis structure can be used to tell if a molecule's (or ion's) electron-pair geometry and molecular structure will be identical?

Explain the difference between electron-pair geometry and molecular structure.

Space must be provided for each pair of electrons whether they are in a bond or are present as lone pairs. Electron-pair geometry considers the placement of all electrons. Molecular structure considers only the bonding-pair geometry.

Why is the H–N–H angle in NH_3 smaller than the H–C–H bond angle in CH_4? Why is the H–N–H angle in $\mathbf{NH_4^+}$ identical to the H–C–H bond angle in CH_4?

Explain how a molecule that contains polar bonds can be nonpolar.

As long as the polar bonds are compensated (for example. two identical atoms are found directly across the central atom from one another), the molecule can be nonpolar.

As a general rule, MX_n molecules (where M represents a central atom and X represents terminal atoms; n = 2 – 5) are polar if there is one or more lone pairs of electrons on M. NH_3 (M = N, X = H, n = 3) is an example. There are two molecular structures with lone pairs that are exceptions to this rule. What are they?

Predict the electron pair geometry and the molecular structure of each of the following molecules or ions:

1. SF_6
2. PCl_5
3. (c) BeH_2
4. $\mathbf{CH_3^+}$

1. Both the electron geometry and the molecular structure are octahedral.
2. Both the electron geometry and the molecular structure are trigonal bipyramid.
3. (c) Both the electron geometry and the molecular structure are linear.
4. Both the electron geometry and the molecular structure are trigonal planar.

Identify the electron pair geometry and the molecular structure of each of the following molecules or ions:

1. $\mathbf{IF_6^+}$
2. CF_4
3. (c) BF_3
4. $\mathbf{SiF_5^-}$
5. $BeCl_2$

What are the electron-pair geometry and the molecular structure of each of the following molecules or ions?

1. ClF_5
2. $\mathbf{ClO_2^-}$
3. (c) $\mathbf{TeCl_4^{2-}}$
4. PCl_3
5. SeF_4

6. $\mathbf{PH_2^-}$

electron-pair geometry: octahedral, molecular structure: square pyramidal; electron-pair geometry: tetrahedral, molecular structure: bent; (c) electron-pair geometry: octahedral, molecular structure: square planar; electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal; electron-pair geometry: trigonal bypyramidal, molecular structure: seesaw; electron-pair geometry: tetrahedral, molecular structure: bent (109°)

Predict the electron pair geometry and the molecular structure of each of the following ions:

1. H_3O^+
2. $\mathbf{PCl_4^-}$
3. (c) $\mathbf{SnCl_3^-}$
4. $\mathbf{BrCl_4^-}$
5. ICl_3
6. XeF_4
7. (g) SF_2

Identify the electron pair geometry and the molecular structure of each of the following molecules:

1. ClNO (N is the central atom)
2. CS_2
3. (c) Cl_2CO (C is the central atom)
4. Cl_2SO (S is the central atom)
5. SO_2F_2 (S is the central atom)
6. XeO_2F_2 (Xe is the central atom)
7. (g) $\mathbf{ClOF_2^+}$ (Cl is the central atom)

electron-pair geometry: trigonal planar, molecular structure: bent (120°); electron-pair geometry: linear, molecular structure: linear; (c) electron-pair geometry: trigonal planar, molecular structure: trigonal planar; electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal; electron-pair geometry: tetrahedral, molecular structure: tetrahedral; electron-pair geometry: trigonal bipyramidal, molecular structure: seesaw; (g) electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal

Predict the electron pair geometry and the molecular structure of each of the following:

1. IOF_5 (I is the central atom)
2. $POCl_3$ (P is the central atom)
3. (c) Cl_2SeO (Se is the central atom)
4. $ClSO^+$ (S is the central atom)
5. F_2SO (S is the central atom)
6. $\mathbf{NO_2^-}$
7. (g) $\mathbf{SiO_4^{4-}}$

Which of the following molecules and ions contain polar bonds? Which of these molecules and ions have dipole moments?

1. ClF_5
2. $\mathbf{ClO_2^-}$
3. (c) $\mathbf{TeCl_4^{2-}}$
4. PCl_3
5. SeF_4
6. $\mathbf{PH_2^-}$
7. (g) XeF_2

All of these molecules and ions contain polar bonds. Only ClF_5, $\mathbf{ClO_2^-}$, PCl_3, SeF_4, and $\mathbf{PH_2^-}$ have dipole moments.

Which of the molecules and ions in Exercise contain polar bonds? Which of these molecules and ions have dipole moments?

1. H_3O^+
2. $\mathbf{PCl_4^-}$

3. (c) $\mathbf{SnCl_3^-}$
4. $\mathbf{BrCl_4^-}$
5. ICl_3
6. XeF_4
7. (g) SF_2

Which of the following molecules have dipole moments?

1. CS_2
2. SeS_2
3. (c) CCl_2F_2
4. PCl_3 (P is the central atom)
5. ClNO (N is the central atom)

SeS_2, CCl_2F_2, PCl_3, and ClNO all have dipole moments.

Identify the molecules with a dipole moment:

1. SF_4
2. CF_4
3. (c) Cl_2CCBr_2
4. CH_3Cl
5. H_2CO

The molecule XF_3 has a dipole moment. Is X boron or phosphorus?

P

The molecule XCl_2 has a dipole moment. Is X beryllium or sulfur?

Is the Cl_2BBCl_2 molecule polar or nonpolar?

nonpolar

There are three possible structures for PCl_2F_3 with phosphorus as the central atom. Draw them and discuss how measurements of dipole moments could help distinguish among them.

Describe the molecular structure around the indicated atom or atoms:

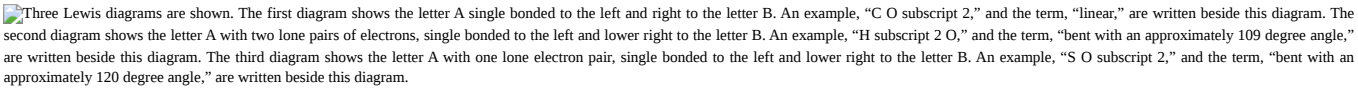
1. the sulfur atom in sulfuric acid, H_2SO_4 [$(HO)_2SO_2$]
2. the chlorine atom in chloric acid, $HClO_3$ [$HOClO_2$]
3. (c) the oxygen atom in hydrogen peroxide, HOOH
4. the nitrogen atom in nitric acid, HNO_3 [$HONO_2$]
5. the oxygen atom in the OH group in nitric acid, HNO_3 [$HONO_2$]
6. the central oxygen atom in the ozone molecule, O_3
7. (g) each of the carbon atoms in propyne, CH_3CCH
8. (h) the carbon atom in Freon, CCl_2F_2
9. (i) each of the carbon atoms in allene, H_2CCCH_2

tetrahedral; trigonal pyramidal; (c) bent (109°); trigonal planar; bent (109°); bent (109°); (g) CH_3CCH tetrahedral, CH_3CCH linear; (h) tetrahedral; (i) H_2CCCH_2 linear; H_2CCCH_2 trigonal planar

Draw the Lewis structures and predict the shape of each compound or ion:

1. CO_2
2. $\mathbf{NO_2^-}$
3. (c) SO_3
4. $\mathbf{SO_3^{2-}}$

A molecule with the formula AB_2, in which A and B represent different atoms, could have one of three different shapes. Sketch and name the three different shapes that this molecule might have. Give an example of a molecule or ion for each shape.



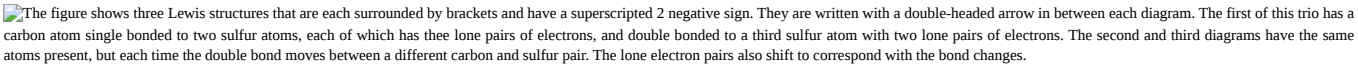
A molecule with the formula AB_3, in which A and B represent different atoms, could have one of three different shapes. Sketch and name the three different shapes that this molecule might have. Give an example of a molecule or ion that has each shape.

Draw the Lewis electron dot structures for these molecules, including resonance structures where appropriate:

1. CS_3^{2-}
2. CS_2
3. (c) CS

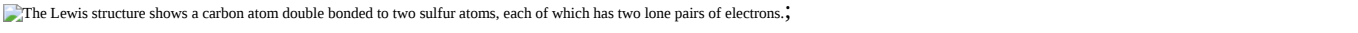
predict the molecular shapes for CS_3^{2-} and CS_2 and explain how you arrived at your predictions

(a)

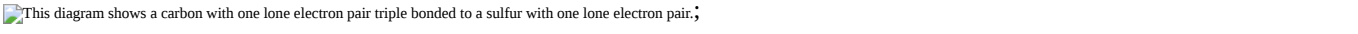


;

(b)



(c)

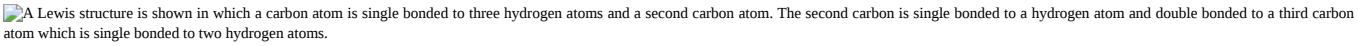


CS_3^{2-} includes three regions of electron density (all are bonds with no lone pairs); the shape is trigonal planar; CS_2 has only two regions of electron density (all bonds with no lone pairs); the shape is linear

What is the molecular structure of the stable form of FNO_2? (N is the central atom.)

A compound with a molar mass of about 42 g/mol contains 85.7% carbon and 14.3% hydrogen. What is its molecular structure?

The Lewis structure is made from three units, but the atoms must be rearranged:



Use the simulation to perform the following exercises for a two-atom molecule:

1. Adjust the electronegativity value so the bond dipole is pointing toward B. Then determine what the electronegativity values must be to switch the dipole so that it points toward A.
2. With a partial positive charge on A, turn on the electric field and describe what happens.
3. (c) With a small partial negative charge on A, turn on the electric field and describe what happens.
4. Reset all, and then with a large partial negative charge on A, turn on the electric field and describe what happens.

Use the simulation to perform the following exercises for a real molecule. You may need to rotate the molecules in three dimensions to see certain dipoles.

1. Sketch the bond dipoles and molecular dipole (if any) for O_3. Explain your observations.
2. Look at the bond dipoles for NH_3. Use these dipoles to predict whether N or H is more electronegative.
3. (c) Predict whether there should be a molecular dipole for NH_3 and, if so, in which direction it will point. Check the molecular dipole box to test your hypothesis.

The molecular dipole points away from the hydrogen atoms.

Use the Molecule Shape simulator to build a molecule. Starting with the central atom, click on the double bond to add one double bond. Then add one single bond and one lone pair. Rotate the molecule to observe the complete geometry. Name the electron group geometry and molecular structure and predict the bond angle. Then click the check boxes at the bottom and right of the simulator to check your answers.

Use the Molecule Shape simulator to explore real molecules. On the Real Molecules tab, select H_2O. Switch between the “real” and “model” modes. Explain the difference observed.

The structures are very similar. In the model mode, each electron group occupies the same amount of space, so the bond angle is shown as 109.5°. In the “real” mode, the lone pairs are larger, causing the hydrogens to be compressed. This leads to the smaller angle of 104.5°.

Use the Molecule Shape simulator to explore real molecules. On the Real Molecules tab, select “model” mode and S_2O. What is the model bond angle? Explain whether the “real” bond angle should be larger or smaller than the ideal model angle.

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CHAPTER OVERVIEW

7: Advanced Theories of Covalent Bonding

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General Chemistry

We have examined the basic ideas of bonding, showing that atoms share electrons to form molecules with stable Lewis structures and that we can predict the shapes of those molecules by valence shell electron pair repulsion (VSEPR) theory. These ideas provide an important starting point for understanding chemical bonding. But these models sometimes fall short in their abilities to predict the behavior of real substances. How can we reconcile the geometries of *s*, *p*, and *d* atomic orbitals with molecular shapes that show angles like 120° and 109.5°? Furthermore, we know that electrons and magnetic behavior are related through electromagnetic fields.

7.1: Prelude to Covalent Bonding
7.2: Valence Bond Theory
7.3: Hybrid Atomic Orbitals
7.4: Multiple Bonds
7.5: Molecular Orbital Theory
7.E: Advanced Theories of Covalent Bonding (Exercises)

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7.1: Prelude to Covalent Bonding

We have examined the basic ideas of bonding, showing that atoms share electrons to form molecules with stable Lewis structures and that we can predict the shapes of those molecules by valence shell electron pair repulsion (VSEPR) theory. These ideas provide an important starting point for understanding chemical bonding. But these models sometimes fall short in their abilities to predict the behavior of real substances. How can we reconcile the geometries of *s*, *p*, and *d* atomic orbitals with molecular shapes that show angles like 120° and 109.5°? Furthermore, we know that electrons and magnetic behavior are related through electromagnetic fields. Both N_2 and O_2 have fairly similar Lewis structures that contain lone pairs of electrons.



Two Lewis diagrams are shown. The diagram on the left shows two nitrogen atoms, represented by the letter N connected by three lines and with a lone pair of electrons on each end of the structure. The diagram on the right shows two oxygen atoms, depicted by the letter O, connected by two lines. Two pairs of electrons surround each oxygen to the top and ends of the structure.

Yet oxygen demonstrates very different magnetic behavior than nitrogen. We can pour liquid nitrogen through a magnetic field with no visible interactions, while liquid oxygen is attracted to the magnet and floats in the magnetic field. We need to understand the additional concepts of valence bond theory, orbital hybridization, and molecular orbital theory to understand these observations.

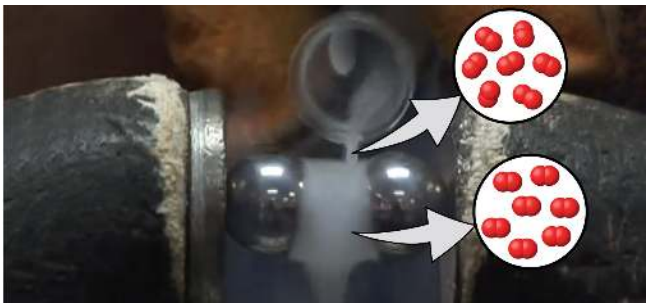


Figure 7.1.1: Oxygen molecules orient randomly most of the time, as shown in the top magnified view. However, when we pour liquid oxygen through a magnet, the molecules line up with the magnetic field, and the attraction allows them to stay suspended between the poles of the magnet where the magnetic field is strongest. Other diatomic molecules (like N_2) flow past the magnet. The detailed explanation of bonding described in this chapter allows us to understand this phenomenon. (credit: modification of work by Jefferson Lab)

A pitcher is shown pouring liquid oxygen through the gap between two magnets, where it has formed a solid disk. A call out box near the stream of liquid oxygen shows an image of six pairs of spheres, spread apart from one another. Another call out box near the solid disk shows ten pairs of spheres much closer together.

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7.2: Valence Bond Theory

Learning Objectives

- Describe the formation of covalent bonds in terms of atomic orbital overlap
- Define and give examples of σ and π bonds

As we know, a scientific theory is a strongly supported explanation for observed natural laws or large bodies of experimental data. For a theory to be accepted, it must explain experimental data and be able to predict behavior. For example, VSEPR theory has gained widespread acceptance because it predicts three-dimensional molecular shapes that are consistent with experimental data collected for thousands of different molecules. However, VSEPR theory does not provide an explanation of chemical bonding.

There are successful theories that describe the electronic structure of atoms. We can use quantum mechanics to predict the specific regions around an atom where electrons are likely to be located: A spherical shape for an *s* orbital, a dumbbell shape for a *p* orbital, and so forth. However, these predictions only describe the orbitals around free atoms. When atoms bond to form molecules, atomic orbitals are not sufficient to describe the regions where electrons will be located in the molecule. A more complete understanding of electron distributions requires a model that can account for the electronic structure of molecules. One popular theory holds that a covalent bond forms when a pair of electrons is shared by two atoms and is simultaneously attracted by the nuclei of both atoms. In the following sections, we will discuss how such bonds are described by valence bond theory and hybridization.

Valence bond theory describes a covalent bond as the overlap of half-filled atomic orbitals (each containing a single electron) that yield a pair of electrons shared between the two bonded atoms. We say that orbitals on two different atoms overlap when a portion of one orbital and a portion of a second orbital occupy the same region of space. According to valence bond theory, a covalent bond results when two conditions are met:

1. an orbital on one atom overlaps an orbital on a second atom and
2. the single electrons in each orbital combine to form an electron pair.

The mutual attraction between this negatively charged electron pair and the two atoms' positively charged nuclei serves to physically link the two atoms through a force we define as a covalent bond. The strength of a covalent bond depends on the extent of overlap of the orbitals involved. Orbitals that overlap extensively form bonds that are stronger than those that have less overlap.

The energy of the system depends on how much the orbitals overlap. Figure **7.2.1** illustrates how the sum of the energies of two hydrogen atoms (the colored curve) changes as they approach each other. When the atoms are far apart there is no overlap, and by convention we set the sum of the energies at zero. As the atoms move together, their orbitals begin to overlap. Each electron begins to feel the attraction of the nucleus in the other atom. In addition, the electrons begin to repel each other, as do the nuclei. While the atoms are still widely separated, the attractions are slightly stronger than the repulsions, and the energy of the system decreases. (A bond begins to form.) As the atoms move closer together, the overlap increases, so the attraction of the nuclei for the electrons continues to increase (as do the repulsions among electrons and between the nuclei). At some specific distance between the atoms, which varies depending on the atoms involved, the energy reaches its lowest (most stable) value. This optimum distance between the two bonded nuclei is the bond distance between the two atoms. The bond is stable because at this point, the attractive and repulsive forces combine to create the lowest possible energy configuration. If the distance between the nuclei were to decrease further, the repulsions between nuclei and the repulsions as electrons are confined in closer proximity to each other would become stronger than the attractive forces. The energy of the system would then rise (making the system destabilized), as shown at the far left of Figure **7.2.1**.

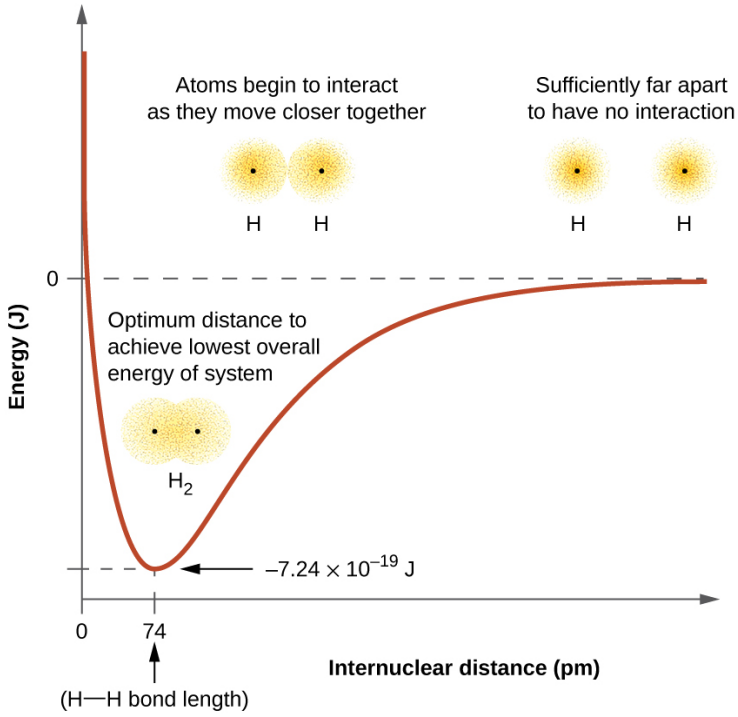


Figure 7.2.1: The interaction of two hydrogen atoms changes as a function of distance. The energy of the system changes as the atoms interact. The lowest (most stable) energy occurs at a distance of 74 pm, which is the bond length observed for the H_2 molecule.

A pair of diagrams are shown and labeled “a” and “b”. Diagram a shows three consecutive images. The first image depicts two separated blurry circles, each labeled with a positive sign and the term “H atom.” The phrase written under them reads, “Sufficiently far apart to have no interaction.” The second image shows the same two circles, but this time they are much closer together and are labeled, “Atoms begin to interact as they move closer together.” The third image shows the two circles overlapping, labeled, “H subscript 2,” and, “Optimum distance to achieve lowest overall energy of system.” Diagram b shows a graph on which the y-axis is labeled “Energy (J),” and the x-axis is labeled, “Internuclear distance (p m).” The midpoint of the y-axis is labeled as zero. The curve on the graph begins at zero p m and high on the y-axis. The graph slopes downward steeply to a point far below the zero joule line on the y-axis and the lowest point reads “0.74 p m” and “H bonded to H bond length.” It is also labeled “ negative 7.24 times 10 superscript negative 19 J.” The graph then rises again to zero J. The graph is accompanied by the same images from diagram a; the first image correlates to the point in the graph where it crosses the zero point on the y-axis, the third image where the graph is lowest.

The bond energy is the difference between the energy minimum (which occurs at the bond distance) and the energy of the two separated atoms. This is the quantity of energy released when the bond is formed. Conversely, the same amount of energy is required to break the bond. For the H_2 molecule shown in Figure 7.2.1, at the bond distance of 74 pm the system is $7.24 \times 10^{-19}\ J$ lower in energy than the two separated hydrogen atoms. This may seem like a small number. However, we know from our earlier description of thermochemistry that bond energies are often discussed on a per-mole basis. For example, it requires $7.24 \times 10^{-19}\ J$ to break one H–H bond, but it takes $4.36 \times 10^{5}\ J$ to break 1 mole of H–H bonds. A comparison of some bond lengths and energies is shown in Table 7.2.1. We can find many of these bonds in a variety of molecules, and this table provides average values. For example, breaking the first C–H bond in CH4 requires 439.3 kJ/mol, while breaking the first C–H bond in $H{-}CH_2C_6H_5$ (a common paint thinner) requires 375.5 kJ/mol.

Table 7.2.1: Representative Bond Energies and Lengths

Bond	Length (pm)	Energy (kJ/mol)	Bond	Length (pm)	Energy (kJ/mol)
H–H	74	436	C–O	140.1	358
H–C	106.8	413	C = O	119.7	745
H–N	101.5	391	C ≡ O	113.7	1072
H–O	97.5	467	H–Cl	127.5	431
C–C	150.6	347	H–Br	141.4	366
C = C	133.5	614	H–I	160.9	298
C ≡ C	120.8	839	O–O	148	146
C–N	142.1	305	O = O	120.8	498
C = N	130.0	615	F–F	141.2	159
C ≡ N	116.1	891	Cl–Cl	198.8	243

In addition to the distance between two orbitals, the orientation of orbitals also affects their overlap (other than for two *s* orbitals, which are spherically symmetric). Greater overlap is possible when orbitals are oriented such that they overlap on a direct line between the two nuclei. Figure **7.2.2** illustrates this for two *p* orbitals from different atoms; the overlap is greater when the orbitals overlap end to end rather than at an angle.

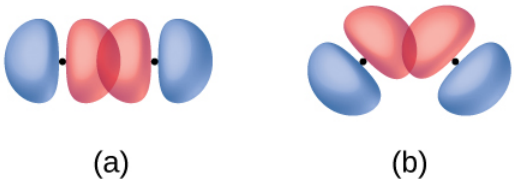


Figure **7.2.2**: (a) The overlap of two p orbitals is greatest when the orbitals are directed end to end. (b) Any other arrangement results in less overlap. The dots indicate the locations of the nuclei.

The overlap of two *s* orbitals (as in H_2), the overlap of an *s* orbital and a *p* orbital (as in HCl), and the end-to-end overlap of two *p* orbitals (as in Cl_2) all produce sigma bonds (σ bonds), as illustrated in Figure **7.2.3**. A σ bond is a covalent bond in which the electron density is concentrated in the region along the internuclear axis; that is, a line between the nuclei would pass through the center of the overlap region. Single bonds in Lewis structures are described as σ bonds in valence bond theory.

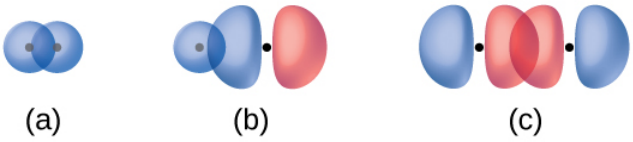


Figure **7.2.3**: Sigma (σ) bonds form from the overlap of the following: (a) two s orbitals, (b) an s orbital and a p orbital, and (c) two p orbitals. The dots indicate the locations of the nuclei.

Three diagrams are shown and labeled “a,” “b,” and “c.” Diagram a shows two spherical orbitals lying side by side and overlapping. Diagram b shows one spherical and one peanut-shaped orbital lying near one another so that the spherical orbital overlaps with one end of the peanut-shaped orbital. Diagram c shows two peanut-shaped orbitals lying end to end so that one end of each orbital overlaps the other.

A pi bond (π bond) is a type of covalent bond that results from the side-by-side overlap of two *p* orbitals, as illustrated in Figure **7.2.4**. In a π bond, the regions of orbital overlap lie on opposite sides of the internuclear axis. Along the axis itself, there is a node, that is, a plane with no probability of finding an electron.

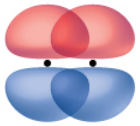
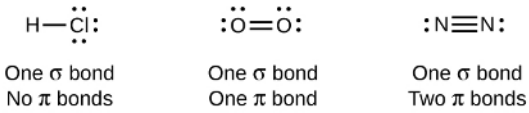


Figure 7.2.4: Pi (π) bonds form from the side-by-side overlap of two p orbitals. The dots indicate the location of the nuclei.

While all single bonds are σ bonds, multiple bonds consist of both σ and π bonds. As the Lewis structures suggest, O_2 contains a double bond, and N_2 contains a triple bond. The double bond consists of one σ bond and one π bond, and the triple bond consists of one σ bond and two π bonds. Between any two atoms, the first bond formed will always be a σ bond, but there can only be one σ bond in any one location. In any multiple bond, there will be one σ bond, and the remaining one or two bonds will be π bonds. These bonds are described in more detail later in this chapter.

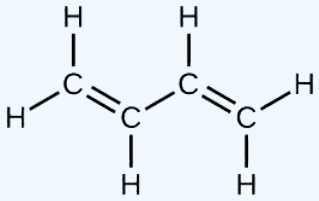


A diagram contains three Lewis structures. The left most structure shows an H atom bonded to a C l atom by a single bond. The C l atom has three lone pairs of electrons. The phrase “One sigma bond No pi bonds” is written below the drawing. The center structure shows two O atoms bonded by a double bond. The O atoms each have two lone pairs of electrons. The phrase “One sigma bond One pi bond” is written below the drawing. The right most structure shows two N atoms bonded by a triple bond. Each N atom has a lone pairs of electrons. The phrase “One sigma bond Two pi bonds” is written below the drawing.

As seen in Table 7.2.1, an average carbon-carbon single bond is 347 kJ/mol, while in a carbon-carbon double bond, the π bond increases the bond strength by 267 kJ/mol. Adding an additional π bond causes a further increase of 225 kJ/mol. We can see a similar pattern when we compare other σ and π bonds. Thus, each individual π bond is generally weaker than a corresponding σ bond between the same two atoms. In a σ bond, there is a greater degree of orbital overlap than in a π bond.

Example 7.2.1: Counting σ and π Bonds

Butadiene, C_4H_6, is used to make synthetic rubber. Identify the number of σ and π bonds contained in this molecule.



Butadiene

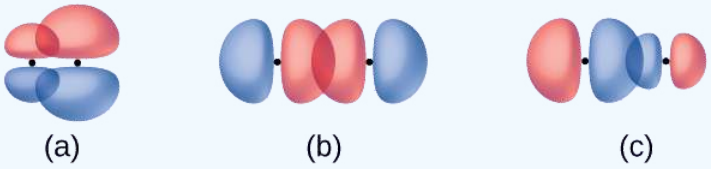
Solution

There are six σ C–H bonds and one σ C–C bond, for a total of seven from the single bonds. There are two double bonds that each have a π bond in addition to the σ bond. This gives a total nine σ and two π bonds overall.

Exercise 7.2.1

Identify each illustration as depicting a σ or π bond:

a. side-by-side overlap of a 4*p* and a 2*p* orbital
b. end-to-end overlap of a 4*p* and 4*p* orbital
c. end-to-end overlap of a 4*p* and a 2*p* orbital



Answer

(a) is a π bond with a node along the axis connecting the nuclei while (b) and (c) are σ bonds that overlap along the axis.

Summary

Valence bond theory describes bonding as a consequence of the overlap of two separate atomic orbitals on different atoms that creates a region with one pair of electrons shared between the two atoms. When the orbitals overlap along an axis containing the nuclei, they form a σ bond. When they overlap in a fashion that creates a node along this axis, they form a π bond.

Glossary

overlap
coexistence of orbitals from two different atoms sharing the same region of space, leading to the formation of a covalent bond

node
plane separating different lobes of orbitals, where the probability of finding an electron is zero

pi bond (π bond)
covalent bond formed by side-by-side overlap of atomic orbitals; the electron density is found on opposite sides of the internuclear axis

sigma bond (σ bond)
covalent bond formed by overlap of atomic orbitals along the internuclear axis

valence bond theory
description of bonding that involves atomic orbitals overlapping to form σ or π bonds, within which pairs of electrons are shared

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7.3: Hybrid Atomic Orbitals

Learning Objectives

- Explain the concept of atomic orbital hybridization
- Determine the hybrid orbitals associated with various molecular geometries

Thinking in terms of overlapping atomic orbitals is one way for us to explain how chemical bonds form in diatomic molecules. However, to understand how molecules with more than two atoms form stable bonds, we require a more detailed model. As an example, let us consider the water molecule, in which we have one oxygen atom bonding to two hydrogen atoms. Oxygen has the electron configuration $1s^2 2s^2 2p^4$, with two unpaired electrons (one in each of the two 2*p* orbitals). Valence bond theory would predict that the two O–H bonds form from the overlap of these two 2*p* orbitals with the 1*s* orbitals of the hydrogen atoms. If this were the case, the bond angle would be 90°, as shown in Figure **7.3.1**, because *p* orbitals are perpendicular to each other. Experimental evidence shows that the bond angle is 104.5°, not 90°. The prediction of the valence bond theory model does not match the real-world observations of a water molecule; a different model is needed.

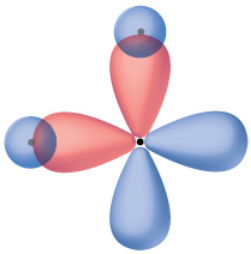


Figure **7.3.1**: The hypothetical overlap of two of the 2p orbitals on an oxygen atom (red) with the 1s orbitals of two hydrogen atoms (blue) would produce a bond angle of 90°. This is not consistent with experimental evidence.[1]

Two peanut-shaped orbitals lie perpendicular to one another. They overlap with spherical orbitals to the left and top of the diagram.

Quantum-mechanical calculations suggest why the observed bond angles in H_2O differ from those predicted by the overlap of the 1*s* orbital of the hydrogen atoms with the 2*p* orbitals of the oxygen atom. The mathematical expression known as the wave function, ψ, contains information about each orbital and the wavelike properties of electrons in an isolated atom. When atoms are bound together in a molecule, the wave functions combine to produce new mathematical descriptions that have different shapes. This process of combining the wave functions for atomic orbitals is called hybridization and is mathematically accomplished by the *linear combination of atomic orbitals*, LCAO, (a technique that we will encounter again later). The new orbitals that result are called hybrid orbitals. The valence orbitals in an *isolated* oxygen atom are a 2*s* orbital and three 2*p* orbitals. The valence orbitals in an oxygen atom in a water molecule differ; they consist of four equivalent hybrid orbitals that point approximately toward the corners of a tetrahedron (Figure **7.3.2**). Consequently, the overlap of the O and H orbitals should result in a tetrahedral bond angle (109.5°). The observed angle of 104.5° is experimental evidence for which quantum-mechanical calculations give a useful explanation: Valence bond theory must include a hybridization component to give accurate predictions.

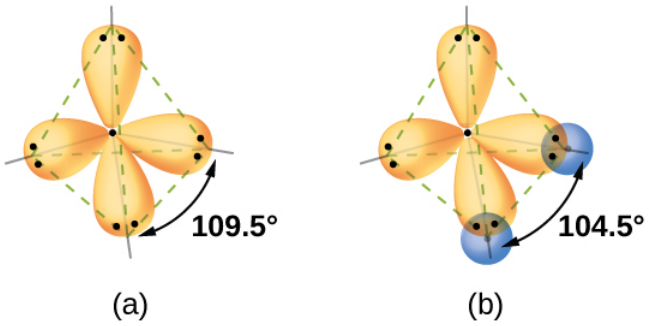


Figure **7.3.2**: (a) A water molecule has four regions of electron density, so VSEPR theory predicts a tetrahedral arrangement of hybrid orbitals. (b) Two of the hybrid orbitals on oxygen contain lone pairs, and the other two overlap with the 1s orbitals of hydrogen atoms to form the O–H bonds in H_2O. This description is more consistent with the experimental structure.

Two diagrams are shown and labeled “a” and “b.” Diagram a shows two peanut-shaped orbitals lying in a tetrahedral arrangement around the letter “O.” Diagram b shows the same two orbitals, but they now overlap to the top and to the left with two spherical orbitals, each labeled “H.” A pair of electrons occupies each lobe of the peanut-shaped orbitals.

The following ideas are important in understanding hybridization:

1. Hybrid orbitals do not exist in isolated atoms. They are formed only in covalently bonded atoms.
2. Hybrid orbitals have shapes and orientations that are very different from those of the atomic orbitals in isolated atoms.
3. A set of hybrid orbitals is generated by combining atomic orbitals. The number of hybrid orbitals in a set is equal to the number of atomic orbitals that were combined to produce the set.
4. All orbitals in a set of hybrid orbitals are equivalent in shape and energy.
5. The type of hybrid orbitals formed in a bonded atom depends on its electron-pair geometry as predicted by the VSEPR theory.
6. Hybrid orbitals overlap to form σ bonds. Unhybridized orbitals overlap to form π bonds.

In the following sections, we shall discuss the common types of hybrid orbitals.

sp Hybridization

The beryllium atom in a gaseous $BeCl_2$ molecule is an example of a central atom with no lone pairs of electrons in a linear arrangement of three atoms. There are two regions of valence electron density in the $BeCl_2$ molecule that correspond to the two covalent Be–Cl bonds. To accommodate these two electron domains, two of the Be atom’s four valence orbitals will mix to yield two hybrid orbitals. This hybridization process involves mixing of the valence *s* orbital with one of the valence *p* orbitals to yield two equivalent *sp* hybrid orbitals that are oriented in a linear geometry (Figure **7.3.3**). In this figure, the set of *sp* orbitals appears similar in shape to the original *p* orbital, but there is an important difference. The number of atomic orbitals combined always equals the number of hybrid orbitals formed. The *p* orbital is one orbital that can hold up to two electrons. The *sp* set is two equivalent orbitals that point 180° from each other. The two electrons that were originally in the *s* orbital are now distributed to the two *sp* orbitals, which are half filled. In gaseous $BeCl_2$, these half-filled hybrid orbitals will overlap with orbitals from the chlorine atoms to form two identical σ bonds.

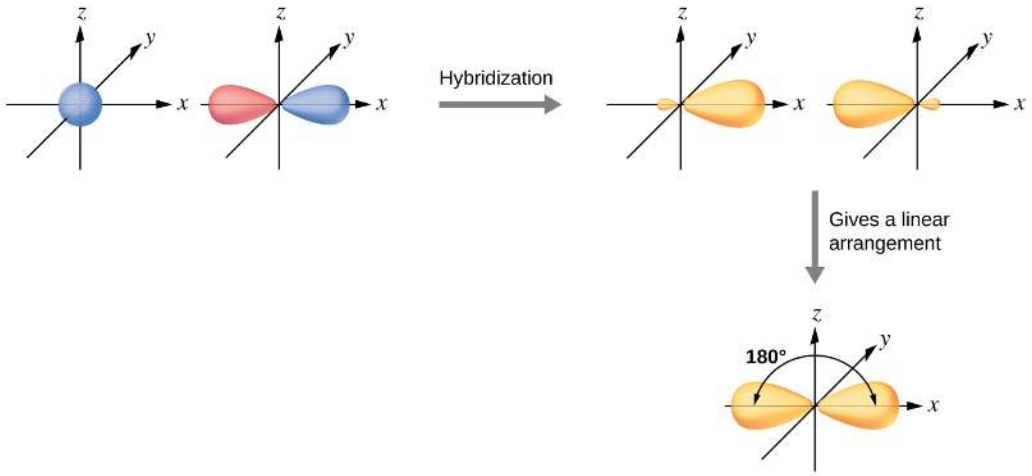


Figure **7.3.3**: Hybridization of an s orbital (blue) and a p orbital (red) of the same atom produces two sp hybrid orbitals (yellow). Each hybrid orbital is oriented primarily in just one direction. Note that each sp orbital contains one lobe that is significantly larger than the other. The set of two sp orbitals are oriented at 180°, which is consistent with the geometry for two domains.

A series of three diagrams connected by a right-facing arrow that is labeled, “Hybridization,” and a downward-facing arrow labeled, “Gives a linear arrangement,” are shown. The first diagram shows a blue spherical orbital and a red, peanut-shaped orbital, each placed on an X, Y, Z axis system. The second diagram shows the same two orbitals, but they are now purple and have one enlarged lobe and one smaller lobe. Each lies along the x-axis in the drawing. The third diagram shows the same two orbitals, but their smaller lobes now overlap along the x-axis while their larger lobes are located at and labeled as “180 degrees” from one another.

We illustrate the electronic differences in an isolated Be atom and in the bonded Be atom in the orbital energy-level diagram in Figure **7.3.4**. These diagrams represent each orbital by a horizontal line (indicating its energy) and each electron by an arrow. Energy increases toward the top of the diagram. We use one upward arrow to indicate one electron in an orbital and two arrows (up and down) to indicate two electrons of opposite spin.

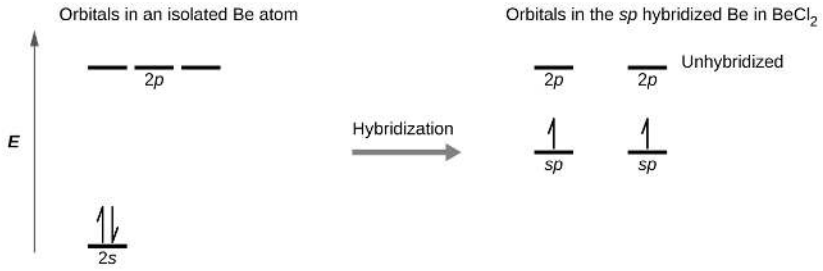


Figure **7.3.4**: This orbital energy-level diagram shows the sp hybridized orbitals on Be in the linear $BeCl_2$ molecule. Each of the two sp hybrid orbitals holds one electron and is thus half filled and available for bonding via overlap with a Cl 3p orbital.

A diagram is shown in two parts, connected by a right facing arrow labeled, “Hybridization.” The left diagram shows an up-facing arrow labeled, “E.” To the lower right of the arrow is a short, horizontal line labeled, “2 s,” that has two vertical half-arrows facing up and down on it. To the upper right of the arrow are a series of three short, horizontal lines labeled, “2 p.” Above these two sets of lines is the phrase, “Orbitals in an isolated B e atom.” The right side of the diagram shows two short, horizontal lines placed halfway up the space and each labeled, “s p.” An upward-facing half arrow is drawn vertically on each line. Above these lines are two other short, horizontal lines, each labeled, “2 p.” Above these two sets of lines is the phrase, “Orbitals in the s p hybridized B e in B e C l subscript 2.”

When atomic orbitals hybridize, the valence electrons occupy the newly created orbitals. The Be atom had two valence electrons, so each of the *sp* orbitals gets one of these electrons. Each of these electrons pairs up with the unpaired electron on a chlorine atom when a hybrid orbital and a chlorine orbital overlap during the formation of the Be–Cl bonds. Any central atom surrounded by just two regions of valence electron density in a molecule will exhibit *sp* hybridization. Other examples include the mercury atom in the linear $HgCl_2$ molecule, the zinc atom in $Zn(CH_3)_2$, which contains a linear C–Zn–C arrangement, and the carbon atoms in HCCH and CO_2.

sp^2 Hybridization

The valence orbitals of a central atom surrounded by three regions of electron density consist of a set of three sp^2 hybrid orbitals and one unhybridized p orbital. This arrangement results from sp^2 hybridization, the mixing of one s orbital and two p orbitals to produce three identical hybrid orbitals oriented in a trigonal planar geometry (Figure **7.3.5**).

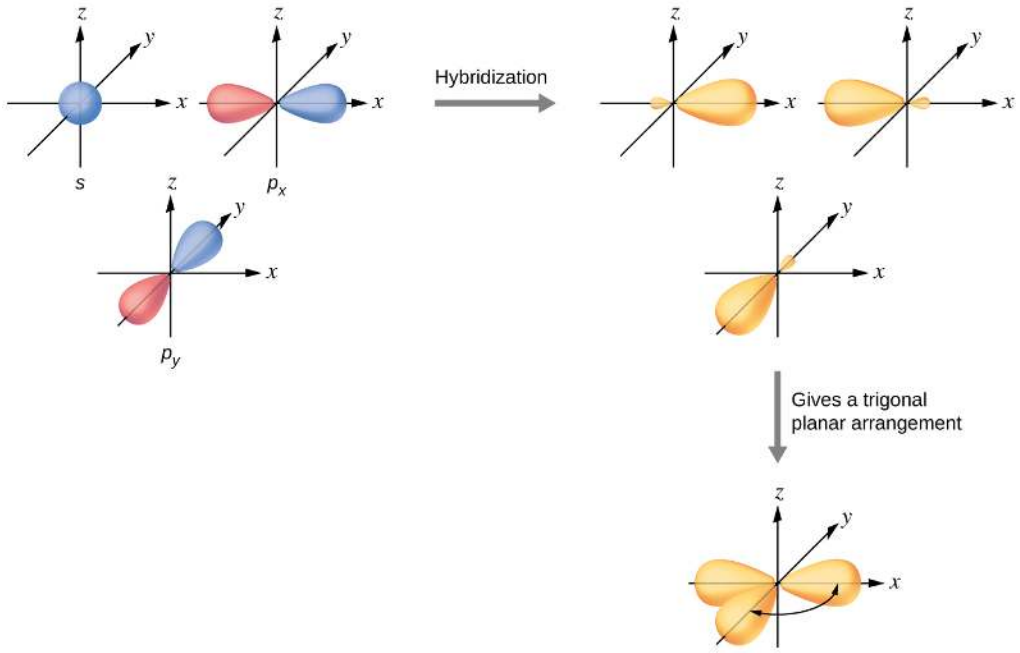


Figure **7.3.5**: The hybridization of an s orbital (blue) and two p orbitals (red) produces three equivalent sp^2 hybridized orbitals (yellow) oriented at 120° with respect to each other. The remaining unhybridized p orbital is not shown here, but is located along the z axis.

A series of three diagrams connected by a right-facing arrow that is labeled, “Hybridization,” and a downward-facing arrow labeled, “Gives a trigonal planar arrangement,” are shown. The first diagram shows a blue spherical orbital and two red, peanut-shaped orbitals, each placed on an X, Y, Z axis system. The two red orbitals are located on the x and z axes, respectively. The second diagram shows the same three orbitals, but they are now purple and have one enlarged lobe and one smaller lobe. Each lies in a different axis in the drawing. The third diagram shows the same three orbitals, but their smaller lobes now overlap while their larger lobes are located at and labeled as “120 degrees” from one another.

Although quantum mechanics yields the “plump” orbital lobes as depicted in Figure **7.3.5**, sometimes for clarity these orbitals are drawn thinner and without the minor lobes, as in Figure **7.3.6**, to avoid obscuring other features of a given illustration. We will use these “thinner” representations whenever the true view is too crowded to easily visualize.

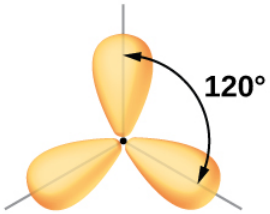


Figure **7.3.6**: This alternate way of drawing the trigonal planar sp^2 hybrid orbitals is sometimes used in more crowded figures.

Three balloon-like orbitals are shown, and connect together near their narrower ends in one plane. The angle between a pair of lobes is labeled, “120 degrees.”

The observed structure of the borane molecule, BH_3, suggests sp^2 hybridization for boron in this compound. The molecule is trigonal planar, and the boron atom is involved in three bonds to hydrogen atoms (Figure **7.3.7**).

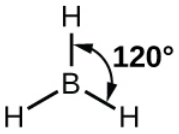


Figure **7.3.7**: BH_3 is an electron-deficient molecule with a trigonal planar structure.

A boron atom is shown connected to three hydrogen atoms, which are arranged around it like a pyramid. The angle from one line connecting the boron atom to a hydrogen atom to another line connecting the boron atom to a hydrogen atom is labeled, “120 degrees.”

We can illustrate the comparison of orbitals and electron distribution in an isolated boron atom and in the bonded atom in BH_3 as shown in the orbital energy level diagram in Figure **7.3.8**. We redistribute the three valence electrons of the boron atom in the three sp^2 hybrid orbitals, and each boron electron pairs with a hydrogen electron when B–H bonds form.

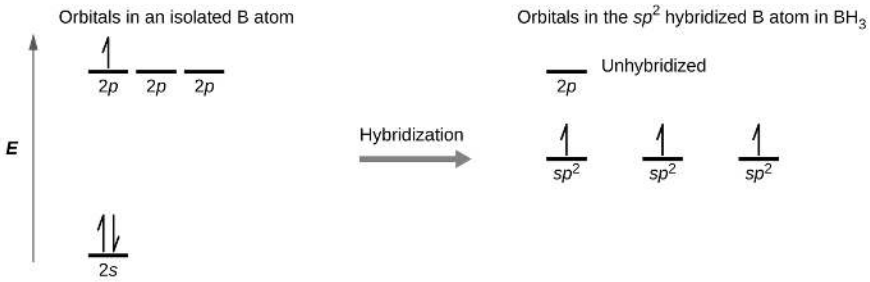


Figure **7.3.8**: In an isolated B atom, there are one 2s and three 2p valence orbitals. When boron is in a molecule with three regions of electron density, three of the orbitals hybridize and create a set of three sp^2 orbitals and one unhybridized 2p orbital. The three half-filled hybrid orbitals each overlap with an orbital from a hydrogen atom to form three σ bonds in BH_3.

A diagram is shown in two parts, connected by a right facing arrow labeled, “Hybridization.” The left diagram shows an up-facing arrow labeled “E.” To the lower right of the arrow is a short, horizontal line labeled, “2 s,” that has two vertical half-arrows facing up and down on it. To the upper right of the arrow are a series of three short, horizontal lines labeled, “2 p.” Above both sets of these lines is the phrase, “Orbitals in an isolated B atom.” One of the lines has a vertical, up-facing arrow drawn on it. The right side of the diagram shows three short, horizontal lines placed halfway up the space and each labeled, “s p superscript 2.” An upward-facing half arrow is drawn vertically on each line. Above these lines is one other short, horizontal line, labeled, “2 p.” Above both sets of lines is the phrase, “Orbitals in the s p superscript 2 hybridized B atom in B H subscript 3.”

Any central atom surrounded by three regions of electron density will exhibit sp^2 hybridization. This includes molecules with a lone pair on the central atom, such as ClNO (Figure **7.3.9**), or molecules with two single bonds and a double bond connected to the central atom, as in formaldehyde, CH_2O, and ethene, H_2CCH_2.

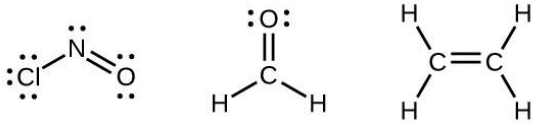


Figure **7.3.9**: The central atom(s) in each of the structures shown contain three regions of electron density and are sp^2 hybridized. As we know from the discussion of VSEPR theory, a region of electron density contains all of the electrons that point in one direction. A lone pair, an unpaired electron, a single bond, or a multiple bond would each count as one region of electron density.

Three Lewis structures are shown. The left-hand structure shows a chlorine atom surrounded by three lone pairs of electrons single bonded to a nitrogen atom with one lone pair of electrons and double bonded to an oxygen atom with two lone pairs of electrons. The middle structure shows a carbon atom single bonded to two hydrogen atoms and double bonded to an oxygen atom that has two lone pairs of electrons. The right-hand structure shows two carbon atoms, double bonded to one another and each single bonded to two hydrogen atoms.

sp^3 Hybridization

The valence orbitals of an atom surrounded by a tetrahedral arrangement of bonding pairs and lone pairs consist of a set of four sp^3 hybrid orbitals. The hybrids result from the mixing of one *s* orbital and all three *p* orbitals that produces four identical sp^3 hybrid orbitals (Figure **7.3.10**). Each of these hybrid orbitals points toward a different corner of a tetrahedron.

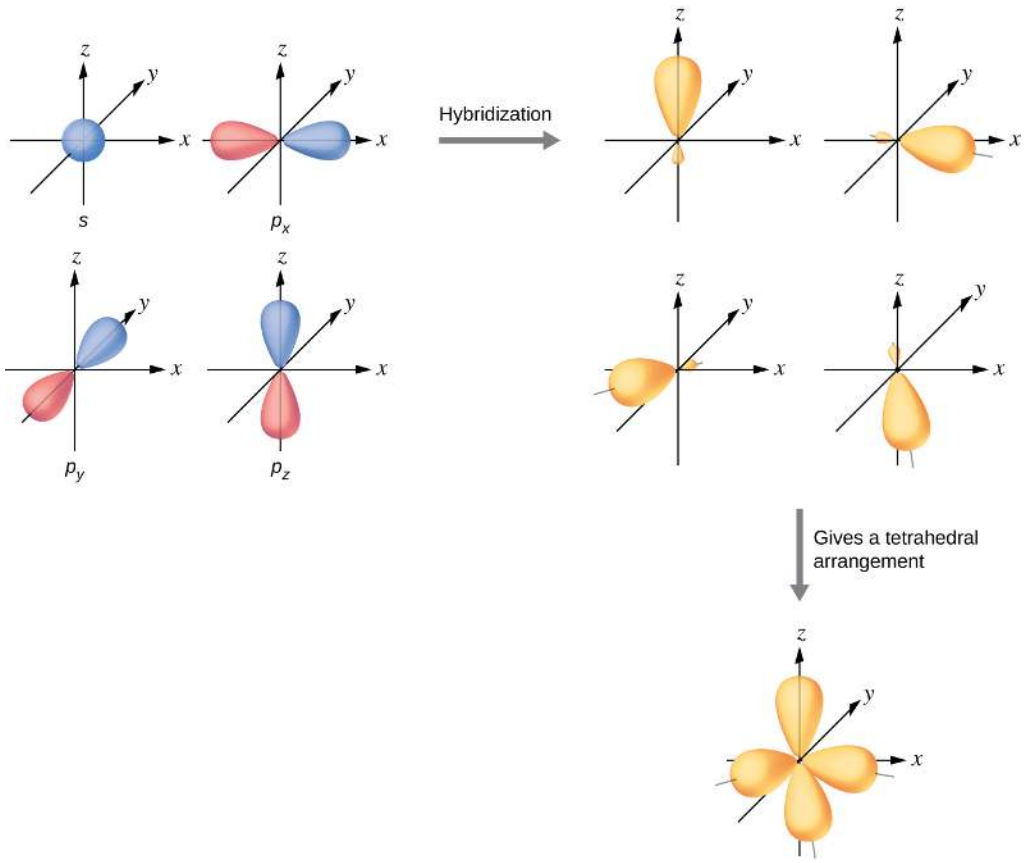


Figure **7.3.10**: The hybridization of an s orbital (blue) and three p orbitals (red) produces four equivalent sp^3 hybridized orbitals (yellow) oriented at 109.5° with respect to each other.

A series of three diagrams connected by a right-facing arrow that is labeled, “Hybridization,” and a downward-facing arrow labeled, “Gives a tetrahedral arrangement,” are shown. The first diagram shows a blue spherical orbital and three red, peanut-shaped orbitals, each placed on an x, y, z axis system. The three red orbitals are located on the x , y and z axes, respectively. The second diagram shows the same four orbitals, but they are now purple and have one enlarged lobe and one smaller lobe. Each lies in a different axis in the drawing. The third diagram shows the same four orbitals, but their smaller lobes now overlap to form a tetrahedral structure.

A molecule of methane, CH_4, consists of a carbon atom surrounded by four hydrogen atoms at the corners of a tetrahedron. The carbon atom in methane exhibits sp^3 hybridization. We illustrate the orbitals and electron distribution in an isolated carbon atom and in the bonded atom in CH_4 in Figure **7.3.11**. The four valence electrons of the carbon atom are distributed equally in the hybrid orbitals, and each carbon electron pairs with a hydrogen electron when the C–H bonds form.

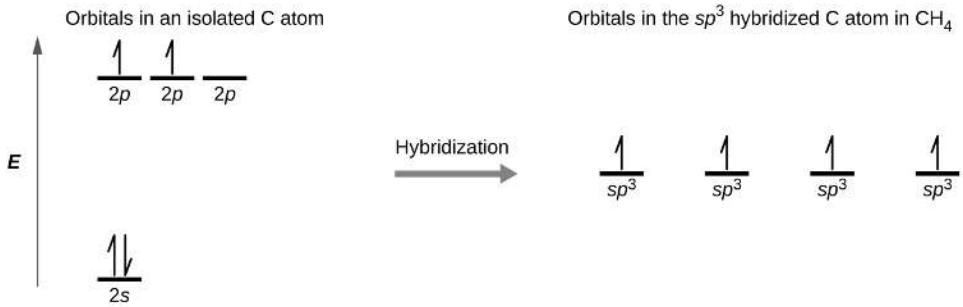


Figure **7.3.11**: The four valence atomic orbitals from an isolated carbon atom all hybridize when the carbon bonds in a molecule like CH_4 with four regions of electron density. This creates four equivalent sp^3 hybridized orbitals. Overlap of each of the hybrid orbitals with a hydrogen orbital creates a C–H σ bond.

A diagram is shown in two parts, connected by a right facing arrow labeled, “Hybridization.” The left diagram shows an up-facing arrow labeled “E.” To the lower right of the arrow is a short, horizontal line labeled, “2 s,” that has two vertical half-arrows facing up and down on it. To the upper right of the arrow are a series of three short, horizontal lines labeled, “2 p.” Two of the lines have a vertical, up-facing arrow drawn on them. Above both sets of lines is the phrase, “Orbitals in an isolated C atom.” The right side of the diagram shows four short, horizontal lines placed halfway up the space and each labeled, “s p superscript 3.” An upward-facing half arrow is drawn vertically on each line. Above these lines is the phrase, “Orbitals in the s p superscript 3 hybridized C atom in C H subscript 4.”

In a methane molecule, the 1*s* orbital of each of the four hydrogen atoms overlaps with one of the four sp^3 orbitals of the carbon atom to form a sigma (σ) bond. This results in the formation of four strong, equivalent covalent bonds between the carbon atom and each of the hydrogen atoms to produce the methane molecule, CH_4.

The structure of ethane, C_2H_6, is similar to that of methane in that each carbon in ethane has four neighboring atoms arranged at the corners of a tetrahedron—three hydrogen atoms and one carbon atom (Figure **7.3.10**). However, in ethane an sp^3 orbital of one carbon atom overlaps end to end with an sp^3 orbital of a second carbon atom to form a σ bond between the two carbon atoms. Each of the remaining sp^3 hybrid orbitals overlaps with an *s* orbital of a hydrogen atom to form carbon–hydrogen σ bonds. The structure and overall outline of the bonding orbitals of ethane are shown in Figure **7.3.12**. The orientation of the two CH_3 groups is not fixed relative to each other. Experimental evidence shows that rotation around σ bonds occurs easily.

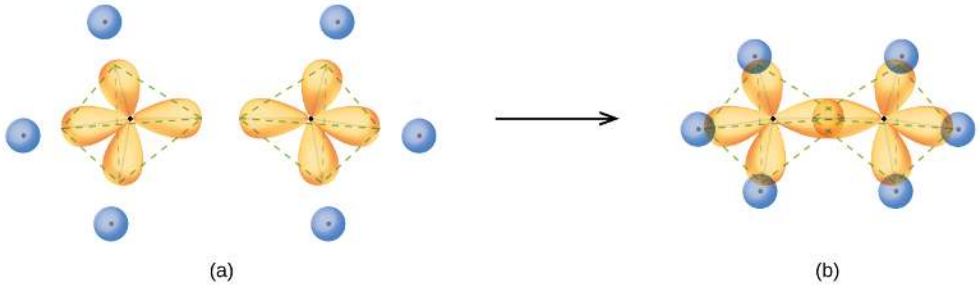


Figure **7.3.12**: (a) In the ethane molecule, C_2H_6, each carbon has four sp^3 orbitals. (b) These four orbitals overlap to form seven σ bonds.

Two diagrams are shown and labeled “a” and “b.” Diagram a shows two carbon atoms, each surrounded by their four s p subscript three hybridized orbitals in a three dimensional arrangement. Each of the orbitals is shown overlapping with a spherical hydrogen atom. Diagram b shows the same general arrangement, but the hydrogen atoms are just represented by an, “H” and their spherical orbitals are not shown.

An sp^3 hybrid orbital can also hold a lone pair of electrons. For example, the nitrogen atom in ammonia is surrounded by three bonding pairs and a lone pair of electrons directed to the four corners of a tetrahedron. The nitrogen atom is sp^3 hybridized with one hybrid orbital occupied by the lone pair.

The molecular structure of water is consistent with a tetrahedral arrangement of two lone pairs and two bonding pairs of electrons. Thus we say that the oxygen atom is sp^3 hybridized, with two of the hybrid orbitals occupied by lone pairs and two by bonding pairs. Since lone pairs occupy more space than bonding pairs, structures that contain lone pairs have bond angles slightly distorted from the ideal. Perfect tetrahedra have angles of 109.5°, but the observed angles in ammonia (107.3°) and water (104.5°) are slightly smaller. Other examples of sp^3 hybridization include CCl_4, PCl_3, and NCl_3.

sp^3d and sp^3d^2 Hybridization

To describe the five bonding orbitals in a trigonal bipyramidal arrangement, we must use five of the valence shell atomic orbitals (the *s* orbital, the three *p* orbitals, and one of the *d* orbitals), which gives five sp^3d hybrid orbitals. With an octahedral arrangement of six hybrid orbitals, we must use six valence shell atomic orbitals (the *s* orbital, the three *p* orbitals, and two of the *d* orbitals in its valence shell), which gives six sp^3d^2 hybrid orbitals. These hybridizations are only possible for atoms that have *d* orbitals in their valence subshells (that is, not those in the first or second period).

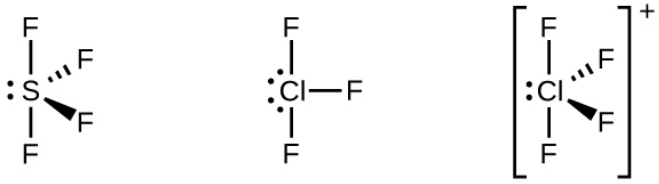


Figure **7.3.13**: The three compounds pictured exhibit sp^3d hybridization in the central atom and a trigonal bipyramid form. SF_4 and $\mathbf{ClF_4^+}$ *have one lone pair of electrons on the central atom, and* ClF_3 *has two lone pairs giving it the T-shape shown.*

Three Lewis structures are shown along with designations of molecular shape. The left image shows a sulfur atom singly bonded to four fluorine atoms. The sulfur atom has one lone pair of electrons while each fluorine has three. Two fluorine atoms are drawn vertically up and down from the sulfur while the other two are shown going into and out of the page. The second structure shows one chlorine atom singly bonded to three fluorine atoms. The chlorine has two lone pairs of electrons while each fluorine has three. Two fluorine atoms are drawn vertically up and down from the sulfur while the other is shown horizontally. The right structure shows a chlorine atom singly bonded to four fluorine atoms. The chlorine atom has one lone pair of electrons and a superscript plus sign, while each fluorine has three lone pairs of electrons. Two fluorine atoms are drawn vertically up and down from the sulfur while the other two are shown going into and out of the page.

In a molecule of phosphorus pentachloride, PCl_5, there are five P–Cl bonds (thus five pairs of valence electrons around the phosphorus atom) directed toward the corners of a trigonal bipyramid. We use the 3*s* orbital, the three 3*p* orbitals, and one of the 3*d* orbitals to form the set of five sp^3d hybrid orbitals (Figure **7.3.13**) that are involved in the P–Cl bonds. Other atoms that exhibit sp^3d hybridization include the sulfur atom in SF_4 and the chlorine atoms in ClF_3 and in $\mathbf{ClF_4^+}$. (The electrons on fluorine atoms are omitted for clarity.)

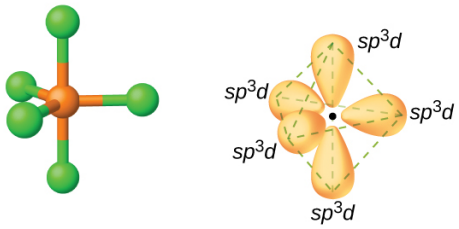


Figure **7.3.14**: (a) The five regions of electron density around phosphorus in PCl_5 require five hybrid sp^3d orbitals. (b) These orbitals combine to form a trigonal bipyramidal structure with each large lobe of the hybrid orbital pointing at a vertex. As before, there are also small lobes pointing in the opposite direction for each orbital (not shown for clarity).

Two images are shown and labeled “a” and “b.” Image a depicts a ball-and-stick model in a trigonal bipyramidal arrangement. Image b depicts the hybrid orbitals in the same arrangement and each is labeled, “s p superscript three d.”

The sulfur atom in sulfur hexafluoride, SF_6, exhibits sp^3d^2 hybridization. A molecule of sulfur hexafluoride has six bonding pairs of electrons connecting six fluorine atoms to a single sulfur atom. There are no lone pairs of electrons on the central atom. To bond six fluorine atoms, the 3*s* orbital, the three 3*p* orbitals, and two of the 3*d* orbitals form six equivalent sp^3d^2 hybrid orbitals, each directed toward a different corner of an octahedron. Other atoms that exhibit sp^3d^2 hybridization include the phosphorus atom in $\mathbf{PCl_6^-}$, the iodine atom in the interhalogens $\mathbf{IF_6^+}$, IF_5, $\mathbf{ICl_4^-}$, $\mathbf{IF_4^-}$ and the xenon atom in XeF_4.

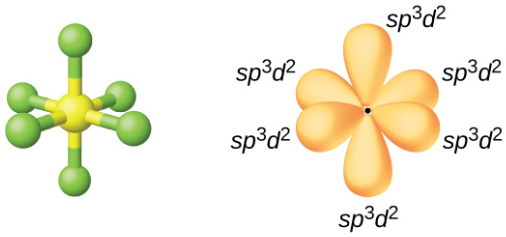


Figure **7.3.15**: (a) Sulfur hexafluoride, SF_6, has an octahedral structure that requires sp^3d^2 hybridization. (b) The six sp^3d^2 orbitals form an octahedral structure around sulfur. Again, the minor lobe of each orbital is not shown for clarity.

Two images are shown and labeled “a” and “b.” Image a depicts a ball-and-stick model in an octahedral arrangement. Image b depicts the hybrid orbitals in the same arrangement and each is labeled, “s p superscript three d superscript two.”

Assignment of Hybrid Orbitals to Central Atoms

The hybridization of an atom is determined based on the number of regions of electron density that surround it. The geometrical arrangements characteristic of the various sets of hybrid orbitals are shown in Figure **7.3.16**. These arrangements are identical to those of the electron-pair geometries predicted by VSEPR theory. VSEPR theory predicts the shapes of molecules, and hybrid orbital theory provides an explanation for how those shapes are formed. To find the hybridization of a central atom, we can use the following guidelines:

1. Determine the Lewis structure of the molecule.
2. Determine the number of regions of electron density around an atom using VSEPR theory, in which single bonds, multiple bonds, radicals, and lone pairs each count as one region.
3. Assign the set of hybridized orbitals from Figure **7.3.16** that corresponds to this geometry.

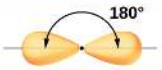
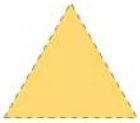
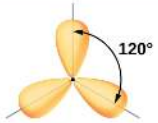
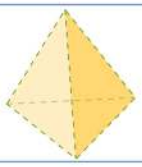
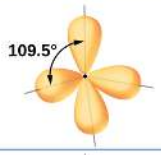
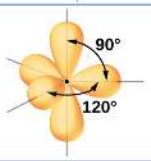
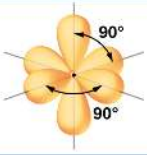
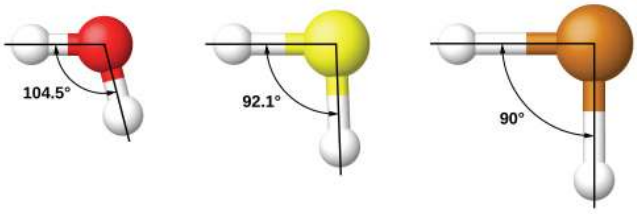
Regions of Electron Density	Arrangement		Hybridization	
2		linear	sp	
3		trigonal planar	sp^2	
4		tetrahedral	sp^3	
5		trigonal bipyramidal	sp^3d	
6		octahedral	sp^3d^2	

Figure **7.3.16**: The shapes of hybridized orbital sets are consistent with the electron-pair geometries. For example, an atom surrounded by three regions of electron density is sp^2 hybridized, and the three sp^2 orbitals are arranged in a trigonal planar fashion.

A table is shown that is composed of five columns and six rows. The header row contains the phrases, “Regions of electron density,” “Arrangement,” (which has two columns below it), and “Hybridization,” (which has two columns below it). The first column contains the numbers “2,” “3,” “4,” “5,” and “6.” The second column contains images of a line, a triangle, a three sided pyramid, a trigonal bipyramid, and an eight-faced ocatahedron. The third column contains the terms, “Linear,” “Trigonal planar,” “Tetrahedral,” “Trigonal bipyramidal,” and “Octahedral.” The fourth column contains the terms “s p,” “s p superscript 2,” “s p superscript 3,” “s p superscript 3 d,” and “s p superscript 3 d superscript 2.” The last column contains drawings of the molecules beginning with a peanut-shaped structure marked with an angle of “180 degrees.” The second structure is made up of three equal-sized, rounded structures connected at one point with an angle of “120 degrees,” while the third structure is a three-dimensional arrangement of four equal-sized, rounded structures labeled as “109.5 degrees.” The fourth structure is made up of five equal-sized, rounded structures connected at “120 and 90 degrees,” while the fifth structure has six equal-sized, rounded structures connected at “90 degrees.”

> *It is important to remember that hybridization was devised to rationalize experimentally observed molecular geometries, not the other way around.*

The model works well for molecules containing small central atoms, in which the valence electron pairs are close together in space. However, for larger central atoms, the valence-shell electron pairs are farther from the nucleus, and there are fewer repulsions. Their compounds exhibit structures that are often not consistent with VSEPR theory, and hybridized orbitals are not necessary to explain the observed data.



Three Lewis structures are shown. The left structure shows an oxygen atom with two lone pairs of electrons single bonded to two hydrogen atoms. The middle structure is made up of a sulfur atom with two lone pairs of electrons single bonded to two hydrogen atoms. The right structure is made up of a tellurium atom with two lone pairs of electrons single bonded to two hydrogen atoms. From left to right, the bond angles of each molecule decrease.

For example, we have discussed the H–O–H bond angle in H_2O, 104.5°, which is more consistent with sp^3 hybrid orbitals (109.5°) on the central atom than with 2*p* orbitals (90°). Sulfur is in the same group as oxygen, and H_2S has a similar Lewis structure. However, it has a much smaller bond angle (92.1°), which indicates much less hybridization on sulfur than oxygen. Continuing down the group, tellurium is even larger than sulfur, and for H_2Te, the observed bond angle (90°) is consistent with overlap of the 5*p* orbitals, without invoking hybridization. We invoke hybridization where it is necessary to explain the observed structures.

Example 7.3.1: Assigning Hybridization

Ammonium sulfate is important as a fertilizer. What is the hybridization of the sulfur atom in the sulfate ion, SO_4^{2-}?

Solution

The Lewis structure of sulfate shows there are four regions of electron density.

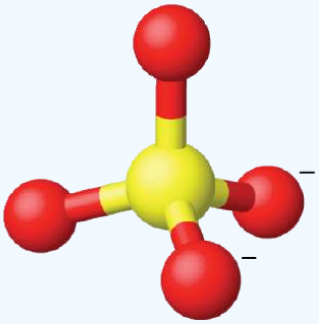


Figure 7.3.16).

A structure is shown in which a sulfur atom is bonded to four oxygen atoms in a tetrahedral arrangement. Two of the oxygen atoms have a negative charge.

Exercise 7.3.1

What is the hybridization of the selenium atom in SeF_4?



A Lewis structure is shown in which four fluorine atoms are each attached to one sulfur atom. Two of the attached fluorine atoms are vertically attached up and down, while two are attached into and out of the page to the right. The sulfur also has one lone pair of electrons attached to the left of the structure.

Answer

The selenium atom is sp^3d hybridized.

Example 7.3.2: Assigning Hybridization

Urea, $NH_2C(O)NH_2$, is sometimes used as a source of nitrogen in fertilizers. What is the hybridization of each nitrogen and carbon atom in urea?

Solution

The Lewis structure of urea is

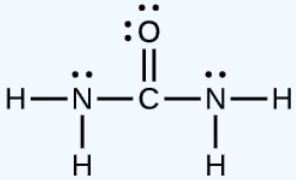


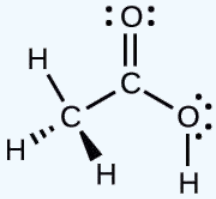
Figure 7.3.16). This is the hybridization of the nitrogen atoms in urea.

A Lewis structure is shown in which a carbon atom is double bonded to an oxygen atom that has two lone pairs of electrons. The carbon atom forms single bonds to two nitrogen atoms. Each nitrogen is single bonded to two hydrogen atoms, and each nitrogen atoms has one lone pair of electrons.

The carbon atom is surrounded by three regions of electron density, positioned in a trigonal planar arrangement. The hybridization in a trigonal planar electron pair geometry is sp^2 (Figure 7.3.16), which is the hybridization of the carbon atom in urea.

Exercise 7.3.1

Acetic acid, $H_3CC(O)OH$, is the molecule that gives vinegar its odor and sour taste. What is the hybridization of the two carbon atoms in acetic acid?



A Lewis structure is shown in which a carbon atom is double bonded to an oxygen atom that has two lone pairs of electrons and single bonded to another oxygen atom that is single boned to a hydrogen atom. This second oxygen atom has two lone pairs of electrons. The carbon is also single bonded to a carbon atom that is single bonded to three hydrogen atoms.

Answer

$H_3\underline{C}$, sp^3; $\underline{C}(O)OH$, sp^2

Summary

We can use hybrid orbitals, which are mathematical combinations of some or all of the valence atomic orbitals, to describe the electron density around covalently bonded atoms. These hybrid orbitals either form sigma (σ) bonds directed toward other atoms of the molecule or contain lone pairs of electrons. We can determine the type of hybridization around a central atom from the geometry of the regions of electron density about it. Two such regions imply *sp* hybridization; three, sp^2 hybridization; four, sp^3 hybridization; five, sp^3d hybridization; and six, sp^3d^2 hybridization. Pi (π) bonds are formed from unhybridized atomic orbitals (*p* or *d* orbitals).

Footnotes

1. Note that orbitals may sometimes be drawn in an elongated “balloon” shape rather than in a more realistic “plump” shape in order to make the geometry easier to visualize.

Glossary

hybrid orbital
orbital created by combining atomic orbitals on a central atom

hybridization
model that describes the changes in the atomic orbitals of an atom when it forms a covalent compound

***sp* hybrid orbital**
one of a set of two orbitals with a linear arrangement that results from combining one *s* and one *p* orbital

***sp*^{2} hybrid orbital**
one of a set of three orbitals with a trigonal planar arrangement that results from combining one *s* and two *p* orbitals

***sp*^{3} hybrid orbital**
one of a set of four orbitals with a tetrahedral arrangement that results from combining one *s* and three *p* orbitals

***sp*^{3}*d* hybrid orbital**
one of a set of five orbitals with a trigonal bipyramidal arrangement that results from combining one *s*, three *p*, and one *d* orbital

***sp*^{3}*d*^{2} hybrid orbital**
one of a set of six orbitals with an octahedral arrangement that results from combining one *s*, three *p*, and two *d* orbitals

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7.4: Multiple Bonds

Learning Objectives

- Describe multiple covalent bonding in terms of atomic orbital overlap
- Relate the concept of resonance to π-bonding and electron delocalization

The hybrid orbital model appears to account well for the geometry of molecules involving single covalent bonds. Is it also capable of describing molecules containing double and triple bonds? We have already discussed that multiple bonds consist of σ and π bonds. Next we can consider how we visualize these components and how they relate to hybrid orbitals. The Lewis structure of ethene, C_2H_4, shows us that each carbon atom is surrounded by one other carbon atom and two hydrogen atoms.

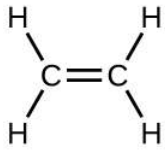


Figure **7.4.2**).

A Lewis structure is shown in which two carbon atoms are bonded together by a double bond. Each carbon atom is bonded to two hydrogen atoms by a single bond.

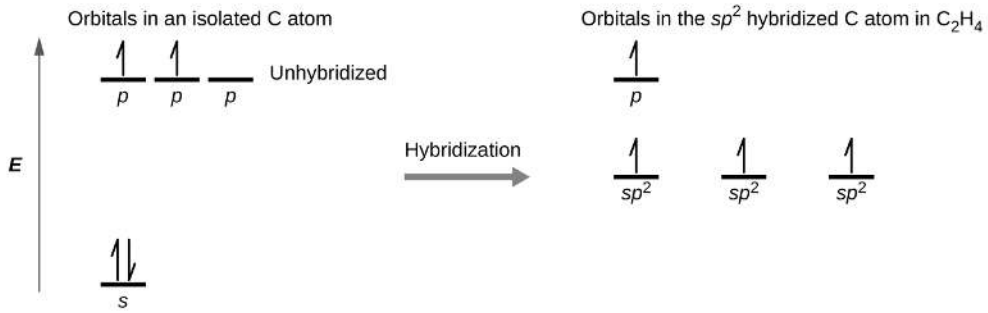


Figure **7.4.1**: In ethene, each carbon atom is sp^2 hybridized, and the sp^2 orbitals and the *p* orbital are singly occupied. The hybrid orbitals overlap to form σ bonds, while the *p* orbitals on each carbon atom overlap to form a π bond.

A diagram is shown in two parts, connected by a right facing arrow labeled, “Hybridization.” The left diagram shows an up-facing arrow labeled, “E.” To the lower right of the arrow is a short, horizontal line labeled, “2 s,” that has two vertical half-arrows facing up and down on it. To the upper right of the arrow are a series of three short, horizontal lines labeled, “2 p.” Above both sets of lines is the phrase, “Orbitals in an isolated C atom.” Two of the lines have vertical, up-facing arrows drawn on them. The right side of the diagram shows three short, horizontal lines placed halfway up the space and each labeled, “s p superscript 2.” An upward-facing half arrow is drawn vertically on each line. Above these lines is one other short, horizontal line, labeled, “p.” Above both sets of lines is the phrase, “Orbitals in the s p superscript 2 hybridized C atom in C subscript 2 H subscript 4.”

The π bond in the C=C double bond results from the overlap of the third (remaining) 2*p* orbital on each carbon atom that is not involved in hybridization. This unhybridized *p* orbital (lobes shown in red and blue in Figure **7.4.2**) is perpendicular to the plane of the sp^2 hybrid orbitals. Thus the unhybridized 2*p* orbitals overlap in a side-by-side fashion, above and below the internuclear axis and form a π bond.

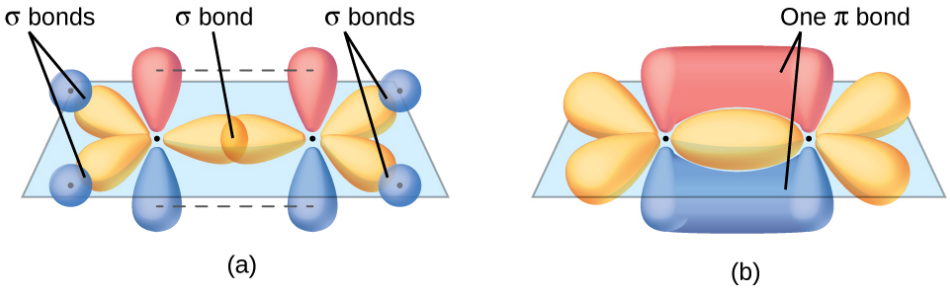
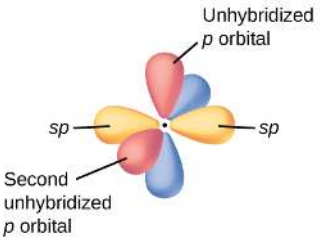


Figure **7.4.2**: In the ethene molecule, C_2H_4, there are (a) five σ bonds. One C–C σ bond results from overlap of sp^2 hybrid orbitals on the carbon atom with one sp^2 hybrid orbital on the other carbon atom. Four C–H bonds result from the overlap between the C atoms' sp^2 orbitals with s orbitals on the hydrogen atoms. (b) The π bond is formed by the side-by-side overlap of the two unhybridized p orbitals in the two carbon atoms. The two lobes of the π bond are above and below the plane of the σ system.

Two diagrams are shown labeled, “a” and “b.” Diagram a shows two carbon atoms with three purple balloon-like orbitals arranged in a plane around them and two red balloon-like orbitals arranged vertically and perpendicularly to the plane. There is an overlap of two of the purple orbitals in between the two carbon atoms, and the other four purple orbitals that face the outside of the molecule are shown interacting with spherical blue orbitals from four hydrogen atoms. Diagram b depicts a similar image to diagram a, but the red, vertical orbitals are interacting above and below the plane of the molecule to form two areas labeled, “One pi bond.”

In an ethene molecule, the four hydrogen atoms and the two carbon atoms are all in the same plane. If the two planes of sp^2 hybrid orbitals tilted relative to each other, the *p* orbitals would not be oriented to overlap efficiently to create the π bond. The planar configuration for the ethene molecule occurs because it is the most stable bonding arrangement. This is a significant difference between σ and π bonds; rotation around single (σ) bonds occurs easily because the end-to-end orbital overlap does not depend on the relative orientation of the orbitals on each atom in the bond. In other words, rotation around the internuclear axis does not change the extent to which the σ bonding orbitals overlap because the bonding electron density is symmetric about the axis. Rotation about the internuclear axis is much more difficult for multiple bonds; however, this would drastically alter the off-axis overlap of the π bonding orbitals, essentially breaking the π bond.



A diagram of a carbon atom with two balloon-like purple orbitals labeled, “sp” arranged in a linear fashion around it is shown. Four red balloon-like orbitals are aligned in pairs in the y and z axes around the carbon and are labeled, “unhybridized p orbital,” and, “Second unhybridized p orbital.”

Figure **7.4.3**: Diagram of the two linear sp hybrid orbitals of a carbon atom, which lie in a straight line, and the two unhybridized p orbitals at perpendicular angles.

In molecules with sp hybrid orbitals, two unhybridized p orbitals remain on the atom (Figure **7.4.3**). We find this situation in acetylene, H−C≡C−H, which is a linear molecule. The sp hybrid orbitals of the two carbon atoms overlap end to end to form a σ bond between the carbon atoms (Figure **7.4.4**). The remaining *sp* orbitals form σ bonds with hydrogen atoms. The two unhybridized *p* orbitals per carbon are positioned such that they overlap side by side and, hence, form two π bonds. The two carbon atoms of acetylene are thus bound together by one σ bond and two π bonds, giving a triple bond.

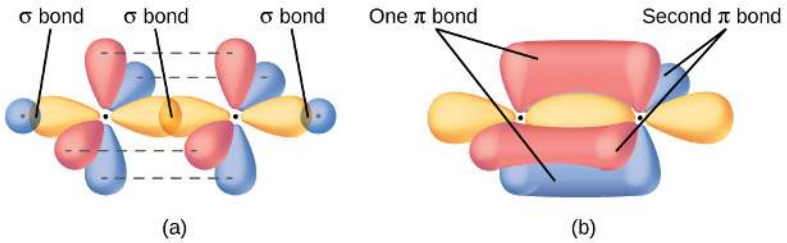
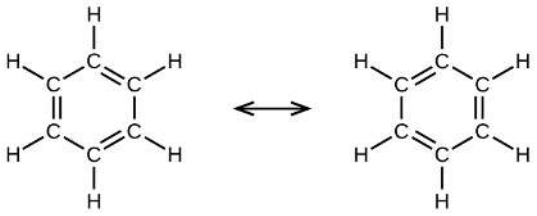


Figure **7.4.4**: (a) In the acetylene molecule, C_2H_2, there are two C–H σ bonds and a C≡C triple bond involving one C–C σ bond and two C–C π bonds. The dashed lines, each connecting two lobes, indicate the side-by-side overlap of the four unhybridized p orbitals. (b) This shows the overall outline of the bonds in C_2H_2. The two lobes of each of the π bonds are positioned across from each other around the line of the C–C σ bond.

Two diagrams are shown and labeled, “a” and “b.” Diagram a shows two carbon atoms with two purple balloon-like orbitals arranged in a plane around each of them, and four red balloon-like orbitals arranged along the y and z axes perpendicular to the plane of the molecule. There is an overlap of two of the purple orbitals in between the two carbon atoms. The other two purple orbitals that face the outside of the molecule are shown interacting with spherical blue orbitals from two hydrogen atoms. Diagram b depicts a similar image to diagram a, but the red, vertical orbitals are interacting above and below and to the front and back of the plane of the molecule to form two areas labeled, “One pi bond,” and, “Second pi bond,” each respectively.

Hybridization involves only σ bonds, lone pairs of electrons, and single unpaired electrons (radicals). Structures that account for these features describe the correct hybridization of the atoms. However, many structures also include resonance forms. Remember that resonance forms occur when various arrangements of π bonds are possible. Since the arrangement of π bonds involves only the unhybridized orbitals, resonance does not influence the assignment of hybridization.

For example, molecule benzene has two resonance forms (Figure **7.4.5**). We can use either of these forms to determine that each of the carbon atoms is bonded to three other atoms with no lone pairs, so the correct hybridization is sp^2. The electrons in the unhybridized *p* orbitals form π bonds. Neither resonance structure completely describes the electrons in the π bonds. They are not located in one position or the other, but in reality are delocalized throughout the ring. Valence bond theory does not easily address delocalization. Bonding in molecules with resonance forms is better described by molecular orbital theory.



A diagram is shown that is made up of two Lewis structures connected by a double ended arrow. The left image shows six carbon atoms bonded together with alternating double and single bonds to form a six-sided ring. Each carbon is also bonded to a hydrogen atom by a single bond. The right image shows the same structure, but the double and single bonds in between the carbon atoms have changed positions.

Figure **7.4.5**: Each carbon atom in benzene, C_6H_6, is sp^2 hybridized, independently of which resonance form is considered. The electrons in the π bonds are not located in one set of p orbitals or the other, but rather delocalized throughout the molecule.

✔ Example 7.4.1: Assignment of Hybridization Involving Resonance

Some acid rain results from the reaction of sulfur dioxide with atmospheric water vapor, followed by the formation of sulfuric acid. Sulfur dioxide, SO_2, is a major component of volcanic gases as well as a product of the combustion of sulfur-containing coal. What is the hybridization of the S atom in SO_2?

Solution

The resonance structures of SO_2 are



Two Lewis structures connected by a double-ended arrow are shown. The left structure shows a sulfur atom with one lone pair of electrons and a positive sign which is single bonded on one side to an oxygen atom with three lone pairs of electrons and a negative sign. The sulfur atom is double bonded on the other side to another oxygen atom with two lone pairs of electrons. The right-hand structure is the same as the left except that the position of the double bonded oxygen atom is switched. In both structures the attached oxygen atoms form an acute angle in terms of the sulfur atom.

The sulfur atom is surrounded by two bonds and one lone pair of electrons in either resonance structure. Therefore, the electron-pair geometry is trigonal planar, and the hybridization of the sulfur atom is sp^2.

? Exercise 7.4.1

Another acid in acid rain is nitric acid, HNO_3, which is produced by the reaction of nitrogen dioxide, NO_2, with atmospheric water vapor. What is the hybridization of the nitrogen atom in NO_2? (Note: the lone electron on nitrogen occupies a hybridized orbital just as a lone pair would.)

Answer

sp^2

Summary

Multiple bonds consist of a σ bond located along the axis between two atoms and one or two π bonds. The σ bonds are usually formed by the overlap of hybridized atomic orbitals, while the π bonds are formed by the side-by-side overlap of unhybridized orbitals. Resonance occurs when there are multiple unhybridized orbitals with the appropriate alignment to overlap, so the placement of π bonds can vary.

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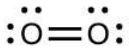
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7.5: Molecular Orbital Theory

Learning Objectives

- Outline the basic quantum-mechanical approach to deriving molecular orbitals from atomic orbitals
- Describe traits of bonding and antibonding molecular orbitals
- Calculate bond orders based on molecular electron configurations
- Write molecular electron configurations for first- and second-row diatomic molecules
- Relate these electron configurations to the molecules' stabilities and magnetic properties

For almost every covalent molecule that exists, we can now draw the Lewis structure, predict the electron-pair geometry, predict the molecular geometry, and come close to predicting bond angles. However, one of the most important molecules we know, the oxygen molecule O_2, presents a problem with respect to its Lewis structure. We would write the following Lewis structure for O_2:



A Lewis structure is shown. It is made up of two oxygen atoms, each with two lone pairs of electrons, bonded together with a double bond.

This electronic structure adheres to all the rules governing Lewis theory. There is an O=O double bond, and each oxygen atom has eight electrons around it. However, this picture is at odds with the magnetic behavior of oxygen. By itself, O_2 is not magnetic, but it is attracted to magnetic fields. Thus, when we pour liquid oxygen past a strong magnet, it collects between the poles of the magnet and defies gravity. Such attraction to a magnetic field is called paramagnetism, and it arises in molecules that have unpaired electrons. And yet, the Lewis structure of O_2 indicates that all electrons are paired. How do we account for this discrepancy?

Magnetic susceptibility measures the force experienced by a substance in a magnetic field. When we compare the weight of a sample to the weight measured in a magnetic field (Figure **7.5.1**), paramagnetic samples that are attracted to the magnet will appear heavier because of the force exerted by the magnetic field. We can calculate the number of unpaired electrons based on the increase in weight.

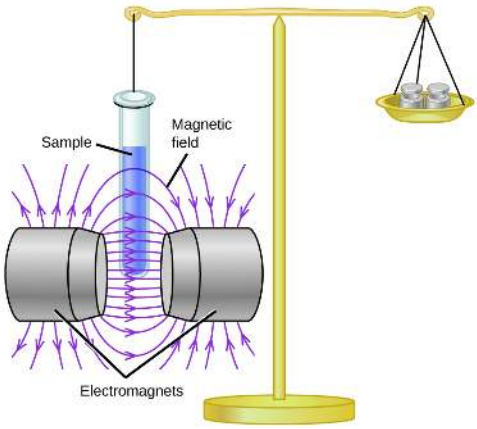


Figure **7.5.1**: A Gouy balance compares the mass of a sample in the presence of a magnetic field with the mass with the electromagnet turned off to determine the number of unpaired electrons in a sample.

Experiments show that each O_2 molecule has two unpaired electrons. The Lewis-structure model does not predict the presence of these two unpaired electrons. Unlike oxygen, the apparent weight of most molecules decreases slightly in the presence of an inhomogeneous magnetic field. Materials in which all of the electrons are paired are diamagnetic and weakly repel a magnetic field. Paramagnetic and diamagnetic materials do not act as permanent magnets. Only in the presence of an applied magnetic field do they demonstrate attraction or repulsion.



Video 7.5.1: Water, like most molecules, contains all paired electrons. Living things contain a large percentage of water, so they demonstrate diamagnetic behavior. If you place a frog near a sufficiently large magnet, it will levitate. You can see videos of diamagnetic floating frogs, strawberries, and more (levitating frog [www.youtube.com])

Molecular orbital theory (MO theory) provides an explanation of chemical bonding that accounts for the paramagnetism of the oxygen molecule. It also explains the bonding in a number of other molecules, such as violations of the octet rule and more molecules with more complicated bonding (beyond the scope of this text) that are difficult to describe with Lewis structures. Additionally, it provides a model for describing the energies of electrons in a molecule and the probable location of these electrons. Unlike valence bond theory, which uses hybrid orbitals that are assigned to one specific atom, MO theory uses the combination of atomic orbitals to yield molecular orbitals that are delocalized over the entire molecule rather than being localized on its constituent atoms. MO theory also helps us understand why some substances are electrical conductors, others are semiconductors, and still others are insulators. Table 7.5.1 summarizes the main points of the two complementary bonding theories. Both theories provide different, useful ways of describing molecular structure.

Table \(\PageIndex{1}\): Comparison of Bonding Theories

Valence Bond Theory	Molecular Orbital Theory
considers bonds as localized between one pair of atoms	considers electrons delocalized throughout the entire molecule
creates bonds from overlap of atomic orbitals (*s*, *p*, *d*…) and hybrid orbitals (*sp*, sp^2, sp^3…)	combines atomic orbitals to form molecular orbitals (σ, σ*, π, π*)
forms σ or π bonds	creates bonding and antibonding interactions based on which orbitals are filled
predicts molecular shape based on the number of regions of electron density	predicts the arrangement of electrons in molecules
needs multiple structures to describe resonance	

Molecular orbital theory describes the distribution of electrons in molecules in much the same way that the distribution of electrons in atoms is described using atomic orbitals. Using quantum mechanics, the behavior of an electron in a molecule is still described by a wave function, Ψ, analogous to the behavior in an atom. Just like electrons around isolated atoms, electrons around atoms in molecules are limited to discrete (quantized) energies. The region of space in which a valence electron in a molecule is likely to be found is called a molecular orbital (Ψ^2). Like an atomic orbital, a molecular orbital is full when it contains two electrons with opposite spin.

We will consider the molecular orbitals in molecules composed of two identical atoms (H_2 or Cl_2, for example). Such molecules are called homonuclear diatomic molecules. In these diatomic molecules, several types of molecular orbitals occur.

The mathematical process of combining atomic orbitals to generate molecular orbitals is called the linear combination of atomic orbitals (LCAO). The wave function describes the wavelike properties of an electron. Molecular orbitals are combinations of atomic orbital wave functions. Combining waves can lead to constructive interference, in which peaks line up with peaks, or

destructive interference, in which peaks line up with troughs (Figure **7.5.2**). In orbitals, the waves are three dimensional, and they combine with in-phase waves producing regions with a higher probability of electron density and out-of-phase waves producing nodes, or regions of no electron density.



Figure **7.5.2**: (a) When in-phase waves combine, constructive interference produces a wave with greater amplitude. (b) When out-of-phase waves combine, destructive interference produces a wave with less (or no) amplitude.

A pair of diagrams are shown and labeled, “a” and “b.” Diagram a shows two identical waves with two crests and two troughs. They are drawn one above the other with a plus sign in between and an equal sign to the right. To the right of the equal sign is a much taller wave with a same number of troughs and crests. Diagram b shows two waves with two crests and two troughs, but they are mirror images of one another rotated over a horizontal axis. They are drawn one above the other with a plus sign in between and an equal sign to the right. To the right of the equal sign is a flat line.

There are two types of molecular orbitals that can form from the overlap of two atomic *s* orbitals on adjacent atoms. The two types are illustrated in Figure **7.5.3**. The in-phase combination produces a lower energy σ_s molecular orbital (read as "sigma-s") in which most of the electron density is directly between the nuclei. The out-of-phase addition (which can also be thought of as subtracting the wave functions) produces a higher energy σ_s^* molecular orbital (read as "sigma-s-star") molecular orbital in which there is a node between the nuclei. The asterisk signifies that the orbital is an antibonding orbital. Electrons in a σ_s orbital are attracted by both nuclei at the same time and are more stable (of lower energy) than they would be in the isolated atoms. Adding electrons to these orbitals creates a force that holds the two nuclei together, so we call these orbitals bonding orbitals. Electrons in the σ_s^* orbitals are located well away from the region between the two nuclei. The attractive force between the nuclei and these electrons pulls the two nuclei apart. Hence, these orbitals are called antibonding orbitals. Electrons fill the lower-energy bonding orbital before the higher-energy antibonding orbital, just as they fill lower-energy atomic orbitals before they fill higher-energy atomic orbitals.

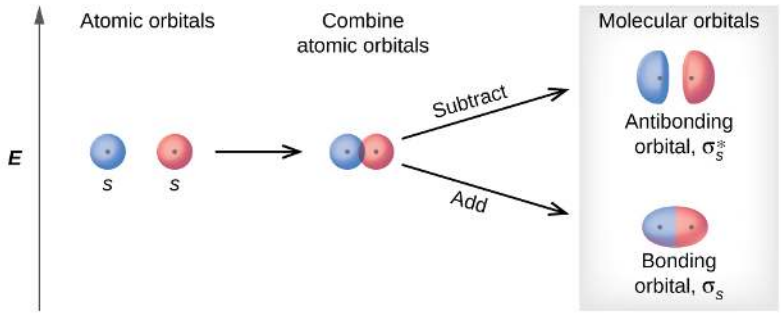
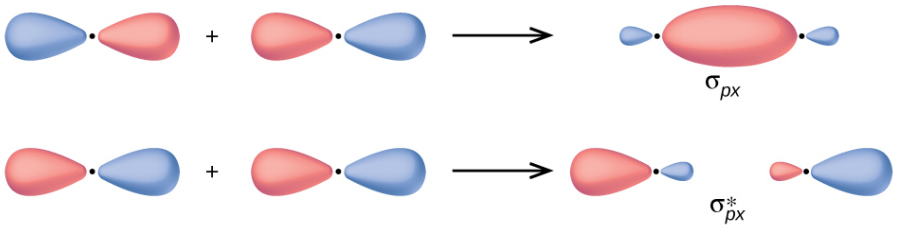


Figure **7.5.3**: Sigma (σ) and sigma-star (σ*) molecular orbitals are formed by the combination of two s atomic orbitals. The plus (+) signs indicate the locations of nuclei.

A diagram is shown that depicts a vertical upward-facing arrow that lies to the left of all the other portions of the diagram and is labeled, “E.” To the immediate right of the midpoint of the arrow are two circles each labeled with a positive sign, the letter S, and the phrase, “Atomic orbitals.” These are followed by a right-facing horizontal arrow that points to the same two circles labeled with plus signs, but they are now touching and are labeled, “Combine atomic orbitals.” Two right-facing arrows lead to the last portion of the diagram, one facing upward and one facing downward. The upper arrow is labeled, “Subtract,” and points to two oblong ovals labeled with plus signs, and the phrase, “Antibonding orbitals sigma subscript s superscript asterisk.” The lower arrow is labeled, “Add,” and points to an elongated oval with two plus signs that is labeled, “Bonding orbital sigma subscript s.” The heading over the last section of the diagram are the words, “Molecular orbitals.”

In *p* orbitals, the wave function gives rise to two lobes with opposite phases, analogous to how a two-dimensional wave has both parts above and below the average. We indicate the phases by shading the orbital lobes different colors. When orbital lobes of the same phase overlap, constructive wave interference increases the electron density. When regions of opposite phase overlap, the destructive wave interference decreases electron density and creates nodes. When *p* orbitals overlap end to end, they create σ and σ* orbitals (Figure **7.5.4**). If two atoms are located along the *x*-axis in a Cartesian coordinate system, the two p_x orbitals overlap end

to end and form σ_{px} (bonding) and σ^*_{px} (antibonding) (read as "sigma-p-x" and "sigma-p-x star," respectively). Just as with *s*-orbital overlap, the asterisk indicates the orbital with a node between the nuclei, which is a higher-energy, antibonding orbital.



Two horizontal rows of diagrams are shown. The upper diagram shows two equally-sized peanut-shaped orbitals with a plus sign in between them connected to a merged orbital diagram by a right facing arrow. The merged diagram has a much larger oval at the center and much smaller ovular orbitals on the edge. It is labeled, “sigma subscript p x.” The lower diagram shows two equally-sized peanut-shaped orbitals with a plus sign in between them connected to a split orbital diagram by a right facing arrow. The split diagram has a much larger oval at the outer ends and much smaller ovular orbitals on the inner edges. It is labeled, “sigma subscript p x superscript asterisk”.

Figure **7.5.4**: Combining wave functions of two p atomic orbitals along the internuclear axis creates two molecular orbitals, σp and σ^*_p.

The side-by-side overlap of two *p* orbitals gives rise to a pi (π) bonding molecular orbital and a \(π^*\) antibonding molecular orbital, as shown in Figure **7.5.5**. In valence bond theory, we describe π bonds as containing a nodal plane containing the internuclear axis and perpendicular to the lobes of the *p* orbitals, with electron density on either side of the node. In molecular orbital theory, we describe the π orbital by this same shape, and a π bond exists when this orbital contains electrons. Electrons in this orbital interact with both nuclei and help hold the two atoms together, making it a bonding orbital. For the out-of-phase combination, there are two nodal planes created, one along the internuclear axis and a perpendicular one between the nuclei.

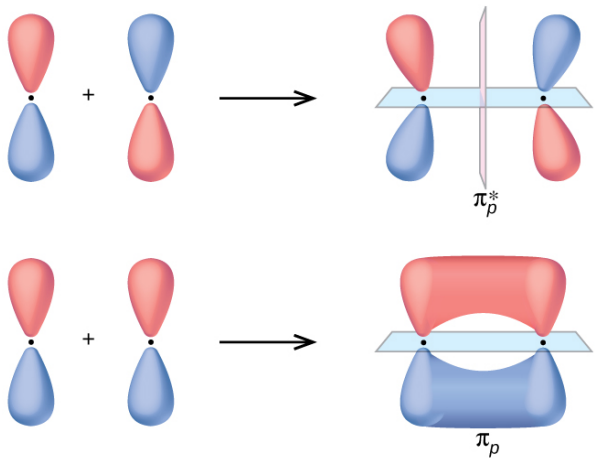


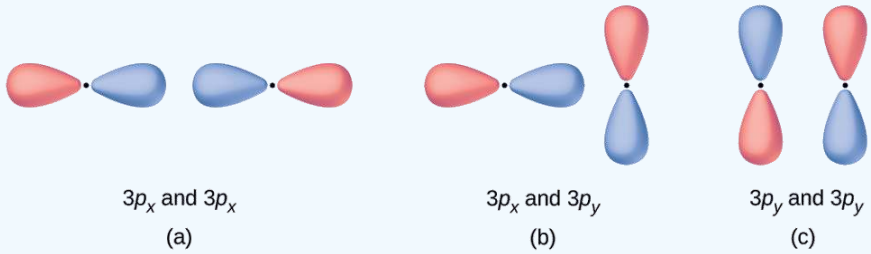
Figure **7.5.5**: Side-by-side overlap of each two p orbitals results in the formation of two π molecular orbitals. Combining the out-of-phase orbitals results in an antibonding molecular orbital with two nodes. One contains the internuclear axis, and one is perpendicular to the axis. Combining the in-phase orbitals results in a bonding orbital. There is a node (blue plane) containing the internuclear axis with the two lobes of the orbital located above and below this node.

Two horizontal rows of diagrams are shown. The upper and lower diagrams both begin with two vertical peanut-shaped orbitals with a plus sign in between followed by a right-facing arrow. The upper diagram shows the same vertical peanut orbitals bending slightly away from one another and separated by a dotted line. It is labeled, “pi subscript p superscript asterisk.” The lower diagram shows the horizontal overlap of the two orbitals and is labeled, “pi subscript p.”

In the molecular orbitals of diatomic molecules, each atom also has two sets of *p* orbitals oriented side by side (p_y and p_z), so these four atomic orbitals combine pairwise to create two π orbitals and two π^* orbitals. The π_{py} and π^*_{py} orbitals are oriented at right angles to the π_{pz} and π^*_{pz} orbitals. Except for their orientation, the π_{py} and π_{pz} orbitals are identical and have the same energy; they are degenerate orbitals. The π^*_{py} and π^*_{pz} antibonding orbitals are also degenerate and identical except for their orientation. A total of six molecular orbitals results from the combination of the six atomic *p* orbitals in two atoms: σ_{px} and σ^*_{px}, π_{py} and π^*_{py}, π_{pz} and π^*_{pz}.

Example 7.5.1: Molecular Orbitals

Predict what type (if any) of molecular orbital would result from adding the wave functions so each pair of orbitals shown overlap. The orbitals are all similar in energy.



Three diagrams are shown and labeled “a,” “b,” and “c.” Diagram a shows two horizontal peanut-shaped orbitals laying side-by-side. They are labeled, “3 p subscript x and 3 p subscript x.” Diagram b shows one vertical and one horizontal peanut-shaped orbital which are at right angles to one another. They are labeled, “3 p subscript x and 3 p subscript y.” Diagram c shows two vertical peanut-shaped orbitals laying side-by-side and labeled, “3 p subscript y and 3 p subscript y.”

Solution

a. This is an in-phase combination, resulting in a σ_{3p} orbital

b. This will not result in a new orbital because the in-phase component (bottom) and out-of-phase component (top) cancel out. Only orbitals with the correct alignment can combine.

c. This is an out-of-phase combination, resulting in a π^*_{3p} orbital.

Exercise 7.5.1

Label the molecular orbital shown as σ or π, bonding or antibonding and indicate where the node occurs.



Two orbitals are shown lying end-to-end. Each has one enlarged and one small side. The small sides are facing one another

Answer

The orbital is located along the internuclear axis, so it is a σ orbital. There is a node bisecting the internuclear axis, so it is an antibonding orbital.



Two orbitals are shown lying end-to-end. Each has one enlarged and one small side. The small sides are facing one another and are separated by a vertical dotted line.

Application: Computational Chemistry in Drug Design

While the descriptions of bonding described in this chapter involve many theoretical concepts, they also have many practical, real-world applications. For example, drug design is an important field that uses our understanding of chemical bonding to develop pharmaceuticals. This interdisciplinary area of study uses biology (understanding diseases and how they operate) to identify specific targets, such as a binding site that is involved in a disease pathway. By modeling the structures of the binding site and potential drugs, computational chemists can predict which structures can fit together and how effectively they will bind (Figure 7.5.6). Thousands of potential candidates can be narrowed down to a few of the most promising candidates. These candidate molecules are then carefully tested to determine side effects, how effectively they can be transported through the

body, and other factors. Dozens of important new pharmaceuticals have been discovered with the aid of computational chemistry, and new research projects are underway.

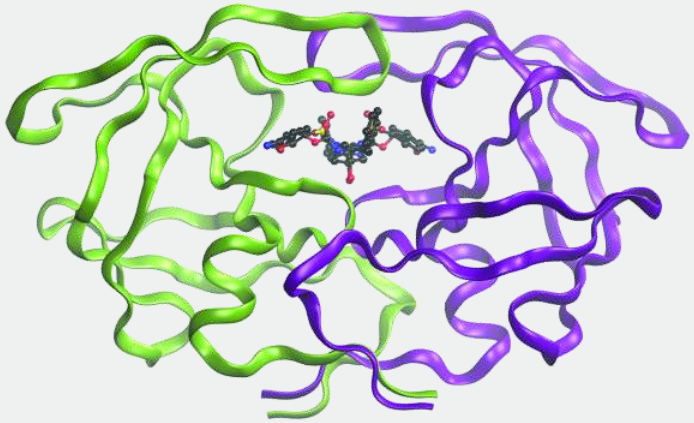


Figure 7.5.6: The molecule shown, HIV-1 protease, is an important target for pharmaceutical research. By designing molecules that bind to this protein, scientists are able to drastically inhibit the progress of the disease.

A diagram of a molecule is shown. The image shows a tangle of ribbon-like, intertwined, pink and green curling lines with a complex ball and stick model in the center.

Molecular Orbital Energy Diagrams

The relative energy levels of atomic and molecular orbitals are typically shown in a molecular orbital diagram (Figure 7.5.7). For a diatomic molecule, the atomic orbitals of one atom are shown on the left, and those of the other atom are shown on the right. Each horizontal line represents one orbital that can hold two electrons. The molecular orbitals formed by the combination of the atomic orbitals are shown in the center. Dashed lines show which of the atomic orbitals combine to form the molecular orbitals. For each pair of atomic orbitals that combine, one lower-energy (bonding) molecular orbital and one higher-energy (antibonding) orbital result. Thus we can see that combining the six 2*p* atomic orbitals results in three bonding orbitals (one σ and two π) and three antibonding orbitals (one σ* and two π*).

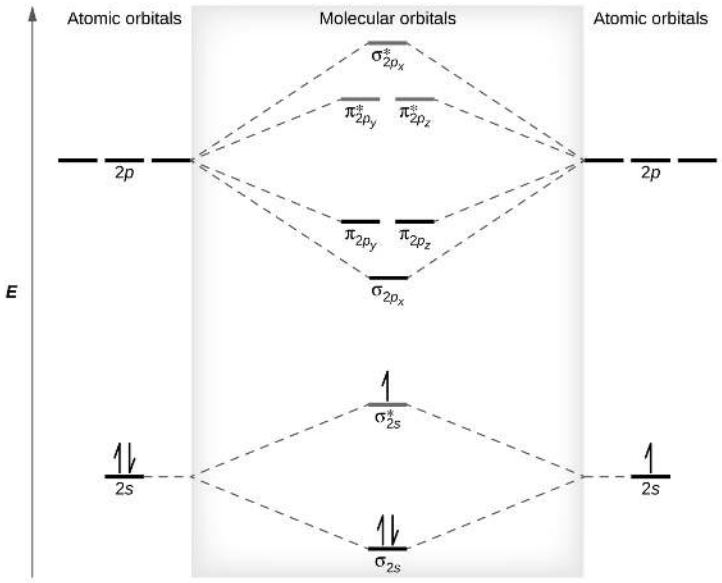


Figure 7.5.7: This is the molecular orbital diagram for the homonuclear diatomic Be_2^+, showing the molecular orbitals of the valence shell only. The molecular orbitals are filled in the same manner as atomic orbitals, using the Aufbau principle and Hund's rule.

A diagram is shown that has an upward-facing vertical arrow running along the left side labeled, "E." At the bottom center of the diagram is a horizontal line labeled, "sigma subscript 2 s," that has two vertical half arrows drawn on it, one facing up and one facing down. This line is connected to the right and left by upward-facing, dotted lines to two more horizontal lines, each labeled, "2 s." The line on the left has two vertical half arrows drawn on it, one facing up and one facing down while the line of the right has one half arrow facing up drawn on it. These two lines are connected by upward-facing dotted lines to another line in the center of the diagram, but further up from the first. It is labeled, "sigma subscript 2 s superscript asterisk." This horizontal line has one upward-facing vertical half-arrow drawn on it. Moving farther up the center of the diagram is a long horizontal line labeled, "sigma subscript 2 p subscript x," which lies below two horizontal lines. These two horizontal lines lie side-by-side, and labeled, "pi subscript 2 p subscript y," and, "pi subscript 2 p subscript z." Both the bottom and top lines are connected to the right and left by upward-facing, dotted lines to three more horizontal lines, each labeled, "2 p." These sets of lines are connected by upward-facing dotted lines to another single line and then pair of double lines in the center of the diagram, but farther up from the lower lines. They are labeled, "sigma subscript 2 p subscript x superscript asterisk," and, ""pi subscript 2 p subscript y superscript asterisk," and, "pi subscript 2 p subscript z superscript asterisk," respectively. The left and right sides of the diagram have headers that read, "Atomic orbitals," while the center is header reads "Molecular orbitals".

We predict the distribution of electrons in these molecular orbitals by filling the orbitals in the same way that we fill atomic orbitals, by the Aufbau principle. Lower-energy orbitals fill first, electrons spread out among degenerate orbitals before pairing, and each orbital can hold a maximum of two electrons with opposite spins (Figure 7.5.7). Just as we write electron configurations for atoms, we can write the molecular electronic configuration by listing the orbitals with superscripts indicating the number of electrons present. For clarity, we place parentheses around molecular orbitals with the same energy. In this case, each orbital is at a different energy, so parentheses separate each orbital. Thus we would expect a diatomic molecule or ion containing seven electrons (such as Be_2^+) would have the molecular electron configuration $(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^1$. It is common to omit the core electrons from molecular orbital diagrams and configurations and include only the valence electrons.

Bond Order

The filled molecular orbital diagram shows the number of electrons in both bonding and antibonding molecular orbitals. The net contribution of the electrons to the bond strength of a molecule is identified by determining the bond order that results from the filling of the molecular orbitals by electrons.

When using Lewis structures to describe the distribution of electrons in molecules, we define bond order as the number of bonding pairs of electrons between two atoms. Thus a single bond has a bond order of 1, a double bond has a bond order of 2, and a triple bond has a bond order of 3. We define bond order differently when we use the molecular orbital description of the distribution of electrons, but the resulting bond order is usually the same. The MO technique is more accurate and can handle cases when the Lewis structure method fails, but both methods describe the same phenomenon.

In the molecular orbital model, an electron contributes to a bonding interaction if it occupies a bonding orbital and it contributes to an antibonding interaction if it occupies an antibonding orbital. The bond order is calculated by subtracting the destabilizing (antibonding) electrons from the stabilizing (bonding) electrons. Since a bond consists of two electrons, we divide by two to get the bond order. We can determine bond order with the following equation:

$$\text{bond order} = \frac{(\text{number of bonding electrons}) - (\text{number of antibonding electrons})}{2}$$

The order of a covalent bond is a guide to its strength; a bond between two given atoms becomes stronger as the bond order increases. If the distribution of electrons in the molecular orbitals between two atoms is such that the resulting bond would have a bond order of zero, a stable bond does not form. We next look at some specific examples of MO diagrams and bond orders.

Bonding in Diatomic Molecules

A dihydrogen molecule (H_2) forms from two hydrogen atoms. When the atomic orbitals of the two atoms combine, the electrons occupy the molecular orbital of lowest energy, the σ_{1s} bonding orbital. A dihydrogen molecule, H_2, readily forms because the energy of a H_2 molecule is lower than that of two H atoms. The σ_{1s} orbital that contains both electrons is lower in energy than either of the two 1*s* atomic orbitals.

A molecular orbital can hold two electrons, so both electrons in the H_2 molecule are in the σ_{1s} bonding orbital; the electron configuration is $(\sigma_{1s})^2$. We represent this configuration by a molecular orbital energy diagram (Figure **7.5.8**) in which a single upward arrow indicates one electron in an orbital, and two (upward and downward) arrows indicate two electrons of opposite spin.

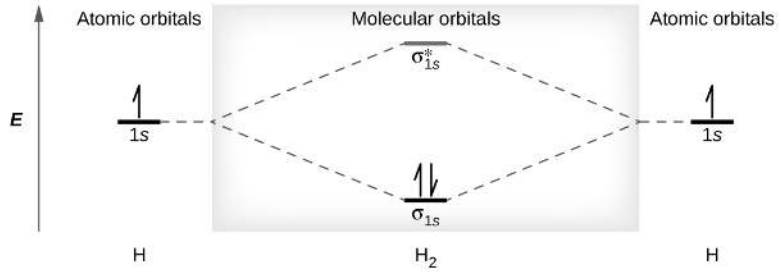


Figure **7.5.8**: The molecular orbital energy diagram predicts that H_2 will be a stable molecule with lower energy than the separated atoms.

A diagram is shown that has an upward-facing vertical arrow running along the left side labeled “E.” At the bottom center of the diagram is a horizontal line labeled, “sigma subscript 1 s,” that has two vertical half arrows drawn on it, one facing up and one facing down. This line is connected to the right and left by upward-facing, dotted lines to two more horizontal lines, each labeled, “1 s,” and each with one vertical half-arrow facing up drawn on it. These two lines are connected by upward-facing dotted lines to another line in the center of the diagram, but farther up from the first, and labeled, “sigma subscript 1 s superscript asterisk.” The left and right sides of the diagram have headers that read, ”Atomic orbitals,” while the center header reads, “Molecular orbitals.” The bottom left and right are labeled “H” while the center is labeled “H subscript 2.”

A dihydrogen molecule contains two bonding electrons and no antibonding electrons so we have

$$\text{bond order in } H_2 = \frac{(2-0)}{2} = 1$$

Because the bond order for the H–H bond is equal to 1, the bond is a single bond.

A helium atom has two electrons, both of which are in its 1*s* orbital. Two helium atoms do not combine to form a dihelium molecule, He_2, with four electrons, because the stabilizing effect of the two electrons in the lower-energy bonding orbital would be offset by the destabilizing effect of the two electrons in the higher-energy antibonding molecular orbital. We would write the hypothetical electron configuration of He_2 as $(\sigma_{1s})^2(\sigma^*_{1s})^2$ as in Figure **7.5.9**. The net energy change would be zero, so there is no driving force for helium atoms to form the diatomic molecule. In fact, helium exists as discrete atoms rather than as diatomic molecules. The bond order in a hypothetical dihelium molecule would be zero.

$$\text{bond order in } He_2 = \frac{(2-2)}{2} = 0$$

A bond order of zero indicates that no bond is formed between two atoms.

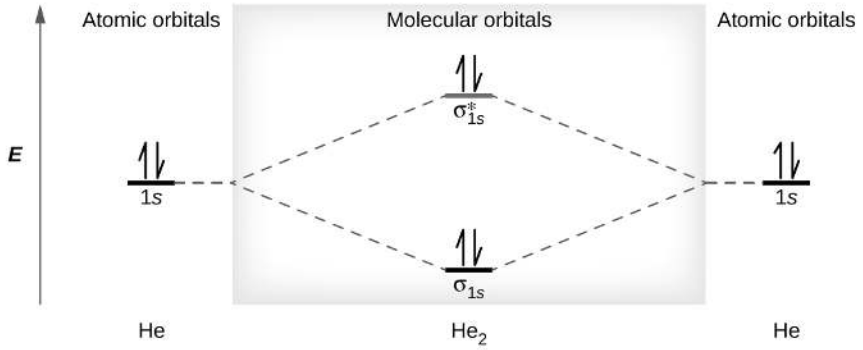


Figure **7.5.9**: The molecular orbital energy diagram predicts that He_2 will not be a stable molecule, since it has equal numbers of bonding and antibonding electrons.

A diagram is shown that has an upward-facing vertical arrow running along the left side labeled, “E.” At the bottom center of the diagram is a horizontal line labeled, “sigma subscript 1 s,” that has two vertical half arrows drawn on it, one facing up and one facing down. This line is connected to the right and left by upward-facing, dotted lines to two more horizontal lines, each labeled, “1 s,” and each with one vertical half-arrow facing up and one facing down drawn on it. These two lines are connected by upward-facing dotted lines to another line in the center of the diagram, but farther up from the first, and labeled, “sigma subscript 1 s superscript asterisk.” This line has one upward-facing and one downward-facing vertical arrow drawn on it. The left and right sides of the diagram have headers that read, “Atomic orbitals,” while the center header reads, “Molecular orbitals.” The bottom left and right are labeled, “H e,” while the center is labeled, “H e subscript 2.”

The Diatomic Molecules of the Second Period

Eight possible homonuclear diatomic molecules might be formed by the atoms of the second period of the periodic table: Li_2, Be_2, B_2, C_2, N_2, O_2, F_2, and Ne_2. However, we can predict that the Be_2 molecule and the Ne_2 molecule would not be stable. We can see this by a consideration of the molecular electron configurations (Table **7.5.1**).

Table **7.5.1**: Electron Configuration and Bond Order for Molecular Orbitals in Homonuclear Diatomic Molecules of Period Two Elements

Molecule	Electron Configuration	Bond Order
Li_2	$(\sigma_{2s})^2$	1
Be_2 (unstable)	$(\sigma_{2s})^2(\sigma^*_{2s})^2$	0
B_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2py}, \pi_{2pz})^2$	1
C_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2py}, \pi_{2pz})^4$	2
N_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2py}, \pi_{2pz})^4(\sigma_{2px})^2$	3
O_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2px})^2(\pi_{2py}, \pi_{2pz})^4(\pi^*_{2py}, \pi^*_{2pz})^2$	2
F_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2px})^2(\pi_{2py}, \pi_{2pz})^4(\pi^*_{2py}, \pi^*_{2pz})^4$	1
Ne_2 (unstable)	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2px})^2(\pi_{2py}, \pi_{2pz})^4(\pi^*_{2py}, \pi^*_{2pz})^4(\sigma^*_{2px})^2$	0

We predict valence molecular orbital electron configurations just as we predict electron configurations of atoms. Valence electrons are assigned to valence molecular orbitals with the lowest possible energies. Consistent with Hund’s rule, whenever there are two or more degenerate molecular orbitals, electrons fill each orbital of that type singly before any pairing of electrons takes place.

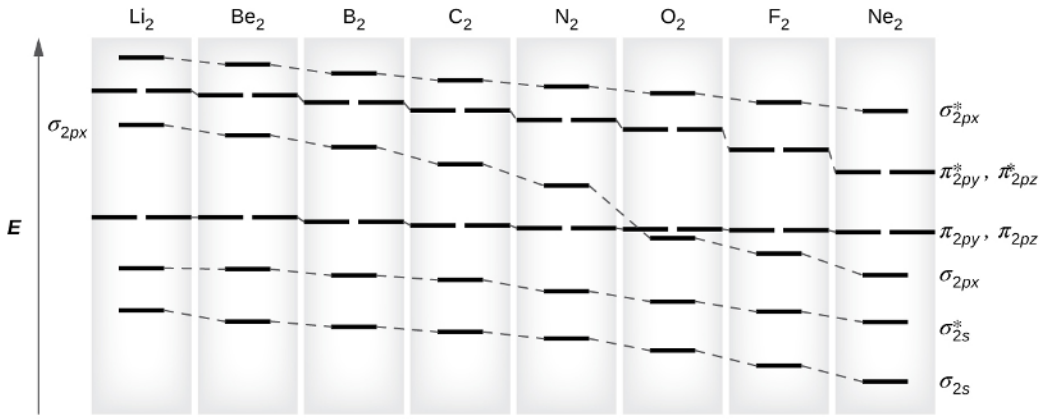


Figure **7.5.10**: This shows the MO diagrams for each homonuclear diatomic molecule in the second period. The orbital energies decrease across the period as the effective nuclear charge increases and atomic radius decreases. Between N_2 and O_2, the order of the orbitals changes.

A graph is shown in which the y-axis is labeled, “E,” and appears as a vertical, upward-facing arrow. Across the top, the graph reads, “L i subscript 2,” “B e subscript 2,” “B subscript 2,” “C subscript 2,” “N subscript 2,” “O subscript 2,” “F subscript 2,” and “Ne subscript 2.” Directly below each of these element terms is a single pink line, and all lines are connected to one another by a dashed line, to create an overall line that decreases in height as it moves from left to right across the graph. This line is labeled, “sigma subscript 2 p x superscript asterisk”. Directly below each of these lines is a set of two pink lines, and all lines are connected to one another by a dashed line, to create an overall line that decreases in height as it moves from left to right across the graph. It is consistently lower than the first line. This line is labeled, “pi subscript 2 p y superscript asterisk,” and, “pi subscript 2 p z superscript asterisk.” Directly below each of these double lines is a single pink line, and all lines are connected to one another by a dashed line, to create an overall line that decreases in height as it moves from left to right across the graph. It has a distinctive drop at the label, “O subscript 2.” This line is labeled, “sigma subscript 2 p x.” Directly below each of these lines is a set of two pink lines, and all lines are connected to one another by a dashed line to create an overall line that decreases very slightly in height as it moves from left to right across the graph. It is consistently lower than the third line until it reaches the point labeled, “O subscript 2.” This line is labeled, “pi subscript 2 p y,” and, “pi subscript 2 p z.” Directly below each of these lines is a single blue line, and all lines are connected to one another by a dashed line to create an overall line that decreases in height as it moves from left to right across the graph. This line is labeled, “sigma subscript 2 s superscript asterisk.” Finally, directly below each of these lines is a single blue line, and all lines are connected to one another by a dashed line to create an overall line that decreases in height as it moves from left to right across the graph. This line is labeled. “sigma subscript 2 s.”

As we saw in valence bond theory, σ bonds are generally more stable than π bonds formed from degenerate atomic orbitals. Similarly, in molecular orbital theory, σ orbitals are usually more stable than π orbitals. However, this is not always the case. The MOs for the valence orbitals of the second period are shown in Figure **7.5.10**. Looking at Ne_2 molecular orbitals, we see that the order is consistent with the generic diagram shown in the previous section. However, for atoms with three or fewer electrons in the *p* orbitals (Li through N) we observe a different pattern, in which the σ_p orbital is higher in energy than the π_p set. Obtain the molecular orbital diagram for a homonuclear diatomic ion by adding or subtracting electrons from the diagram for the neutral molecule.

This switch in orbital ordering occurs because of a phenomenon called s-p mixing. s-p mixing does not create new orbitals; it merely influences the energies of the existing molecular orbitals. The σ_s wavefunction mathematically combines with the σ_p wavefunction, with the result that the σ_s orbital becomes more stable, and the σ_p orbital becomes less stable (Figure **7.5.11**). Similarly, the antibonding orbitals also undergo s-p mixing, with the σ_{s*} becoming more stable and the σ_{p*} becoming less stable.

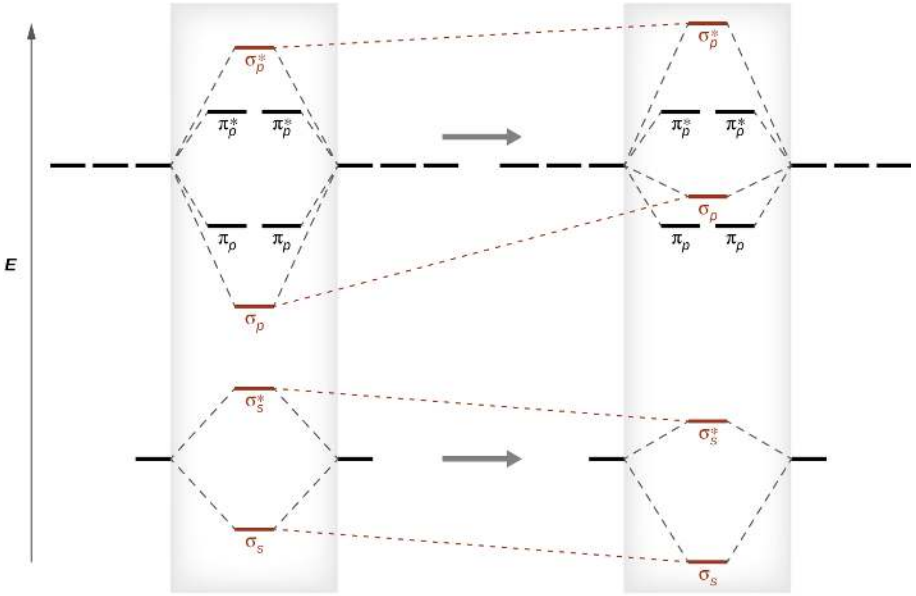


Figure **7.5.11**: Without mixing, the MO pattern occurs as expected, with the σ_p orbital lower in energy than the σ_p orbitals. When s-p mixing occurs, the orbitals shift as shown, with the σ_p orbital higher in energy than the π_p orbitals.

A diagram is shown. At the bottom left of the diagram is a horizontal line that is connected to the right and left by upward-facing, dotted lines to two more horizontal lines. Those two lines are connected by upward-facing dotted lines to another line in the center of the diagram but farther up from the first. Each of the bottom two central lines has a vertical downward-facing arrow. Above this structure is a horizontal line that is connected to the right and left by upward-facing, dotted lines to two sets of three horizontal lines and those two lines are connected by upward-facing dotted lines to another line in the center of the diagram, but further up from the first. In between the horizontal lines of this structure are two pairs of horizontal lines that are above the first line but below the second and connected by dotted lines to the side horizontal lines. The bottom and top central lines each have an upward-facing vertical arrow. These two structures are redrawn on the right side of the diagram, but this time, the central lines of the bottom structure are moved downward in relation to the side lines. The upper portion of the structure has its central lines shifted upward in relation to the side lines. This structure also shows the bottom line appearing above the set of two lines.

s-p mixing occurs when the *s* and *p* orbitals have similar energies. The energy difference between 2*s* and 2*p* orbitals in O, F, and Ne is greater than that in Li, Be, B, C, and N. Because of this, O_2, F_2, and Ne exhibit negligible s-p mixing (not sufficient to change the energy ordering), and their MO diagrams follow the normal pattern, as shown in Figure **7.5.7**. All of the other period 2 diatomic molecules do have s-p mixing, which leads to the pattern where the σ_p orbital is raised above the π_p set.

Using the MO diagrams shown in Figure **7.5.11**, we can add in the electrons and determine the molecular electron configuration and bond order for each of the diatomic molecules. As shown in Table **7.5.1**, Be_2 and Ne_2 molecules would have a bond order of 0, and these molecules do not exist.

The combination of two lithium atoms to form a lithium molecule, Li_2, is analogous to the formation of H_2, but the atomic orbitals involved are the valence 2*s* orbitals. Each of the two lithium atoms has one valence electron. Hence, we have two valence electrons available for the σ_{2s} bonding molecular orbital. Because both valence electrons would be in a bonding orbital, we would predict the Li_2 molecule to be stable. The molecule is, in fact, present in an appreciable concentration in lithium vapor at temperatures near the boiling point of the element. All of the other molecules in Table **7.5.1** with a bond order greater than zero are also known.

The O_2 molecule has enough electrons to half fill the (π^*_{2py}, π^*_{2pz}) level. We expect the two electrons that occupy these two degenerate orbitals to be unpaired, and this molecular electronic configuration for O_2 is in accord with the fact that the oxygen molecule has two unpaired electrons (Figure **7.5.10**). The presence of two unpaired electrons has proved to be difficult to explain using Lewis structures, but the molecular orbital theory explains it quite well. In fact, the unpaired electrons of the oxygen molecule provide a strong piece of support for the molecular orbital theory.

Application: Band Theory in Extended Systems

When two identical atomic orbitals on different atoms combine, two molecular orbitals result (e.g., H_2 in Figure 7.5.8). The bonding orbital is lower in energy than the original atomic orbitals because the atomic orbitals are in-phase in the molecular orbital. The antibonding orbital is higher in energy than the original atomic orbitals because the atomic orbitals are out-of-phase.

In a solid, similar things happen, but on a much larger scale. Remember that even in a small sample there are a huge number of atoms (typically > 10^{23} atoms), and therefore a huge number of atomic orbitals that may be combined into molecular orbitals. When *N* valence atomic orbitals, all of the same energy and each containing one (1) electron, are combined, *N*/2 (filled) bonding orbitals and *N*/2 (empty) antibonding orbitals will result. Each bonding orbital will show an energy lowering as the atomic orbitals are *mostly* in-phase, but each of the bonding orbitals will be a little different and have slightly different energies. The antibonding orbitals will show an increase in energy as the atomic orbitals are *mostly* out-of-phase, but each of the antibonding orbitals will also be a little different and have slightly different energies. The allowed energy levels for all the bonding orbitals are so close together that they form a band, called the valence band. Likewise, all the antibonding orbitals are very close together and form a band, called the conduction band. Figure 7.5.12) shows the bands for three important classes of materials: insulators, semiconductors, and conductors.

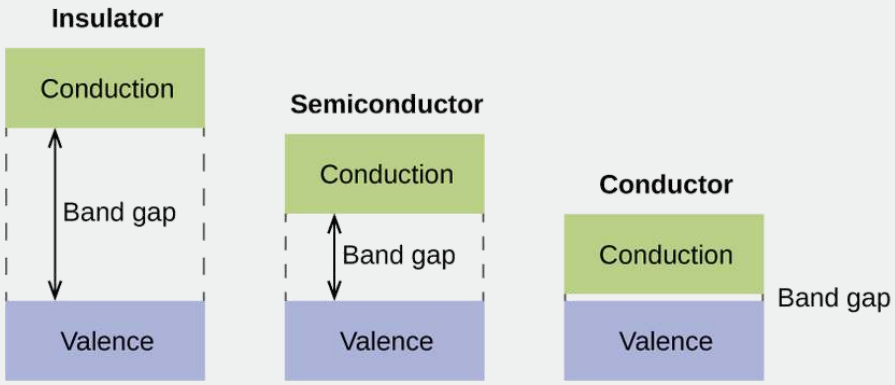


Figure 7.5.12: Molecular orbitals in solids are so closely spaced that they are described as bands. The valence band is lower in energy and the conduction band is higher in energy. The type of solid is determined by the size of the "band gap" between the valence and conduction bands. Only a very small amount of energy is required to move electrons from the valence band to the conduction band in a conductor, and so they conduct electricity well. In an insulator, the band gap is large, so that very few electrons move, and they are poor conductors of electricity. Semiconductors are in between: they conduct electricity better than insulators, but not as well as conductors.

This figure shows three diagrams. The first is labeled, "Insulator," and it consists of two boxes. The "conduction" box is above and the "valence" box is below. A large gap marked by 4 dashed lines contains a double-headed arrow. One head pointing towards the "conduction box" and the other towards the "valence" box. The arrow is labeled, "Band gap." The second diagram is similar to the first, but the band gap is about half as large. This diagram is labeled, "Semiconductor." The third diagram is similar to the other two, but the band gap is about a fifth that of the "Semiconductor" diagram. This diagram is labeled, "Conductor."

In order to conduct electricity, electrons must move from the filled valence band to the empty conduction band where they can move throughout the solid. The size of the band gap, or the energy difference between the top of the valence band and the bottom of the conduction band, determines how easy it is to move electrons between the bands. Only a small amount of energy is required in a conductor because the band gap is very small. This small energy difference is "easy" to overcome, so they are good conductors of electricity. In an insulator, the band gap is so "large" that very few electrons move into the conduction band; as a result, insulators are poor conductors of electricity. Semiconductors conduct electricity when "moderate" amounts of energy are provided to move electrons out of the valence band and into the conduction band. Semiconductors, such as silicon, are found in many electronics.

Semiconductors are used in devices such as computers, smartphones, and solar cells. Solar cells produce electricity when light provides the energy to move electrons out of the valence band. The electricity that is generated may then be used to power a light or tool, or it can be stored for later use by charging a battery. As of December 2014, up to 46% of the energy in sunlight could be converted into electricity using solar cells.

Example 7.5.2: Molecular Orbital Diagrams, Bond Order, and Number of Unpaired Electrons

Draw the molecular orbital diagram for the oxygen molecule, O_2. From this diagram, calculate the bond order for O_2. How does this diagram account for the paramagnetism of O_2?

Solution

We draw a molecular orbital energy diagram similar to that shown in Figure 7.5.7. Each oxygen atom contributes six electrons, so the diagram appears as shown in Figure 7.5.7.

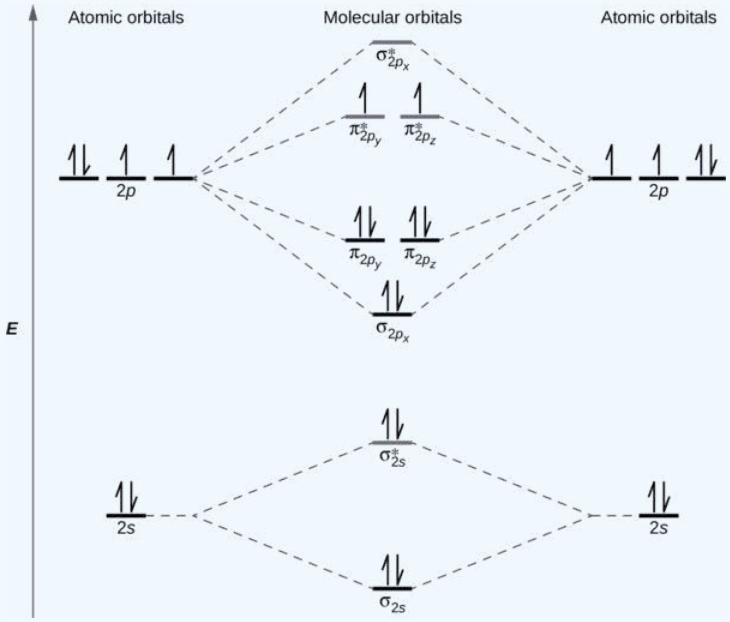


Figure 7.5.13: The molecular orbital energy diagram for O_2 predicts two unpaired electrons.

We calculate the bond order as

$$O_2 = \frac{(8-4)}{2} = 2$$

Oxygen's paramagnetism is explained by the presence of two unpaired electrons in the $(\pi_{2py}, \pi_{2pz})^*$ molecular orbitals.

Exercise 7.5.2

The main component of air is N_2. From the molecular orbital diagram of N_2, predict its bond order and whether it is diamagnetic or paramagnetic.

Answer

N_2 has a bond order of 3 and is diamagnetic.

Example 7.5.3: Ion Predictions with MO Diagrams

Give the molecular orbital configuration for the valence electrons in C_2^{2-}. Will this ion be stable?

Solution

Looking at the appropriate MO diagram, we see that the π orbitals are lower in energy than the σ_p orbital. The valence electron configuration for C_2 is

$$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2py}, \pi_{2pz})^4.$$

Adding two more electrons to generate the C_2^{2-} anion will give a valence electron configuration of

$$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2py},\ \pi_{2pz})^4(\sigma_{2px})^2$$

Since this has six more bonding electrons than antibonding, the bond order will be 3, and the ion should be stable.

? Exercise 7.5.3

How many unpaired electrons would be present on a Be_2^{2-} ion? Would it be paramagnetic or diamagnetic?

Answer

two, paramagnetic

Key Concepts and Summary

Molecular orbital (MO) theory describes the behavior of electrons in a molecule in terms of combinations of the atomic wave functions. The resulting molecular orbitals may extend over all the atoms in the molecule. Bonding molecular orbitals are formed by in-phase combinations of atomic wave functions, and electrons in these orbitals stabilize a molecule. Antibonding molecular orbitals result from out-of-phase combinations of atomic wave functions and electrons in these orbitals make a molecule less stable. Molecular orbitals located along an internuclear axis are called σ MOs. They can be formed from *s* orbitals or from *p* orbitals oriented in an end-to-end fashion. Molecular orbitals formed from *p* orbitals oriented in a side-by-side fashion have electron density on opposite sides of the internuclear axis and are called π orbitals.

We can describe the electronic structure of diatomic molecules by applying molecular orbital theory to the valence electrons of the atoms. Electrons fill molecular orbitals following the same rules that apply to filling atomic orbitals; Hund's rule and the Aufbau principle tell us that lower-energy orbitals will fill first, electrons will spread out before they pair up, and each orbital can hold a maximum of two electrons with opposite spins. Materials with unpaired electrons are paramagnetic and attracted to a magnetic field, while those with all-paired electrons are diamagnetic and repelled by a magnetic field. Correctly predicting the magnetic properties of molecules is in advantage of molecular orbital theory over Lewis structures and valence bond theory.

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7.E: Advanced Theories of Covalent Bonding (Exercises)

8.1: Valence Bond Theory

Chapter Exercises

1. Explain how σ and π bonds are similar and how they are different.
2. Draw a curve that describes the energy of a system with H and Cl atoms at varying distances. Then, find the minimum energy of this curve two ways.
   a. Use the bond energy found in Table 8.2.1 to calculate the energy for one single HCl bond (Hint: How many bonds are in a mole?)
   b. Use the enthalpy of reaction and the bond energies for H_2 and Cl_2 to solve for the energy of one mole of HCl bonds.

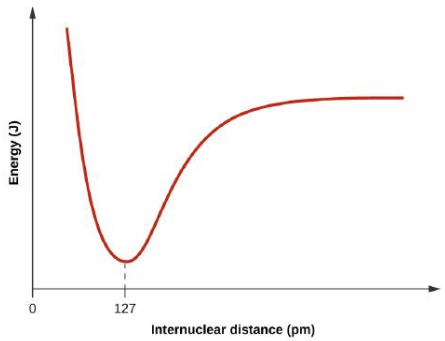
$$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)} \quad \Delta H^\circ_{rxn} = -184.7\ kJ/mol \tag{7.E.1}$$

3. Explain why bonds occur at specific average bond distances instead of the atoms approaching each other infinitely close.
4. Use valence bond theory to explain the bonding in F_2, HF, and ClBr. Sketch the overlap of the atomic orbitals involved in the bonds.
5. Use valence bond theory to explain the bonding in O_2. Sketch the overlap of the atomic orbitals involved in the bonds in O_2.
6. How many σ and π bonds are present in the molecule HCN?
7. A friend tells you N_2 has three π bonds due to overlap of the three *p*-orbitals on each N atom. Do you agree?
8. Draw the Lewis structures for CO_2 and CO, and predict the number of σ and π bonds for each molecule.
   a. CO_2
   b. CO

Solutions

1. **Similarities**: Both types of bonds result from overlap of atomic orbitals on adjacent atoms and contain a maximum of two electrons. **Differences**: σ bonds are stronger and result from end-to-end overlap and all single bonds are σ bonds; π bonds between the same two atoms are weaker because they result from side-by-side overlap, and multiple bonds contain one or more π bonds (in addition to a σ bond).

2



When H and Cl are separate (the x axis) the energy is at a particular value. As they approach, it decreases to a minimum at 127 pm (the bond distance), and then it increases sharply as you get closer.

a. (a) H–Cl431 kJ/mol 427kJmol×mol6.022×1023bonds×1000 JkJ=7.09×10−19
b. (b) We know Hess's law related to bond energies: ΔH°=ΣΔH∘BDE(broken)−ΣΔH∘BDE(formed) We are given the enthalpy of reaction

$$-184.7kJ/mol = (\Delta H \circ BDE(H–H) + \Delta H \circ BDE(Cl–Cl)) - (2\Delta H \circ BDE(H–Cl)) \tag{7.E.2}$$

$$H–His436kJ/molandCl–Clis243 \tag{7.E.3}$$

$$–184.7kJ/mol = (436 + 243)–2x = 679–2x \tag{7.E.4}$$

$$2x = 863.7 kJ/mol \tag{7.E.5}$$

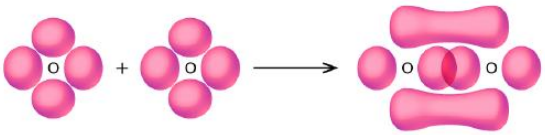
$$x = 432\ kJ/mol \tag{7.E.6}$$

This is very close to the value from part (a).

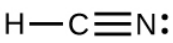
3. The specific average bond distance is the distance with the lowest energy. At distances less than the bond distance, the positive charges on the two nuclei repel each other, and the overall energy increases.

4. The single bond present in each molecule results from overlap of the relevant orbitals: F 2*p* orbitals in F_2, the H 1*s* and F 2*p* orbitals in HF, and the Cl 3*p* orbital and Br 4*p* orbital in ClBr.

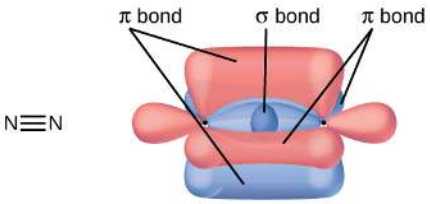
5. Bonding: One σ bond and one π bond. The *s* orbitals are filled and do not overlap. The *p* orbitals overlap along the axis to form a σ bond and side by side to form the π bond.



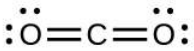
6. **H–C≡N** has two σ (H–C and C–N) and two π (making the CN triple bond).



7. No, two of the *p* orbitals (one on each N) will be oriented end-to-end and will form a σ bond.



8. (a) 2 σ 2 π;



(b) 1 σ 2 π;



8.2: Hybrid Atomic Orbitals

Chemistry End of Chapter Exercises

Why is the concept of hybridization required in valence bond theory?

Hybridization is introduced to explain the geometry of bonding orbitals in valance bond theory.

Give the shape that describes each hybrid orbital set:

(a) sp^2

(b) sp^3d

(c) *sp*

(d) sp^3d^2

Explain why a carbon atom cannot form five bonds using sp^3d hybrid orbitals.

There are no *d* orbitals in the valence shell of carbon.

What is the hybridization of the central atom in each of the following?

(a) BeH_2

(b) SF_6

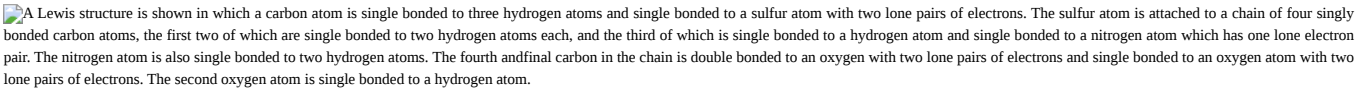
(c) PO_4^{3-}

(d) PCl_5

A molecule with the formula AB_3 could have one of four different shapes. Give the shape and the hybridization of the central A atom for each.

trigonal planar, sp^2; trigonal pyramidal (one lone pair on A) sp^3; T-shaped (two lone pairs on A sp^3d, or (three lone pairs on A) sp^3d^2

Methionine, $CH_3SCH_2CH_2CH(NH_2)CO_2H$, is an amino acid found in proteins. Draw a Lewis structure of this compound. What is the hybridization type of each carbon, oxygen, the nitrogen, and the sulfur?


A Lewis structure is shown in which a carbon atom is single bonded to three hydrogen atoms and single bonded to a sulfur atom with two lone pairs of electrons. The sulfur atom is attached to a chain of four singly bonded carbon atoms, the first two of which are single bonded to two hydrogen atoms each, and the third of which is single bonded to a hydrogen atom and single bonded to a nitrogen atom which has one lone electron pair. The nitrogen atom is also single bonded to two hydrogen atoms. The fourth andfinal carbon in the chain is double bonded to an oxygen with two lone pairs of electrons and single bonded to an oxygen atom with two lone pairs of electrons. The second oxygen atom is single bonded to a hydrogen atom.

Sulfuric acid is manufactured by a series of reactions represented by the following equations:

$$S_8(s) + 8\,O_2(g) \longrightarrow 8\,SO_2(g)$$

$$2\,SO_2(g) + O_2(g) \longrightarrow 2\,SO_3(g)$$

$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(l)$$

Draw a Lewis structure, predict the molecular geometry by VSEPR, and determine the hybridization of sulfur for the following:

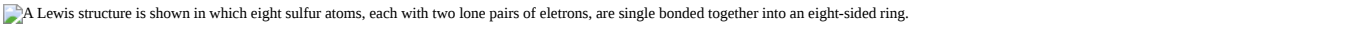
(a) circular S_8 molecule

(b) SO_2 molecule

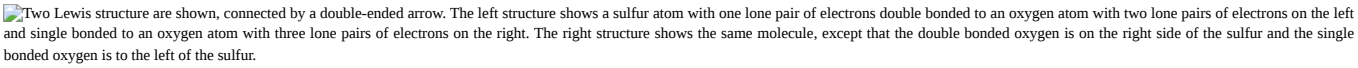
(c) SO_3 molecule

(d) H_2SO_4 molecule (the hydrogen atoms are bonded to oxygen atoms)

(a) Each S has a bent (109°) geometry, sp^3


A Lewis structure is shown in which eight sulfur atoms, each with two lone pairs of eletrons, are single bonded together into an eight-sided ring.

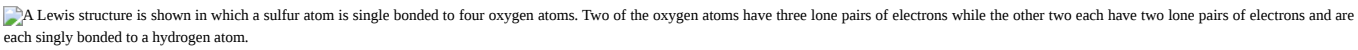
(b) Bent (120°), sp^2


Two Lewis structure are shown, connected by a double-ended arrow. The left structure shows a sulfur atom with one lone pair of electrons double bonded to an oxygen atom with two lone pairs of electrons on the left and single bonded to an oxygen atom with three lone pairs of electrons on the right. The right structure shows the same molecule, except that the double bonded oxygen is on the right side of the sulfur and the single bonded oxygen is to the left of the sulfur.

(c) Trigonal planar, sp^2


A Lewis structure of a sulfur atom singly bonded to two oxygen atoms, each with three lone pairs of electrons, and double bonded to a third oxygen atom with two lone pairs of electrons is shown.

(d) Tetrahedral, sp^3


A Lewis structure is shown in which a sulfur atom is single bonded to four oxygen atoms. Two of the oxygen atoms have three lone pairs of electrons while the other two each have two lone pairs of electrons and are each singly bonded to a hydrogen atom.

Two important industrial chemicals, ethene, C_2H_4, and propene, C_3H_6, are produced by the steam (or thermal) cracking process:

$$2\,C_3H_8(g) \longrightarrow C_2H_4(g) + C_3H_6(g) + CH_4(g) + H_2(g)$$

For each of the four carbon compounds, do the following:

(a) Draw a Lewis structure.

(b) Predict the geometry about the carbon atom.

(c) Determine the hybridization of each type of carbon atom.

For many years after they were discovered, it was believed that the noble gases could not form compounds. Now we know that belief to be incorrect. A mixture of xenon and fluorine gases, confined in a quartz bulb and placed on a windowsill, is found to slowly produce a white solid. Analysis of the compound indicates that it contains 77.55% Xe and 22.45% F by mass.

(a) What is the formula of the compound?

(b) Write a Lewis structure for the compound.

(c) Predict the shape of the molecules of the compound.

(d) What hybridization is consistent with the shape you predicted?

(a) XeF_2

(b)



(c) linear (d) sp^3d

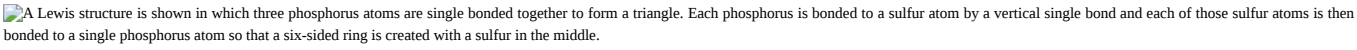
Consider nitrous acid, HNO_2 (HONO).

(a) Write a Lewis structure.

(b) What are the electron pair and molecular geometries of the internal oxygen and nitrogen atoms in the HNO_2 molecule?

(c) What is the hybridization on the internal oxygen and nitrogen atoms in HNO_2?

Strike-anywhere matches contain a layer of $KClO_3$ and a layer of P_4S_3. The heat produced by the friction of striking the match causes these two compounds to react vigorously, which sets fire to the wooden stem of the match. $KClO_3$ contains the ClO_3^- ion. P_4S_3 is an unusual molecule with the skeletal structure.



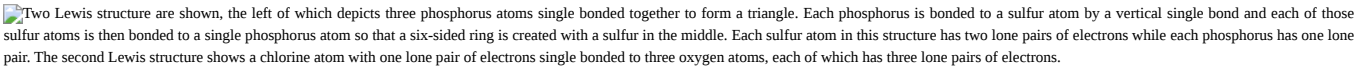
(a) Write Lewis structures for P_4S_3 and the ClO_3^- ion.

(b) Describe the geometry about the P atoms, the S atom, and the Cl atom in these species.

(c) Assign a hybridization to the P atoms, the S atom, and the Cl atom in these species.

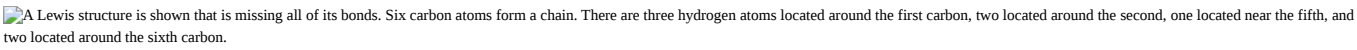
(d) Determine the oxidation states and formal charge of the atoms in P_4S_3 and the ClO_3^- ion.

(a)

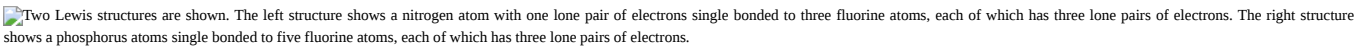


(b) P atoms, trigonal pyramidal; S atoms, bent, with two lone pairs; Cl atoms, trigonal pyramidal; (c) Hybridization about P, S, and Cl is, in all cases, sp^3; (d) Oxidation states P +1, S $-1\frac{1}{3}$, Cl +5, O –2. Formal charges: P 0; S 0; Cl +2: O –1

Identify the hybridization of each carbon atom in the following molecule. (The arrangement of atoms is given; you need to determine how many bonds connect each pair of atoms.)



Write Lewis structures for NF_3 and PF_5. On the basis of hybrid orbitals, explain the fact that NF_3, PF_3, and PF_5 are stable molecules, but NF_5 does not exist.



Phosphorus and nitrogen can form sp^3 hybrids to form three bonds and hold one lone pair in PF_3 and NF_3, respectively. However, nitrogen has no valence *d* orbitals, so it cannot form a set of sp^3d hybrid orbitals to bind five fluorine atoms in NF_5. Phosphorus has *d* orbitals and can bind five fluorine atoms with sp^3d hybrid orbitals in PF_5.

In addition to NF_3, two other fluoro derivatives of nitrogen are known: N_2F_4 and N_2F_2. What shapes do you predict for these two molecules? What is the hybridization for the nitrogen in each molecule?

8.3: Multiple Bonds

Chemistry End of Chapter Exercises

The bond energy of a C–C single bond averages 347 kJ mol^{-1}; that of a C≡C triple bond averages 839 kJ mol^{-1}. Explain why the triple bond is not three times as strong as a single bond.

A triple bond consists of one σ bond and two π bonds. A σ bond is stronger than a π bond due to greater overlap.

For the carbonate ion, CO_3^{2-}, draw all of the resonance structures. Identify which orbitals overlap to create each bond.

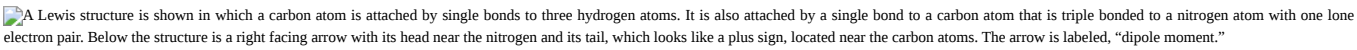
A useful solvent that will dissolve salts as well as organic compounds is the compound acetonitrile, H_3CCN. It is present in paint strippers.

(a) Write the Lewis structure for acetonitrile, and indicate the direction of the dipole moment in the molecule.

(b) Identify the hybrid orbitals used by the carbon atoms in the molecule to form σ bonds.

(c) Describe the atomic orbitals that form the π bonds in the molecule. Note that it is not necessary to hybridize the nitrogen atom.

(a)


A Lewis structure is shown in which a carbon atom is attached by single bonds to three hydrogen atoms. It is also attached by a single bond to a carbon atom that is triple bonded to a nitrogen atom with one lone electron pair. Below the structure is a right facing arrow with its head near the nitrogen and its tail, which looks like a plus sign, located near the carbon atoms. The arrow is labeled, “dipole moment.”

(b) The terminal carbon atom uses sp^3 hybrid orbitals, while the central carbon atom is *sp* hybridized. (c) Each of the two π bonds is formed by overlap of a 2*p* orbital on carbon and a nitrogen 2*p* orbital.

For the molecule allene, $H_2C=C=CH_2$, give the hybridization of each carbon atom. Will the hydrogen atoms be in the same plane or perpendicular planes?

Identify the hybridization of the central atom in each of the following molecules and ions that contain multiple bonds:

(a) ClNO (N is the central atom)

(b) CS_2

(c) Cl_2CO (C is the central atom)

(d) Cl_2SO (S is the central atom)

(e) SO_2F_2 (S is the central atom)

(f) XeO_2F_2 (Xe is the central atom)

(g) $ClOF_2^+$ (Cl is the central atom)

(a) sp^2; (b) *sp*; (c) sp^2; (d) sp^3; (e) sp^3; (f) sp^3d; (g) sp^3

Describe the molecular geometry and hybridization of the N, P, or S atoms in each of the following compounds.

(a) H_3PO_4, phosphoric acid, used in cola soft drinks

(b) NH_4NO_3, ammonium nitrate, a fertilizer and explosive

(c) S_2Cl_2, disulfur dichloride, used in vulcanizing rubber

(d) $K_4[O_3POPO_3]$, potassium pyrophosphate, an ingredient in some toothpastes

For each of the following molecules, indicate the hybridization requested and whether or not the electrons will be delocalized:

(a) ozone (O_3) central O hybridization

(b) carbon dioxide (CO_2) central C hybridization

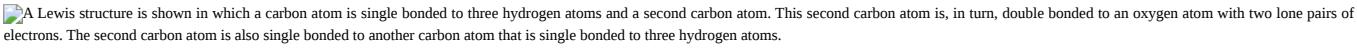
(c) nitrogen dioxide (NO_2) central N hybridization

(d) phosphate ion (PO_4^{3-}) central P hybridization

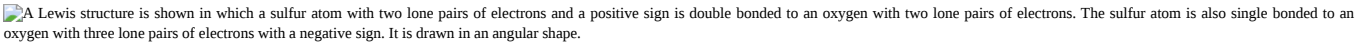
(a) sp^2, delocalized; (b) *sp*, localized; (c) sp^2, delocalized; (d) sp^3, delocalized

For each of the following structures, determine the hybridization requested and whether the electrons will be delocalized:

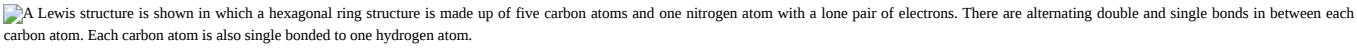
(a) Hybridization of each carbon


A Lewis structure is shown in which a carbon atom is single bonded to three hydrogen atoms and a second carbon atom. This second carbon atom is, in turn, double bonded to an oxygen atom with two lone pairs of electrons. The second carbon atom is also single bonded to another carbon atom that is single bonded to three hydrogen atoms.

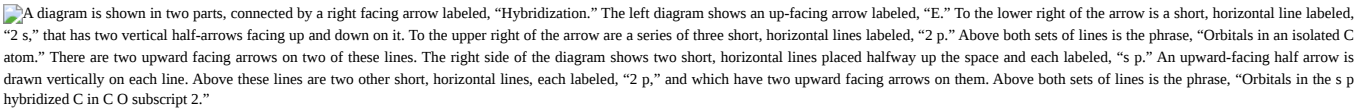
(b) Hybridization of sulfur


A Lewis structure is shown in which a sulfur atom with two lone pairs of electrons and a positive sign is double bonded to an oxygen with two lone pairs of electrons. The sulfur atom is also single bonded to an oxygen with three lone pairs of electrons with a negative sign. It is drawn in an angular shape.

(c) All atoms


A Lewis structure is shown in which a hexagonal ring structure is made up of five carbon atoms and one nitrogen atom with a lone pair of electrons. There are alternating double and single bonds in between each carbon atom. Each carbon atom is also single bonded to one hydrogen atom.

Draw the orbital diagram for carbon in CO_2 showing how many carbon atom electrons are in each orbital.


A diagram is shown in two parts, connected by a right facing arrow labeled, “Hybridization.” The left diagram shows an up-facing arrow labeled, “E.” To the lower right of the arrow is a short, horizontal line labeled, “2 s,” that has two vertical half-arrows facing up and down on it. To the upper right of the arrow are a series of three short, horizontal lines labeled, “2 p.” Above both sets of lines is the phrase, “Orbitals in an isolated C atom.” There are two upward facing arrows on two of these lines. The right side of the diagram shows two short, horizontal lines placed halfway up the space and each labeled, “s p.” An upward-facing half arrow is drawn vertically on each line. Above these lines are two other short, horizontal lines, each labeled, “2 p,” and which have two upward facing arrows on them. Above both sets of lines is the phrase, “Orbitals in the s p hybridized C in C O subscript 2.”

Each of the four electrons is in a separate orbital and overlaps with an electron on an oxygen atom.

8.4: Molecular Orbital Theory

Chemistry End of Chapter Exercises

Sketch the distribution of electron density in the bonding and antibonding molecular orbitals formed from two *s* orbitals and from two *p* orbitals.

How are the following similar, and how do they differ?

(a) σ molecular orbitals and π molecular orbitals

(b) ψ for an atomic orbital and ψ for a molecular orbital

(c) bonding orbitals and antibonding orbitals

(a) Similarities: Both are bonding orbitals that can contain a maximum of two electrons. Differences: σ orbitals are end-to-end combinations of atomic orbitals, whereas π orbitals are formed by side-by-side overlap of orbitals. (b) Similarities: Both are quantum-mechanical constructs that represent the probability of finding the electron about the atom or the molecule. Differences: ψ for an atomic orbital describes the behavior of only one electron at a time based on the atom. For a molecule, ψ represents a mathematical combination of atomic orbitals. (c) Similarities: Both are orbitals that can contain two electrons. Differences: Bonding orbitals result in holding two or more atoms together. Antibonding orbitals have the effect of destabilizing any bonding that has occurred.

If molecular orbitals are created by combining five atomic orbitals from atom A and five atomic orbitals from atom B combine, how many molecular orbitals will result?

Can a molecule with an odd number of electrons ever be diamagnetic? Explain why or why not.

An odd number of electrons can never be paired, regardless of the arrangement of the molecular orbitals. It will always be paramagnetic.

Can a molecule with an even number of electrons ever be paramagnetic? Explain why or why not.

Why are bonding molecular orbitals lower in energy than the parent atomic orbitals?

Bonding orbitals have electron density in close proximity to more than one nucleus. The interaction between the bonding positively charged nuclei and negatively charged electrons stabilizes the system.

Calculate the bond order for an ion with this configuration:

$$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2px})^2(\pi_{2py},\ \pi_{2pz})^4(\pi^*_{2py},\ \pi^*_{2pz})^3$$

Explain why an electron in the bonding molecular orbital in the H_2 molecule has a lower energy than an electron in the 1*s* atomic orbital of either of the separated hydrogen atoms.

The pairing of the two bonding electrons lowers the energy of the system relative to the energy of the nonbonded electrons.

Predict the valence electron molecular orbital configurations for the following, and state whether they will be stable or unstable ions.

(a) Na_2^{2+}

(b) Mg_2^{2+}

(c) Al_2^{2+}

(d) Si_2^{2+}

(e) P_2^{2+}

(f) S_2^{2+}

(g) F_2^{2+}

(h) Ar_2^{2+}

Determine the bond order of each member of the following groups, and determine which member of each group is predicted by the molecular orbital model to have the strongest bond.

(a) H_2, H_2^+, H_2^-

(b) O_2, O_2^{2+}, O_2^{2-}

(c) Li_2, Be_2^+, Be_2

(d) F_2, F_2^+, F_2^-

(e) N_2, N_2^+, N_2^-

(a) H_2 bond order = 1, H_2^+ bond order = 0.5, H_2^- bond order = 0.5, strongest bond is H_2; (b) O_2 bond order = 2, O_2^{2+} bond order = 3; O_2^{2-} bond order = 1, strongest bond is O_2^{2+}; (c) Li_2 bond order = 1, Be_2^+ bond order = 0.5, Be_2 bond order = 0, strongest bond is Li_2;(d) F_2 bond order = 1, F_2^+ bond order = 1.5, F_2^- bond order = 0.5, strongest bond is F_2^+; (e) N_2 bond order = 3, N_2^+ bond order = 2.5, N_2^- bond order = 2.5, strongest bond is N_2

For the first ionization energy for an N_2 molecule, what molecular orbital is the electron removed from?

Compare the atomic and molecular orbital diagrams to identify the member of each of the following pairs that has the highest first ionization energy (the most tightly bound electron) in the gas phase:

(a) H and H_2

(b) N and N_2

(c) O and O_2

(d) C and C_2

(e) B and B_2

(a) H_2; (b) N_2; (c) O; (d) C_2; (e) B_2

Which of the period 2 homonuclear diatomic molecules are predicted to be paramagnetic?

A friend tells you that the 2*s* orbital for fluorine starts off at a much lower energy than the 2*s* orbital for lithium, so the resulting σ_{2s} molecular orbital in F_2 is more stable than in Li_2. Do you agree?

Yes, fluorine is a smaller atom than Li, so atoms in the 2*s* orbital are closer to the nucleus and more stable.

True or false: Boron contains $2s^2 2p^1$ valence electrons, so only one *p* orbital is needed to form molecular orbitals.

What charge would be needed on F_2 to generate an ion with a bond order of 2?

2+

Predict whether the MO diagram for S_2 would show s-p mixing or not.

Explain why N_2^{2+} is diamagnetic, while O_2^{4+}, which has the same number of valence electrons, is paramagnetic.

N_2 has s-p mixing, so the π orbitals are the last filled in N_2^{2+}. O_2 does not have s-p mixing, so the σ_p orbital fills before the π orbitals.

Using the MO diagrams, predict the bond order for the stronger bond in each pair:

(a) B_2 or B_2^+

(b) F_2 or F_2^+

(c) O_2 or O_2^{2+}

(d) C_2^+ or C_2^-

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CHAPTER OVERVIEW

8: Kinetics

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General Chemistry

Chemical kinetics is the study of rates of chemical processes and includes investigations of how different experimental conditions can influence the speed of a chemical reaction and yield information about the reaction's mechanism and transition states, as well as the construction of mathematical models that can describe the characteristics of a chemical reaction.

8.1: Prelude to Kinetics
8.2: Chemical Reaction Rates
8.3: Factors Affecting Reaction Rates
8.4: Rate Laws
8.5: Reaction Mechanisms
8.6: Catalysis
8.E: Kinetics (Exercises)

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8.1: Prelude to Kinetics

The lizard in the photograph is not simply enjoying the sunshine or working on its tan. The heat from the sun's rays is critical to the lizard's survival. A warm lizard can move faster than a cold one because the chemical reactions that allow its muscles to move occur more rapidly at higher temperatures. In the absence of warmth, the lizard is an easy meal for predators.



Figure **8.1.1**: *An agama lizard basks in the sun. As its body warms, the chemical reactions of its metabolism speed up.*

From baking a cake to determining the useful lifespan of a bridge, rates of chemical reactions play important roles in our understanding of processes that involve chemical changes. When planning to run a chemical reaction, we should ask at least two questions. The first is: "Will the reaction produce the desired products in useful quantities?" The second question is: "How rapidly will the reaction occur?" A reaction that takes 50 years to produce a product is about as useful as one that never gives a product at all. A third question is often asked when investigating reactions in greater detail: "What specific molecular-level processes take place as the reaction occurs?" Knowing the answer to this question is of practical importance when the yield or rate of a reaction needs to be controlled.

The study of chemical kinetics concerns the second and third questions—that is, the rate at which a reaction yields products and the molecular-scale means by which a reaction occurs. In this chapter, we will examine the factors that influence the rates of chemical reactions, the mechanisms by which reactions proceed, and the quantitative techniques used to determine and describe the rate at which reactions occur.

- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).

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8.2: Chemical Reaction Rates

Learning Objectives

- Define chemical reaction rate
- Derive rate expressions from the balanced equation for a given chemical reaction
- Calculate reaction rates from experimental data

A *rate* is a measure of how some property varies with time. Speed is a familiar rate that expresses the distance traveled by an object in a given amount of time. Wage is a rate that represents the amount of money earned by a person working for a given amount of time. Likewise, the rate of a chemical reaction is a measure of how much reactant is consumed, or how much product is produced, by the reaction in a given amount of time.

The rate of reaction is the change in the amount of a reactant or product per unit time. Reaction rates are therefore determined by measuring the time dependence of some property that can be related to reactant or product amounts. Rates of reactions that consume or produce gaseous substances, for example, are conveniently determined by measuring changes in volume or pressure. For reactions involving one or more colored substances, rates may be monitored via measurements of light absorption. For reactions involving aqueous electrolytes, rates may be measured via changes in a solution's conductivity.

For reactants and products in solution, their relative amounts (concentrations) are conveniently used for purposes of expressing reaction rates. If we measure the concentration of hydrogen peroxide, H_2O_2, in an aqueous solution, we find that it changes slowly over time as the H_2O_2 decomposes, according to the equation:

$$2\,H_2O_2(aq) \longrightarrow 2\,H_2O(l) + O_2(g)$$

The rate at which the hydrogen peroxide decomposes can be expressed in terms of the rate of change of its concentration, as shown here:

$$\begin{aligned}\text{rate of decomposition of } H_2O_2 &= -\frac{\text{change in concentration of reactant}}{\text{time interval}} \\ &= -\frac{[H_2O_2]_{t_2} - [H_2O_2]_{t_1}}{t_2 - t_1} \\ &= -\frac{\Delta[H_2O_2]}{\Delta t}\end{aligned}$$

This mathematical representation of the change in species concentration over time is the rate expression for the reaction. The brackets indicate molar concentrations, and the symbol delta (Δ) indicates "change in." Thus, $[H_2O_2]_{t_1}$ represents the molar concentration of hydrogen peroxide at some time t_1; likewise, $[H_2O_2]_{t_2}$ represents the molar concentration of hydrogen peroxide at a later time t_2; and $\Delta[H_2O_2]$ represents the change in molar concentration of hydrogen peroxide during the time interval Δt (that is, $t_2 - t_1$). Since the reactant concentration decreases as the reaction proceeds, $\Delta[H_2O_2]$ is a negative quantity; we place a negative sign in front of the expression because reaction rates are, by convention, positive quantities. Figure **8.2.1** provides an example of data collected during the decomposition of H_2O_2.

Time (h)	$[H_2O_2]$ (mol L^{-1})	$\Delta[H_2O_2]$ (mol L^{-1})	Δt (h)	Rate of Decomposition, (mol/L/h)
0.00	1.000			
		−0.500	6.00	−0.0833
6.00	0.500			
		−0.250	6.00	−0.0417
12.00	0.250			
		−0.125	6.00	−0.0208
18.00	0.125			
		−0.062	6.00	−0.0103
24.00	0.0625			

Figure **8.2.1**: The rate of decomposition of H_2O_2 in an aqueous solution decreases as the concentration of H_2O_2 decreases.

To obtain the tabulated results for this decomposition, the concentration of hydrogen peroxide was measured every 6 hours over the course of a day at a constant temperature of 40 °C. Reaction rates were computed for each time interval by dividing the change in concentration by the corresponding time increment, as shown here for the first 6-hour period:

$$\frac{-\Delta[H_2O_2]}{\Delta t} = \frac{-(0.500\ \text{mol/L} - 1.000\ \text{mol/L})}{(6.00\ \text{h} - 0.00\ \text{h})} = 0.0833\ \text{mol L}^{-1}\ \text{h}^{-1}$$

Notice that the reaction rates vary with time, decreasing as the reaction proceeds. Results for the last 6-hour period yield a reaction rate of:

$$\frac{-\Delta[H_2O_2]}{\Delta t} = \frac{-(0.0625\ \text{mol/L} - 0.125\ \text{mol/L})}{(24.00\ \text{h} - 18.00\ \text{h})} = 0.0104\ \text{mol L}^{-1}\ \text{h}^{-1}$$

This behavior indicates the reaction continually slows with time. Using the concentrations at the beginning and end of a time period over which the reaction rate is changing results in the calculation of an average rate for the reaction over this time interval. At any specific time, the rate at which a reaction is proceeding is known as its instantaneous rate. The instantaneous rate of a reaction at "time zero," when the reaction commences, is its initial rate. Consider the analogy of a car slowing down as it approaches a stop sign. The vehicle's initial rate—analogous to the beginning of a chemical reaction—would be the speedometer reading at the moment the driver begins pressing the brakes (t_0). A few moments later, the instantaneous rate at a specific moment—call it t_1—would be somewhat slower, as indicated by the speedometer reading at that point in time. As time passes, the instantaneous rate will continue to fall until it reaches zero, when the car (or reaction) stops. Unlike instantaneous speed, the car's average speed is not indicated by the speedometer; but it can be calculated as the ratio of the distance traveled to the time required to bring the vehicle to a complete stop (Δt). Like the decelerating car, the average rate of a chemical reaction will fall somewhere between its initial and final rates.

The instantaneous rate of a reaction may be determined one of two ways. If experimental conditions permit the measurement of concentration changes over very short time intervals, then average rates computed as described earlier provide reasonably good approximations of instantaneous rates. Alternatively, a graphical procedure may be used that, in effect, yields the results that would be obtained if short time interval measurements were possible. If we plot the concentration of hydrogen peroxide against time, the instantaneous rate of decomposition of H_2O_2 at any time t is given by the slope of a straight line that is tangent to the curve at that time (Figure **8.2.2**). We can use calculus to evaluating the slopes of such tangent lines, but the procedure for doing so is beyond the scope of this chapter.

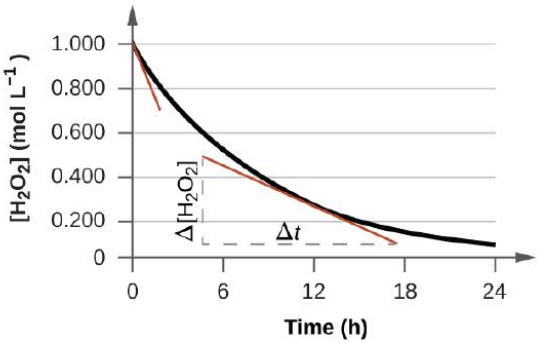


Figure **8.2.1**: This graph shows a plot of concentration versus time for a 1.000 M solution of H_2O_2. The rate at any instant is equal to the opposite of the slope of a line tangential to this curve at that time. Tangents are shown at t = 0 h ("initial rate") and at t = 10 h ("instantaneous rate" at that particular time).

Reaction Rates in Analysis: Test Strips for Urinalysis

Physicians often use disposable test strips to measure the amounts of various substances in a patient's urine (Figure **8.2.2**). These test strips contain various chemical reagents, embedded in small pads at various locations along the strip, which undergo changes in color upon exposure to sufficient concentrations of specific substances. The usage instructions for test strips often stress that proper read time is critical for optimal results. This emphasis on read time suggests that kinetic aspects of the chemical reactions occurring on the test strip are important considerations.

The test for urinary glucose relies on a two-step process represented by the chemical equations shown here:

$$C_6H_{12}O_6 + O_2 \xrightarrow[\text{catalyst}]{} C_6H_{10}O_6 + H_2O_2 \qquad (8.2.1)$$

$$2\,H_2O_2 + 2\,I^- \xrightarrow[\text{catalyst}]{} I_2 + 2\,H_2O + O_2 \tag{8.2.2}$$

Equation 8.2.1 depicts the oxidation of glucose in the urine to yield glucolactone and hydrogen peroxide. The hydrogen peroxide produced subsequently oxidizes colorless iodide ion to yield brown iodine (Equation 8.2.2), which may be visually detected. Some strips include an additional substance that reacts with iodine to produce a more distinct color change.

The two test reactions shown above are inherently very slow, but their rates are increased by special enzymes embedded in the test strip pad. This is an example of *catalysis*, a topic discussed later in this chapter. A typical glucose test strip for use with urine requires approximately 30 seconds for completion of the color-forming reactions. Reading the result too soon might lead one to conclude that the glucose concentration of the urine sample is lower than it actually is (a *false-negative* result). Waiting too long to assess the color change can lead to a *false positive* due to the slower (not catalyzed) oxidation of iodide ion by other substances found in urine.

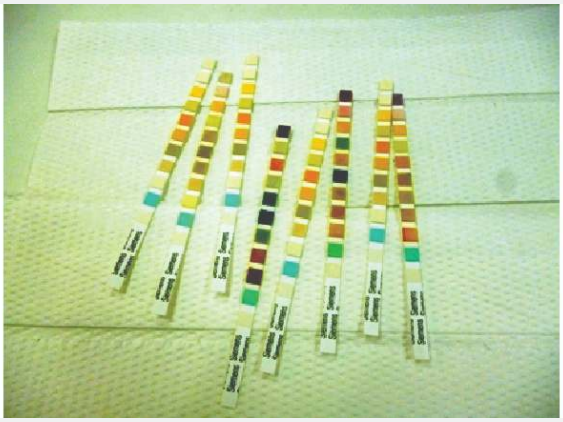


Figure **8.2.2**: Test strips are commonly used to detect the presence of specific substances in a person's urine. Many test strips have several pads containing various reagents to permit the detection of multiple substances on a single strip. (credit: Iqbal Osman).

Relative Rates of Reaction

The rate of a reaction may be expressed in terms of the change in the amount of any reactant or product, and may be simply derived from the stoichiometry of the reaction. Consider the reaction represented by the following equation:

$$2\,NH_3(g) \longrightarrow N_2(g) + 3\,H_2(g)$$

The stoichiometric factors derived from this equation may be used to relate reaction rates in the same manner that they are used to related reactant and product amounts. The relation between the reaction rates expressed in terms of nitrogen production and ammonia consumption, for example, is:

$$-\frac{\Delta \text{mol } NH_3}{\Delta t} \times \frac{1 \text{ mol } N_2}{2 \text{ mol } NH_3} = \frac{\Delta \text{mol } N_2}{\Delta t}$$

We can express this more simply without showing the stoichiometric factor's units:

$$-\frac{1}{2}\frac{\Delta \text{mol } NH_3}{\Delta t} = \frac{\Delta \text{mol } N_2}{\Delta t}$$

Note that a negative sign has been added to account for the opposite signs of the two amount changes (the reactant amount is decreasing while the product amount is increasing). If the reactants and products are present in the same solution, the molar amounts may be replaced by concentrations:

$$-\frac{1}{2}\frac{\Delta[NH_3]}{\Delta t} = \frac{\Delta[N_2]}{\Delta t}$$

Similarly, the rate of formation of H_2 is three times the rate of formation of N_2 because three moles of H_2 form during the time required for the formation of one mole of N_2:

$$\frac{1}{3}\frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[N_2]}{\Delta t}$$

Figure 8.2.3 illustrates the change in concentrations over time for the decomposition of ammonia into nitrogen and hydrogen at 1100 °C. We can see from the slopes of the tangents drawn at t = 500 seconds that the instantaneous rates of change in the concentrations of the reactants and products are related by their stoichiometric factors. The rate of hydrogen production, for example, is observed to be three times greater than that for nitrogen production:

$$\frac{2.91 \times 10^{-6}\ M/s}{9.71 \times 10^{-6}\ M/s} \approx 3$$

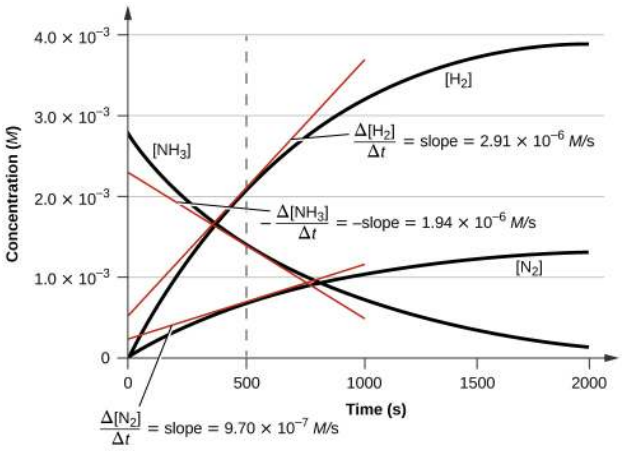


Figure 8.2.3: This graph shows the changes in concentrations of the reactants and products during the reaction $2\,NH_3 \longrightarrow N_2 + 3\,H_2$. *The rates of change of the three concentrations are related by their stoichiometric factors, as shown by the different slopes of the tangents at t = 500 s.*

Example 8.2.1: Expressions for Relative Reaction Rates

The first step in the production of nitric acid is the combustion of ammonia:

$$4\,NH_3(g) + 5\,O_2(g) \longrightarrow 4\,NO(g) + 6\,H_2O(g)$$

Write the equations that relate the rates of consumption of the reactants and the rates of formation of the products.

Solution

Considering the stoichiometry of this homogeneous reaction, the rates for the consumption of reactants and formation of products are:

$$-\frac{1}{4}\frac{\Delta[NH_3]}{\Delta t} = -\frac{1}{5}\frac{\Delta[O_2]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO]}{\Delta t} = \frac{1}{6}\frac{\Delta[H_2O]}{\Delta t}$$

Exercise 8.2.1

The rate of formation of Br_2 is 6.0×10^{-6} mol/L/s in a reaction described by the following net ionic equation:

$$5\,Br^- + BrO_3^- + 6\,H^+ \longrightarrow 3\,Br_2 + 3\,H_2O$$

Write the equations that relate the rates of consumption of the reactants and the rates of formation of the products.

Answer

$$-\frac{1}{5}\frac{\Delta[Br^-]}{\Delta t} = -\frac{\Delta[BrO_3^-]}{\Delta t} = -\frac{1}{6}\frac{\Delta[H^+]}{\Delta t} = \frac{1}{3}\frac{\Delta[Br_2]}{\Delta t} = \frac{1}{3}\frac{\Delta[H_2O]}{\Delta t}$$

Example 8.2.2: Reaction Rate Expressions for Decomposition of H_2O_2

The graph in Figure **8.2.3** shows the rate of the decomposition of H_2O_2 over time:

$$2\,H_2O_2 \longrightarrow 2\,H_2O + O_2$$

Based on these data, the instantaneous rate of decomposition of H_2O_2 at t = 11.1 h is determined to be 3.20×10^{-2} mol/L/h, that is:

$$-\frac{\Delta[H_2O_2]}{\Delta t} = 3.20 \times 10^{-2}\ \text{mol}\ \text{L}^{-1}\ \text{h}^{-1}$$

What is the instantaneous rate of production of H_2O and O_2?

Solution

Using the stoichiometry of the reaction, we may determine that:

$$-\frac{1}{2}\frac{\Delta[H_2O_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[H_2O]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

Therefore:

$$\frac{1}{2} \times 3.20 \times 10^{-2}\ \text{mol}\ \text{L}^{-1}\ \text{h}^{-1} = \frac{\Delta[O_2]}{\Delta t}$$

and

$$\frac{\Delta[O_2]}{\Delta t} = 1.60 \times 10^{-2}\ \text{mol}\ \text{L}^{-1}\ \text{h}^{-1}$$

Exercise 8.2.2

If the rate of decomposition of ammonia, NH_3, at 1150 K is 2.10×10^{-6} mol/L/s, what is the rate of production of nitrogen and hydrogen?

Answer

1.05×10^{-6} mol/L/s, N_2 and 3.15×10^{-6} mol/L/s, H_2.

Summary

The rate of a reaction can be expressed either in terms of the decrease in the amount of a reactant or the increase in the amount of a product per unit time. Relations between different rate expressions for a given reaction are derived directly from the stoichiometric coefficients of the equation representing the reaction.

Glossary

average rate
rate of a chemical reaction computed as the ratio of a measured change in amount or concentration of substance to the time interval over which the change occurred

initial rate
instantaneous rate of a chemical reaction at t = 0 s (immediately after the reaction has begun)

instantaneous rate
rate of a chemical reaction at any instant in time, determined by the slope of the line tangential to a graph of concentration as a function of time

rate of reaction
measure of the speed at which a chemical reaction takes place

rate expression

mathematical representation relating reaction rate to changes in amount, concentration, or pressure of reactant or product species per unit time

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8.3: Factors Affecting Reaction Rates

Learning Objectives

- Describe the effects of chemical nature, physical state, temperature, concentration, and catalysis on reaction rates

The rates at which reactants are consumed and products are formed during chemical reactions vary greatly. We can identify five factors that affect the rates of chemical reactions: the chemical nature of the reacting substances, the state of subdivision (one large lump versus many small particles) of the reactants, the temperature of the reactants, the concentration of the reactants, and the presence of a catalyst.

The Chemical Nature of the Reacting Substances

The rate of a reaction depends on the nature of the participating substances. Reactions that appear similar may have different rates under the same conditions, depending on the identity of the reactants. For example, when small pieces of the metals iron and sodium are exposed to air, the sodium reacts completely with air overnight, whereas the iron is barely affected. The active metals calcium and sodium both react with water to form hydrogen gas and a base. Yet calcium reacts at a moderate rate, whereas sodium reacts so rapidly that the reaction is almost explosive.

The State of Subdivision of the Reactants

Except for substances in the gaseous state or in solution, reactions occur at the boundary, or interface, between two phases. Hence, the rate of a reaction between two phases depends to a great extent on the surface contact between them. A finely divided solid has more surface area available for reaction than does one large piece of the same substance. Thus a liquid will react more rapidly with a finely divided solid than with a large piece of the same solid. For example, large pieces of iron react slowly with acids; finely divided iron reacts much more rapidly (Figure **8.3.1**). Large pieces of wood smolder, smaller pieces burn rapidly, and saw dust burns explosively.



Figure **8.3.1**: (a) Iron powder reacts rapidly with dilute hydrochloric acid and produces bubbles of hydrogen gas because the powder has a large total area: 2Fe(s) + 6HCl(aq) ⟶ 2FeCl3(aq) + 3H2(g). (surfaceb) An iron nail reacts more slowly.

This figure shows two photos labeled (a) and (b). Photo (a) shows the bottom of a test tube. The test tube is filled with a dark gas, and there is a dark substance and bubbles in the bottom. Photo (b) shows a rod and bubbles in a test tube similar to photo (a), but the gas in the test tube is not as dark.



Video* 8.3.1: The reaction of cesium with water in slow motion and a discussion of how the state of reactants and particle size affect reaction rates.*

Temperature of the Reactants

Chemical reactions typically occur faster at higher temperatures. Food can spoil quickly when left on the kitchen counter. However, the lower temperature inside of a refrigerator slows that process so that the same food remains fresh for days. We use a burner or a hot plate in the laboratory to increase the speed of reactions that proceed slowly at ordinary temperatures. In many cases, an increase in temperature of only 10 °C will approximately double the rate of a reaction in a homogeneous system.

Concentrations of the Reactants

The rates of many reactions depend on the concentrations of the reactants. Rates usually increase when the concentration of one or more of the reactants increases. For example, calcium carbonate ($\mathbf{CaCO_3}$) deteriorates as a result of its reaction with the pollutant sulfur dioxide. The rate of this reaction depends on the amount of sulfur dioxide in the air (Figure **8.3.2**). As an acidic oxide, sulfur dioxide combines with water vapor in the air to produce sulfurous acid in the following reaction:

$$\mathbf{SO_{2(g)} + H_2O_{(g)} \longrightarrow H_2SO_{3(aq)}} \tag{8.3.1}$$

Calcium carbonate reacts with sulfurous acid as follows:

$$\mathbf{CaCO_{3(s)} + H_2SO_{3(aq)} \longrightarrow CaSO_{3(aq)} + CO_{2(g)} + H_2O_{(l)}} \tag{8.3.2}$$

In a polluted atmosphere where the concentration of sulfur dioxide is high, calcium carbonate deteriorates more rapidly than in less polluted air. Similarly, phosphorus burns much more rapidly in an atmosphere of pure oxygen than in air, which is only about 20% oxygen.

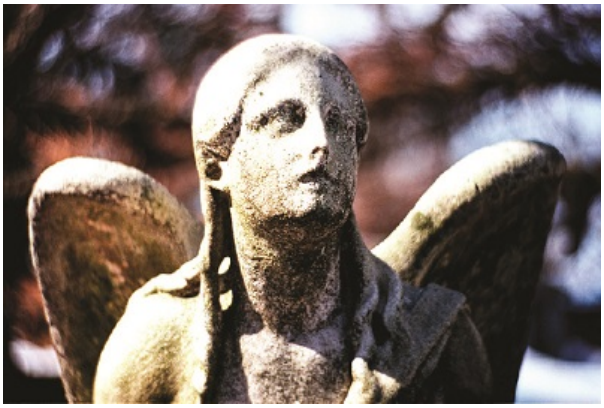


Figure **8.3.2**: Statues made from carbonate compounds such as limestone and marble typically weather slowly over time due to the actions of water, and thermal expansion and contraction. However, pollutants like sulfur dioxide can accelerate weathering. As the concentration of air pollutants increases, deterioration of limestone occurs more rapidly. (credit: James P Fisher III).

A photograph is shown of an angel statue. While some details of the statue, including facial features, are present, effects of weathering appear to be diminishing these features.



***Video* 8.3.2**: *Phosphorous burns rapidly in air, but it will burn even more rapidly if the concentration of oxygen in is higher.*

The Presence of a Catalyst

Hydrogen peroxide solutions foam when poured onto an open wound because substances in the exposed tissues act as catalysts, increasing the rate of hydrogen peroxide's decomposition. However, in the absence of these catalysts (for example, in the bottle in the medicine cabinet) complete decomposition can take months. A catalyst is a substance that increases the rate of a chemical reaction by lowering the activation energy without itself being consumed by the reaction. Activation energy is the minimum amount of energy required for a chemical reaction to proceed in the forward direction. A catalyst increases the reaction rate by providing an alternative pathway or mechanism for the reaction to follow (Figure **8.3.3**). Catalysis will be discussed in greater detail later in this chapter as it relates to mechanisms of reactions.

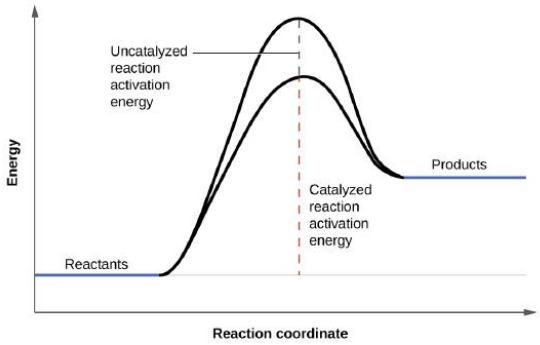


Figure **8.3.3**: The presence of a catalyst increases the rate of a reaction by lowering its activation energy.

A graph is shown with the label, "Reaction coordinate," on the x-axis. The x-axis is depicted as an arrow. The y-axis is also an arrow and is labeled, "Energy." There is a horizontal line that runs the width of the graph and appears just above the x-axis. A segment of this line is blue and is labeled, "Reactants." From the right end of this line segment, a solid black, concave down curve is shown which reaches the level just below the end of the y-axis. The curve ends at another short, blue line labeled, "Products." The "Products" line appears at a higher level than the "Reactants" line. An arrow extends from the horizontal line to the apex of the curve. The arrow is labeled, "Uncatalyzed reaction activation energy." A second, black concave down curve is shown. This curve also meets the reactants and products blue line segments, but only extends to about two-thirds the height of the initial curve. From the horizontal line is another arrow pointing to the apex of the second curve. This arrow is labeled, "Catalyzed reaction activation energy."

> *Chemical reactions occur when molecules collide with each other and undergo a chemical transformation. Before physically performing a reaction in a laboratory, scientists can use molecular modeling simulations to predict how the parameters discussed earlier will influence the rate of a reaction. Use the PhET Reactions & Rates interactive to explore how temperature, concentration, and the nature of the reactants affect reaction rates.*

Summary

The rate of a chemical reaction is affected by several parameters. Reactions involving two phases proceed more rapidly when there is greater surface area contact. If temperature or reactant concentration is increased, the rate of a given reaction generally increases as well. A catalyst can increase the rate of a reaction by providing an alternative pathway that causes the activation energy of the reaction to decrease.

Glossary

catalyst

substance that increases the rate of a reaction without itself being consumed by the reaction

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8.4: Rate Laws

Learning Objectives

- Explain the form and function of a rate law
- Use rate laws to calculate reaction rates
- Use rate and concentration data to identify reaction orders and derive rate laws

As described in the previous module, the rate of a reaction is affected by the concentrations of reactants. Rate laws or rate equations are mathematical expressions that describe the relationship between the rate of a chemical reaction and the concentration of its reactants. In general, a rate law (or differential rate law, as it is sometimes called) takes this form:

$$\text{rate} = k[A]^m[B]^n[C]^p \ldots$$

in which [*A*], [*B*], and [*C*] represent the molar concentrations of reactants, and *k* is the rate constant, which is specific for a particular reaction at a particular temperature. The exponents *m*, *n*, and *p* are usually positive integers (although it is possible for them to be fractions or negative numbers). The rate constant *k* and the exponents *m*, *n*, and *p* must be determined experimentally by observing how the rate of a reaction changes as the concentrations of the reactants are changed. The rate constant *k* is independent of the concentration of *A*, *B*, or *C*, but it does vary with temperature and surface area.

The exponents in a rate law describe the effects of the reactant concentrations on the reaction rate and define the reaction order. Consider a reaction for which the rate law is:

$$\text{rate} = k[A]^m[B]^n$$

If the exponent *m* is 1, the reaction is first order with respect to *A*. If *m* is 2, the reaction is second order with respect to *A*. If *n* is 1, the reaction is first order in *B*. If *n* is 2, the reaction is second order in *B*. If *m* or *n* is zero, the reaction is zero order in *A* or *B*, respectively, and the rate of the reaction is not affected by the concentration of that reactant. The overall reaction order is the sum of the orders with respect to each reactant. If *m* = 1 and *n* = 1, the overall order of the reaction is second order (*m* + *n* = 1 + 1 = 2).

The rate law:

$$\text{rate} = k[\text{H}_2\text{O}_2]$$

describes a reaction that is first order in hydrogen peroxide and first order overall. The rate law:

$$\text{rate} = k[\text{C}_4\text{H}_6]^2$$

describes a reaction that is second order in C_4H_6 and second order overall. The rate law:

$$\text{rate} = k[\text{H}^+][\text{OH}^-]$$

describes a reaction that is first order in H^+, first order in OH^-, and second order overall.

Example 8.4.1: Writing Rate Laws from Reaction Orders

An experiment shows that the reaction of nitrogen dioxide with carbon monoxide:

$$\text{NO}_2(g) + \text{CO}(g) \longrightarrow \text{NO}(g) + \text{CO}_2(g)$$

is second order in NO_2 and zero order in CO at 100 °C. What is the rate law for the reaction?

Solution

The reaction will have the form:

$$\text{rate} = k[\text{NO}_2]^m[\text{CO}]^n$$

The reaction is second order in NO_2; thus *m* = 2. The reaction is zero order in CO; thus *n* = 0. The rate law is:

$$\text{rate} = k[\text{NO}_2]^2[\text{CO}]^0 = k[\text{NO}_2]^2$$

Remember that a number raised to the zero power is equal to 1, thus $[CO]^0 = 1$, which is why we can simply drop the concentration of CO from the rate equation: the rate of reaction is solely dependent on the concentration of NO_2. When we consider rate mechanisms later in this chapter, we will explain how a reactant's concentration can have no effect on a reaction despite being involved in the reaction.

Exercise 8.4.1*A*

The rate law for the reaction:

$$\mathrm{H_2}(g) + 2\,\mathrm{NO}(g) \longrightarrow \mathrm{N_2O}(g) + \mathrm{H_2O}(g)$$

has been experimentally determined to be rate = $k[NO]^2[H_2]$. What are the orders with respect to each reactant, and what is the overall order of the reaction?

Answer

- order in NO = 2;
- order in H_2 = 1;
- overall order = 3

Exercise 8.4.1*B*

In a transesterification reaction, a triglyceride reacts with an alcohol to form an ester and glycerol. Many students learn about the reaction between methanol (CH_3OH) and ethyl acetate ($CH_3CH_2OCOCH_3$) as a sample reaction before studying the chemical reactions that produce biodiesel:

$$\mathrm{CH_3OH} + \mathrm{CH_3CH_2OCOCH_3} \longrightarrow \mathrm{CH_3OCOCH_3} + \mathrm{CH_3CH_2OH}$$

The rate law for the reaction between methanol and ethyl acetate is, under certain conditions, experimentally determined to be:

$$\text{rate} = k[\mathrm{CH_3OH}]$$

What is the order of reaction with respect to methanol and ethyl acetate, and what is the overall order of reaction?

Answer

- order in CH_3OH = 1;
- order in $CH_3CH_2OCOCH_3$ = 0;
- overall order = 1

It is sometimes helpful to use a more explicit algebraic method, often referred to as the method of initial rates, to determine the orders in rate laws. To use this method, we select two sets of rate data that differ in the concentration of only one reactant and set up a ratio of the two rates and the two rate laws. After canceling terms that are equal, we are left with an equation that contains only one unknown, the coefficient of the concentration that varies. We then solve this equation for the coefficient.

Example 8.4.2: Determining a Rate Law from Initial Rates

Ozone in the upper atmosphere is depleted when it reacts with nitrogen oxides. The rates of the reactions of nitrogen oxides with ozone are important factors in deciding how significant these reactions are in the formation of the ozone hole over Antarctica (Figure 8.4.1). One such reaction is the combination of nitric oxide, NO, with ozone, O_3:

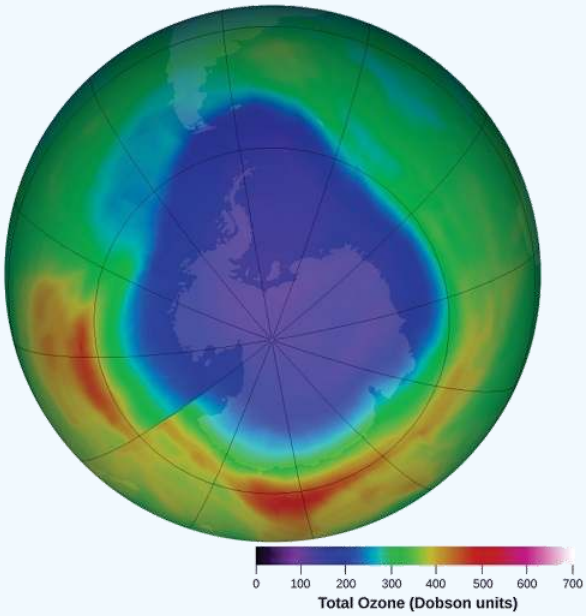


Figure **8.4.1**: Over the past several years, the atmospheric ozone concentration over Antarctica has decreased during the winter. This map shows the decreased concentration as a purple area. (credit: modification of work by NASA)

A view of Earth's southern hemisphere is shown. A nearly circular region of approximately half the diameter of the image is shown in shades of purple, with Antarctica appearing in a slightly lighter color than the surrounding ocean areas. Immediately outside this region is a narrow bright blue zone followed by a bright green zone. In the top half of the figure, the purple region extends slightly outward from the circle and the blue zone extends more outward to the right of the center as compared to the lower half of the image. In the upper half of the image, the majority of the space outside the purple region is shaded green, with a few small strips of interspersed blue regions. The lower half however shows the majority of the space outside the central purple zone in yellow, orange, and red. The red zones appear in the lower central and left regions outside the purple zone. To the lower right of this image is a color scale that is labeled "Total Ozone (Dobsone units)." This scale begins at 0 and increases by 100's up to 700. At the left end of the scale, the value 0 shows a very deep purple color, 100 is indigo, 200 is blue, 300 is green, 400 is a yellow-orange, 500 is red, 600 is pink, and 700 is white.

$$\mathrm{NO}(g) + \mathrm{O_3}(g) \longrightarrow \mathrm{NO_2}(g) + \mathrm{O_2}(g)$$

This reaction has been studied in the laboratory, and the following rate data were determined at 25 °C.

Trial	[NO] (mol/L)	$[O_3]$ (mol/L)	$\frac{\Delta[NO_2]}{\Delta t}$ $(\mathrm{mol\,L^{-1}\,s^{-1}})$
1	1.00×10^{-6}	3.00×10^{-6}	6.60×10^{-5}
2	1.00×10^{-6}	6.00×10^{-6}	1.32×10^{-4}
3	1.00×10^{-6}	9.00×10^{-6}	1.98×10^{-4}
4	2.00×10^{-6}	9.00×10^{-6}	3.96×10^{-4}
5	3.00×10^{-6}	9.00×10^{-6}	5.94×10^{-4}

Determine the rate law and the rate constant for the reaction at 25 °C.

Solution

The rate law will have the form:

$$\text{rate} = k[\mathrm{NO}]^m[\mathrm{O_3}]^n$$

We can determine the values of *m*, *n*, and *k* from the experimental data using the following three-part process:

1. *Determine the value of* m *from the data in which [NO] varies and [O_3] is constant.* In the last three experiments, [NO] varies while [O_3] remains constant. When [NO] doubles from trial 3 to 4, the rate doubles, and when [NO] triples from trial 3 to 5, the rate also triples. Thus, the rate is also directly proportional to [NO], and *m* in the rate law is equal to 1.

2. *Determine the value of* n *from data in which [O_3] varies and [NO] is constant.* In the first three experiments, [NO] is constant and [O_3] varies. The reaction rate changes in direct proportion to the change in [O_3]. When [O_3] doubles from trial 1 to 2, the rate doubles; when [O_3] triples from trial 1 to 3, the rate increases also triples. Thus, the rate is directly proportional to [O_3], and *n* is equal to 1.The rate law is thus:

$$\text{rate} = k[\text{NO}]^1[\text{O}_3]^1 = k[\text{NO}][\text{O}_3]$$

3. *Determine the value of* k *from one set of concentrations and the corresponding rate*.

$$\begin{aligned} k &= \frac{\text{rate}}{[\text{NO}][\text{O}_3]} \\ &= \frac{6.60 \times 10^{-5}\ \cancel{\text{mol L}^{-1}}\ \text{s}^{-1}}{(1.00 \times 10^{-6}\ \cancel{\text{mol L}^{-1}})(3.00 \times 10^{-6}\ \text{mol L}^{-1})} \\ &= 2.20 \times 10^{7}\ \text{L mol}^{-1}\ \text{s}^{-1} \end{aligned}$$

The large value of *k* tells us that this is a fast reaction that could play an important role in ozone depletion if [NO] is large enough.

? Exercise 8.4.2

Acetaldehyde decomposes when heated to yield methane and carbon monoxide according to the equation:

$$\text{CH}_3\text{CHO}(g) \longrightarrow \text{CH}_4(g) + \text{CO}(g)$$

Determine the rate law and the rate constant for the reaction from the following experimental data:

Trial	[CH_3CHO] (mol/L)	$-\frac{\Delta[\text{CH}_3\text{CHO}]}{\Delta t}$ (mol L^{-1} s^{-1})
1	1.75×10^{-3}	2.06×10^{-11}
2	3.50×10^{-3}	8.24×10^{-11}
3	7.00×10^{-3}	3.30×10^{-10}

Answer

$\text{rate} = k[\text{CH}_3\text{CHO}]^2$ with $k = 6.73 \times 10^{-6}$ L/mol/s

✓ Example 8.4.3: Determining Rate Laws from Initial Rates

Using the initial rates method and the experimental data, determine the rate law and the value of the rate constant for this reaction:

$$2\,\text{NO}(g) + \text{Cl}_2(g) \longrightarrow 2\,\text{NOCl}(g)$$

Trial	[NO] (mol/L)	[Cl_2] (mol/L)	$-\frac{\Delta[\text{NO}]}{2\Delta t}$ (mol L^{-1} s^{-1})
1	0.10	0.10	0.00300
2	0.10	0.15	0.00450
3	0.15	0.10	0.00675

Solution

The rate law for this reaction will have the form:

$$\text{rate} = k[\text{NO}]^m[\text{Cl}_2]^n$$

As in Example **8.4.2**, we can approach this problem in a stepwise fashion, determining the values of *m* and *n* from the experimental data and then using these values to determine the value of *k*. In this example, however, we will use a different approach to determine the values of *m* and *n*:

Determine the value of m *from the data in which [NO] varies and [Cl_2] is constant.* We can write the ratios with the subscripts *x* and *y* to indicate data from two different trials:

$$\frac{\text{rate}_x}{\text{rate}_y} = \frac{k[\text{NO}]_x^m[\text{Cl}_2]_x^n}{k[\text{NO}]_y^m[\text{Cl}_2]_y^n}$$

Using the third trial and the first trial, in which [Cl_2] does not vary, gives:

$$\frac{\text{rate 3}}{\text{rate 1}} = \frac{0.00675}{0.00300} = \frac{k(0.15)^m(0.10)^n}{k(0.10)^m(0.10)^n}$$

After canceling equivalent terms in the numerator and denominator, we are left with:

$$\frac{0.00675}{0.00300} = \frac{(0.15)^m}{(0.10)^m}$$

which simplifies to:

$$2.25 = (1.5)^m$$

We can use natural logs to determine the value of the exponent *m*:

$$\ln(2.25) = m\ln(1.5)\frac{\ln(2.25)}{\ln(1.5)} \qquad = m2 = m$$

We can confirm the result easily, since:

$$1.5^2 = 2.25$$

- *Determine the value of* n *from data in which [Cl_2] varies and [NO] is constant.*

  $$\frac{\text{rate 2}}{\text{rate 1}} = \frac{0.00450}{0.00300} = \frac{k(0.10)^m(0.15)^n}{k(0.10)^m(0.10)^n}$$

  Cancelation gives:

  $$\frac{0.0045}{0.0030} = \frac{(0.15)^n}{(0.10)^n}$$

  which simplifies to:

  $$1.5 = (1.5)^n$$

  Thus *n* must be 1, and the form of the rate law is:

  $$\text{Rate} = k[\text{NO}]^m[\text{Cl}_2]^n = k[\text{NO}]^2[\text{Cl}_2]$$

- *Determine the numerical value of the rate constant* k *with appropriate units.* The units for the rate of a reaction are mol/L/s. The units for *k* are whatever is needed so that substituting into the rate law expression affords the appropriate units for the rate. In this example, the concentration units are mol^3/L^3. The units for *k* should be $mol^{-2}\ L^2/s$ so that the rate is in terms of mol/L/s.

  To determine the value of *k* once the rate law expression has been solved, simply plug in values from the first experimental trial and solve for *k*:

  $$0.00300\ \text{mol L}^{-1}\ \text{s}^{-1} = k(0.10\ \text{mol L}^{-1})^2(0.10\ \text{mol L}^{-1})^1$$
  $$k = 3.0\ \text{mol}^{-2}\ \text{L}^2\ \text{s}^{-1}$$

? Exercise 8.4.3

Use the provided initial rate data to derive the rate law for the reaction whose equation is:

$$\text{OCl}^-(aq) + \text{I}^-(aq) \longrightarrow \text{OI}^-(aq) + \text{Cl}^-(aq)$$

Trial	[OCl^-] (mol/L)	[I^-] (mol/L)	Initial Rate (mol/L/s)
1	0.0040	0.0020	0.00184
2	0.0020	0.0040	0.00092
3	0.0020	0.0020	0.00046

Determine the rate law expression and the value of the rate constant k with appropriate units for this reaction.

Answer

$$\frac{\text{rate 2}}{\text{rate 3}} = \frac{0.00092}{0.00046} = \frac{k(0.0020)^x(0.0040)^y}{k(0.0020)^x(0.0020)^y}$$

$$2.00 = 2.00^y$$

$$y = 1$$

$$\frac{\text{rate 1}}{\text{rate 2}} = \frac{0.00184}{0.00092} = \frac{k(0.0040)^x(0.0020)^y}{k(0.0020)^x(0.0040)^y}$$

$$2.00 = \frac{2^x}{2^y}$$

$$2.00 = \frac{2^x}{2^1}$$

$$4.00 = 2^x$$

$$x = 2$$

Substituting the concentration data from trial 1 and solving for k yields:

$$\text{rate} = k[OCl^-]^2[I^-]^1$$

$$0.00184 = k(0.0040)^2(0.0020)^1$$

$$k = 5.75 \times 10^4\ \text{mol}^{-2}\ \text{L}^2\ \text{s}^{-1}$$

Reaction Order and Rate Constant Units

In some of our examples, the reaction orders in the rate law happen to be the same as the coefficients in the chemical equation for the reaction. This is merely a coincidence and very often not the case. Rate laws may exhibit fractional orders for some reactants, and negative reaction orders are sometimes observed when an increase in the concentration of one reactant causes a decrease in reaction rate. A few examples illustrating these points are provided:

$$NO_2 + CO \longrightarrow NO + CO_2 \quad \text{rate} = k[NO_2]^2$$

$$CH_3CHO \longrightarrow CH_4 + CO \quad \text{rate} = k[CH_3CHO]^2$$

$$2\,N_2O_5 \longrightarrow 2\,NO_2 + O_2 \quad \text{rate} = k[N_2O_5]$$

$$2\,NO_2 + F_2 \longrightarrow 2\,NO_2F \quad \text{rate} = k[NO_2][F_2]$$

$$2\,NO_2Cl \longrightarrow 2\,NO_2 + Cl_2 \quad \text{rate} = k[NO_2Cl]$$

> *It is important to note that rate laws are determined by experiment only and are not reliably predicted by reaction stoichiometry.*

Reaction orders also play a role in determining the units for the rate constant k. In Example 8.4.2, a second-order reaction, we found the units for k to be $\text{L mol}^{-1}\ \text{s}^{-1}$, whereas in Example 8.4.3, a third order reaction, we found the units for k to be $\text{mol}^{-2}\ \text{L}^2/\text{s}$. More generally speaking, the units for the rate constant for a reaction of order $(m + n)$ are $\text{mol}^{1-(m+n)}\text{L}^{(m+n)-1}\text{s}^{-1}$. Table 8.4.1 summarizes the rate constant units for common reaction orders.

Table 8.4.1: Rate Constants for Common Reaction Orders

Reaction Order	Units of k
$(m+n)$	$\text{mol}^{1-(m+n)}\text{L}^{(m+n)-1}\text{s}^{-1}$
zero	mol/L/s
first	s^{-1}
second	L/mol/s
third	$mol^{-2}\ L^2\ s^{-1}$

Note that the units in the table can also be expressed in terms of molarity (M) instead of mol/L. Also, units of time other than the second (such as minutes, hours, days) may be used, depending on the situation.

Summary

Rate laws provide a mathematical description of how changes in the amount of a substance affect the rate of a chemical reaction. Rate laws are determined experimentally and cannot be predicted by reaction stoichiometry. The order of reaction describes how much a change in the amount of each substance affects the overall rate, and the overall order of a reaction is the sum of the orders for each substance present in the reaction. Reaction orders are typically first order, second order, or zero order, but fractional and even negative orders are possible.

Glossary

method of initial rates
: use of a more explicit algebraic method to determine the orders in a rate law

overall reaction order
: sum of the reaction orders for each substance represented in the rate law

rate constant (k)
: proportionality constant in the relationship between reaction rate and concentrations of reactants

rate law
: (also, rate equation) mathematical equation showing the dependence of reaction rate on the rate constant and the concentration of one or more reactants

reaction order
: value of an exponent in a rate law, expressed as an ordinal number (for example, zero order for 0, first order for 1, second order for 2, and so on)

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8.5: Reaction Mechanisms

Learning Objectives

- Distinguish net reactions from elementary reactions (steps)
- Identify the molecularity of elementary reactions
- Write a balanced chemical equation for a process given its reaction mechanism
- Derive the rate law consistent with a given reaction mechanism

A balanced equation for a chemical reaction indicates what is reacting and what is produced, but it reveals nothing about how the reaction actually takes place. The reaction mechanism (or reaction path) is the process, or pathway, by which a reaction occurs. A chemical reaction often occurs in steps, although it may not always be obvious to an observer. The decomposition of ozone, for example, appears to follow a mechanism with two steps:

$$\begin{aligned} &O_3(g) \longrightarrow O_2(g) + O \\ &O + O_3(g) \longrightarrow 2\,O_2(g) \end{aligned} \tag{8.5.1}$$

We call each step in a reaction mechanism an elementary reaction. Elementary reactions occur exactly as they are written and cannot be broken down into simpler steps. Elementary reactions add up to the overall reaction, which, for the decomposition, is:

$$2\,O_3(g) \longrightarrow 3\,O_2(g) \tag{8.5.2}$$

Notice that the oxygen atom produced in the first step of this mechanism is consumed in the second step and therefore does not appear as a product in the overall reaction. Species that are produced in one step and consumed in a subsequent step are called intermediates.

While the overall reaction equation for the decomposition of ozone indicates that two molecules of ozone react to give three molecules of oxygen, the mechanism of the reaction does not involve the collision and reaction of two ozone molecules. Rather, it involves a molecule of ozone decomposing to an oxygen molecule and an intermediate oxygen atom; the oxygen atom then reacts with a second ozone molecule to give two oxygen molecules. These two elementary reactions occur exactly as they are shown in the reaction mechanism.

Unimolecular Elementary Reactions

The molecularity of an elementary reaction is the number of reactant species (atoms, molecules, or ions). For example, a unimolecular reaction involves the rearrangement of a *single* reactant species to produce one or more molecules of product:

$$A \longrightarrow \text{products} \tag{8.5.3}$$

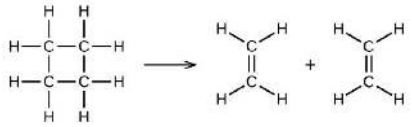
The rate equation for a unimolecular reaction is:

$$\text{rate} = k[A] \tag{8.5.4}$$

A unimolecular reaction may be one of several elementary reactions in a complex mechanism. For example, the reaction:

$$O_3 \longrightarrow O_2 + O \tag{8.5.5}$$

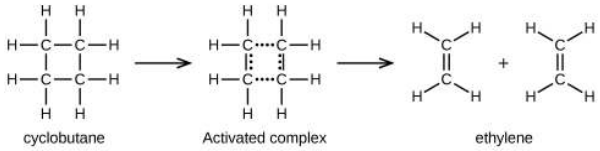
illustrates a unimolecular elementary reaction that occurs as one part of a two-step reaction mechanism. However, some unimolecular reactions may have only a single reaction in the reaction mechanism. (In other words, an elementary reaction can also be an overall reaction in some cases.) For example, the gas-phase decomposition of cyclobutane, C_4H_8, to ethylene, C_2H_4, occurs via a unimolecular, single-step mechanism:



In this figure, structural formulas are used to illustrate a chemical reaction. On the left, a structural formula for cyclobutane is shown. This structure is composed of 4 C atoms connected with single bonds in a square shape. Each C atom is bonded to two other C atoms in the structure, leaving two bonds for H atoms pointing outward above, below, left, and right. An arrow points right to two identical ethane molecules with a plus symbol between them. Each of these molecules contains two C atoms connected with a double bond oriented vertically between them. The C atom at the top of these molecules has H atoms bonded above to the right and left. Similarly, the lower C atom has two H atoms bonded below to the right and left.

For these unimolecular reactions to occur, all that is required is the separation of parts of single reactant molecules into products.

Chemical bonds do not simply fall apart during chemical reactions. Energy is required to break chemical bonds. The activation energy for the decomposition of C_4H_8, for example, is 261 kJ per mole. This means that it requires 261 kilojoules to distort one mole of these molecules into activated complexes that decompose into products:



In this figure, structural formulas are used to illustrate a chemical reaction, including an intermediate step. On the left, a structural formula for cyclobutane is shown. This structure is composed of 4 C atoms connected with single bonds in a square shape. Each C atom is bonded to two other C atoms in the structure, leaving two bonds for H atoms pointing outward above, below, left, and right. This structure is labeled, "Cyclohexane." An arrow points right to a similar structure which has the upper and lower bonds replaced by rows of 4 dots. Similarly, columns of 3 dots appear just inside the line segments indicating the vertically oriented single bonds in the structure. The label "Activated complex" appears beneath this structure. A second arrow points right to two identical ethane molecules with a plus symbol between them. Each of these molecules contains two C atoms connected with a double bond oriented vertically between them. The C atom at the top of these molecules has H atoms bonded above to the right and left. Similarly, the lower C atom has two H atoms bonded below to the right and left. Below these two molecules appears the label "Ethylene."

In a sample of C_4H_8, a few of the rapidly moving C_4H_8 molecules collide with other rapidly moving molecules and pick up additional energy. When the C_4H_8 molecules gain enough energy, they can transform into an activated complex, and the formation of ethylene molecules can occur. In effect, a particularly energetic collision knocks a C_4H_8 molecule into the geometry of the activated complex. However, only a small fraction of gas molecules travel at sufficiently high speeds with large enough kinetic energies to accomplish this. Hence, at any given moment, only a few molecules pick up enough energy from collisions to react.

The rate of decomposition of C_4H_8 is directly proportional to its concentration. Doubling the concentration of C_4H_8 in a sample gives twice as many molecules per liter. Although the fraction of molecules with enough energy to react remains the same, the total number of such molecules is twice as great. Consequently, there is twice as much C_4H_8 per liter, and the reaction rate is twice as fast:

$$\text{rate} = -\frac{\Delta[C_4H_8]}{\Delta t} = k[C_4H_8] \tag{8.5.6}$$

A similar relationship applies to any unimolecular elementary reaction; the reaction rate is directly proportional to the concentration of the reactant, and the reaction exhibits first-order behavior. The proportionality constant is the rate constant for the particular unimolecular reaction.

Bimolecular Elementary Reactions

The collision and combination of two molecules or atoms to form an activated complex in an elementary reaction is called a bimolecular reaction. There are two types of bimolecular elementary reactions:

$$A + B \longrightarrow \text{products} \tag{8.5.7}$$

and

$$2A \longrightarrow \text{products} \tag{8.5.8}$$

For the first type, in which the two reactant molecules are different, the rate law is first-order in A and first order in B:

$$\text{rate} = k[A][B] \tag{8.5.9}$$

For the second type, in which two identical molecules collide and react, the rate law is second order in A:

$$\text{rate} = k[A][A] = k[A]^2 \tag{8.5.10}$$

Some chemical reactions have mechanisms that consist of a single bimolecular elementary reaction. One example is the reaction of nitrogen dioxide with carbon monoxide:

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g) \tag{8.5.11}$$

(see Figure 8.5.1)

Figure 8.5.1: The probable mechanism for the reaction between NO_2 and CO to yield NO and CO_2.

This figure provides an illustration of a reaction between two H I molecules using space filling models. H atoms are shown as white spheres, and I atoms are shown as purple spheres. On the left, two H I molecules are shownwith a small white sphere bonded to a much larger purple sphere. The label, “Two H I molecules,” appears below. An arrow points right to a similar structure in which the two molecules appear pushed together, so that the purple spheres of the two molecules are touching. Below appears the label, “Transition state.” Following another arrow, two white spheres are shown vertically oriented and bonded together with the label, “H subscript 2” above. The H subscript 2 molecule is followed by a plus sign and two purple spheres bonded together with the label, “I subscript 2” above. Below these structures is the label, “Hydrogen iodide molecules decompose to produce hydrogen H subscript 2 and iodine I subscript 2.”

Bimolecular elementary reactions may also be involved as steps in a multistep reaction mechanism. The reaction of atomic oxygen with ozone is one example:

$$O(g) + O_3(g) \longrightarrow 2\,O_2(g) \tag{8.5.12}$$

Termolecular Elementary Reactions

An elementary termolecular reaction involves the simultaneous collision of three atoms, molecules, or ions. Termolecular elementary reactions are uncommon because the probability of three particles colliding simultaneously is less than one one-thousandth of the probability of two particles colliding. There are, however, a few established termolecular elementary reactions. The reaction of nitric oxide with oxygen appears to involve termolecular steps:

$$2\,NO + O_2 \longrightarrow 2\,NO_2 \tag{8.5.13}$$
$$\text{rate} = k[NO]^2[O_2]$$

Likewise, the reaction of nitric oxide with chlorine appears to involve termolecular steps:

$$2\,NO + Cl_2 \longrightarrow 2\,NOCl \tag{8.5.14}$$
$$\text{rate} = k[NO]^2[Cl_2]$$

Relating Reaction Mechanisms to Rate Laws

It's often the case that one step in a multistep reaction mechanism is significantly slower than the others. Because a reaction cannot proceed faster than its slowest step, this step will limit the rate at which the overall reaction occurs. The slowest step is therefore called the rate-limiting step (or rate-determining step) of the reaction Figure 8.5.2.



Figure 8.5.2: A cattle chute is a nonchemical example of a rate-determining step. Cattle can only be moved from one holding pen to another as quickly as one animal can make its way through the chute. (credit: Loren Kerns)

A photo is shown of cattle passing through a narrow chute into a holding pen. A person directs them through the gate with a long white and red pole.

As described earlier, rate laws may be derived directly from the chemical equations for elementary reactions. This is not the case, however, for ordinary chemical reactions. The balanced equations most often encountered represent the overall change for some chemical system, and very often this is the result of some multistep reaction mechanisms. In every case, we must determine the overall rate law from experimental data and deduce the mechanism from the rate law (and sometimes from other data). The reaction of NO_2 and CO provides an illustrative example:

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

For temperatures above 225 °C, the rate law has been found to be:

$$\text{rate} = k[NO_2][CO]$$

The reaction is first order with respect to NO_2 and first-order with respect to CO. This is consistent with a single-step bimolecular mechanism and it is *possible* that this is the mechanism for this reaction at high temperatures.

At temperatures below 225 °C, the reaction is described by a rate law that is second order with respect to NO_2:

$$\text{rate} = k[NO_2]^2$$

This is consistent with a mechanism that involves the following two elementary reactions, the first of which is slower and is therefore the rate-determining step:

$$\begin{aligned} &\mathrm{NO_2}(g) + \mathrm{NO_2}(g) \longrightarrow \mathrm{NO_3}(g) + \mathrm{NO}(g) \text{ (slow)} \\ &\mathrm{NO_3}(g) + \mathrm{CO}(g) \longrightarrow \mathrm{NO_2}(g) + \mathrm{CO_2}(g) \text{ (fast)} \end{aligned}$$

The rate-determining step gives a rate law showing second-order dependence on the NO_2 concentration, and the sum of the two equations gives the net overall reaction.

In general, when the rate-determining (slower) step is the first step in a mechanism, the rate law for the overall reaction is the same as the rate law for this step. However, when the rate-determining step is preceded by a step involving an *equilibrium* reaction, the rate law for the overall reaction may be more difficult to derive.

An elementary reaction is at equilibrium when it proceeds in both the forward and reverse directions at equal rates. Consider the dimerization of NO to N_2O_2, with k_1 used to represent the rate constant of the forward reaction and k_{-1} used to represent the rate constant of the reverse reaction:

$$\mathrm{NO} + \mathrm{NO} \rightleftharpoons \mathrm{N_2O_2}$$

$$\mathrm{rate_{forward}} = \mathrm{rate_{reverse}}$$

$$k_1[\mathrm{NO}]^2 = k_{-1}[\mathrm{N_2O_2}]$$

If N_2O_2 was an intermediate in a mechanism, this expression could be rearranged to represent the concentration of N_2O_2 in the overall rate law expression using algebraic manipulation:

$$\left(\frac{k_1[\mathrm{NO}]^2}{k_{-1}}\right) = [\mathrm{N_2O_2}]$$

However, once again, intermediates cannot be listed as part of the overall rate law expression, though they can be included in an individual elementary reaction of a mechanism. Example **8.5.1** will illustrate how to derive overall rate laws from mechanisms involving equilibrium steps preceding the rate-determining step.

Example 8.5.1: Deriving the Overall Rate Law Expression for a Multistep Reaction

Mechanism Nitryl chloride (NO_2Cl) decomposes to nitrogen dioxide (NO_2) and chlorine gas (Cl_2) according to the following mechanism:

1. $\mathbf{2\,NO_2Cl}(g) \rightleftharpoons \mathbf{ClO_2}(g) + \mathbf{N_2O}(g) + \mathbf{ClO}(g)$ (fast, k_1 represents the rate constant for the forward reaction and k_{-1} the rate constant for the reverse reaction)
2. $\mathbf{N_2O}(g) + \mathbf{ClO_2}(g) \rightleftharpoons \mathbf{NO_2}(g) + \mathbf{NOCl}(g)$ (fast, k_2 for the forward reaction, k_{-2} for the reverse reaction)
3. $\mathbf{NOCl + ClO \longrightarrow NO_2 + Cl_2}$ (slow, k_3 the rate constant for the forward reaction)

Determine the overall reaction, write the rate law expression for each elementary reaction, identify any intermediates, and determine the overall rate law expression.

Solution

For the overall reaction, simply sum the three steps, cancel intermediates, and combine like formulas:

$$2\,\mathrm{NO_2Cl}(g) \longrightarrow 2\,\mathrm{NO_2}(g) + \mathrm{Cl_2}(g)$$

Next, write the rate law expression for each elementary reaction. Remember that for elementary reactions that are part of a mechanism, the rate law expression can be derived directly from the stoichiometry:

$$\begin{aligned} k_1[\mathrm{NO_2Cl}]_2 &= k_{-1}[\mathrm{ClO_2}][\mathrm{N_2O}][\mathrm{ClO}] \\ k_2[\mathrm{N_2O}][\mathrm{ClO_2}] &= k_{-2}[\mathrm{NO_2}][\mathrm{NOCl}] \\ \mathrm{Rate} &= k_3[\mathrm{NOCl}][\mathrm{ClO}] \end{aligned}$$

The third step, which is the slow step, is the rate-determining step. Therefore, the overall rate law expression could be written as Rate = k_3 [NOCl][ClO]. However, both NOCl and ClO are intermediates. Algebraic expressions must be used to represent [NOCl] and [ClO] such that no intermediates remain in the overall rate law expression.

- Using elementary reaction 1, $[\mathrm{ClO}] = \dfrac{k_1[\mathrm{NO_2Cl}]^2}{k_{-1}[\mathrm{ClO_2}][\mathrm{N_2O}]}$.
- Using elementary reaction 2, $[\mathrm{NOCl}] = \dfrac{k_2[\mathrm{N_2O}][\mathrm{ClO_2}]}{k_{-2}[\mathrm{NO_2}]}$.

Now substitute these algebraic expressions into the overall rate law expression and simplify:

$$\begin{aligned} \mathrm{rate} &= k_3\left(\frac{k_2[\mathrm{N_2O}][\mathrm{ClO_2}]}{k_{-2}[\mathrm{NO_2}]}\right)\left(\frac{k_1[\mathrm{NO_2Cl}]^2}{k_{-1}[\mathrm{ClO_2}][\mathrm{N_2O}]}\right) \\ \mathrm{rate} &= \frac{k_3k_2k_1[\mathrm{NO_2Cl}]^2}{k_{-2}k_{-1}[\mathrm{NO_2}]} \end{aligned}$$

Notice that this rate law shows an *inverse* dependence on the concentration of one of the product species, consistent with the presence of an equilibrium step in the reaction mechanism.

Exercise 8.5.1

Atomic chlorine in the atmosphere reacts with ozone in the following pair of elementary reactions:

$$\begin{aligned} &\mathrm{Cl} + \mathrm{O_3}(g) \longrightarrow \mathrm{ClO}(g) + \mathrm{O_2}(g) \quad \text{(rate constant } k_1\text{)} \\ &\mathrm{ClO}(g) + \mathrm{O} \longrightarrow \mathrm{Cl}(g) + \mathrm{O_2}(g) \quad \text{(rate constant } k_2\text{)} \end{aligned}$$

Determine the overall reaction, write the rate law expression for each elementary reaction, identify any intermediates, and determine the overall rate law expression.

Answer

- overall reaction: $\mathbf{O_3}(g) + \mathbf{O} \longrightarrow \mathbf{2\,O_2}(g)$
- $\mathrm{rate}_1 = k_1[\mathrm{O_3}][\mathrm{Cl}]$; $\mathrm{rate}_2 = k_2[\mathrm{ClO}][\mathrm{O}]$
- intermediate: ClO(g)
- overall rate = $k_2k_1[\mathrm{O_3}][\mathrm{Cl}][\mathrm{O}]$

Summary

The sequence of individual steps, or elementary reactions, by which reactants are converted into products during the course of a reaction is called the reaction mechanism. The overall rate of a reaction is determined by the rate of the slowest step, called the rate-determining step. Unimolecular elementary reactions have first-order rate laws, while bimolecular elementary reactions have second-order rate laws. By comparing the rate laws derived from a reaction mechanism to that determined experimentally, the mechanism may be deemed either incorrect or plausible.

Footnotes

1. This question is taken from the Chemistry Advanced Placement Examination and is used with the permission of the Educational Testing Service.

Glossary

bimolecular reaction
elementary reaction involving the collision and combination of two reactant species

elementary reaction
reaction that takes place precisely as depicted in its chemical equation

intermediate
molecule or ion produced in one step of a reaction mechanism and consumed in another

molecularity
number of reactant species (atoms, molecules or ions) involved in an elementary reaction

rate-determining step
(also, rate-limiting step) slowest elementary reaction in a reaction mechanism; determines the rate of the overall reaction

reaction mechanism
stepwise sequence of elementary reactions by which a chemical change takes place

termolecular reaction
elementary reaction involving the simultaneous collision and combination of three reactant species

unimolecular reaction
elementary reaction involving the rearrangement of a single reactant species to produce one or more molecules of product

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8.6: Catalysis

Learning Objectives

- Explain the function of a catalyst in terms of reaction mechanisms and potential energy diagrams
- List examples of catalysis in natural and industrial processes

We have seen that the rate of many reactions can be accelerated by catalysts. A catalyst speeds up the rate of a reaction by lowering the activation energy; in addition, the catalyst is regenerated in the process. Several reactions that are thermodynamically favorable in the absence of a catalyst only occur at a reasonable rate when a catalyst is present. One such reaction is catalytic hydrogenation, the process by which hydrogen is added across an alkene C=C bond to afford the saturated alkane product. A comparison of the reaction coordinate diagrams (also known as energy diagrams) for catalyzed and uncatalyzed alkene hydrogenation is shown in Figure 8.6.1.

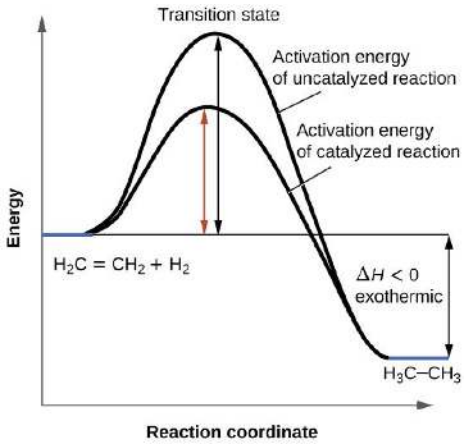


Figure 8.6.1: This graph compares the reaction coordinates for catalyzed and uncatalyzed alkene hydrogenation.

A graph is shown with the label, “Reaction coordinate,” on the x-axis and the label,“Energy,” on the y-axis. Approximately half-way up the y-axis, a short portion of a black concave down curve which has a horizontal line extended from it across the graph. The left end of this line is labeled “H subscript 2 C equals C H subscript 2 plus H subscript 2.” The black concave down curve extends upward to reach a maximum near the height of the y-axis. The peak of this curve is labeled, “Transition state.” A double sided arrow extends from the horizontal line to the peak of the curve. This arrow is labeled, “Activation energy of Uncatalyzed reation.” From the peak, the curve continues downward to a second horizontally flattened region well below the origin of the curve near the x-axis. This flattened region is shaded in blue and is labeled “H subscript 3 C dash C H subscript 3.” A double sided arrow is drawn from the lowers part of this curve at the far right of the graph to the line extending across the graph above it. This arrow is labeled, “capital delta H less than 0 : exothermic.” A second curve is drawn with the same flattened regions at the start and end of the curve. The height of this curve is about two-thirds the height of the first curve. A double sided arrow is drawn from the horizontal line that originates at the left side of the graph to the peak of this second curve. This arrow is labeled, “Activation energy of catalyzed reaction.”

Catalysts function by providing an alternate reaction mechanism that has a lower activation energy than would be found in the absence of the catalyst. In some cases, the catalyzed mechanism may include additional steps, as depicted in the reaction diagrams shown in Figure 8.6.2 This lower activation energy results in an increase in rate as described by the Arrhenius equation. Note that a catalyst decreases the activation energy for both the forward and the reverse reactions and hence *accelerates both the forward and the reverse reactions*. Consequently, the presence of a catalyst will permit a system to reach equilibrium more quickly, but it has no effect on the position of the equilibrium as reflected in the value of its equilibrium constant (see the later chapter on chemical equilibrium).

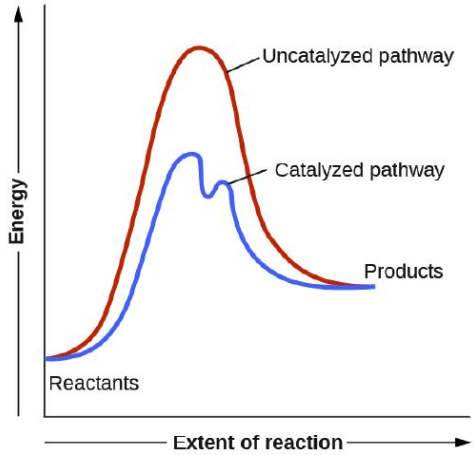
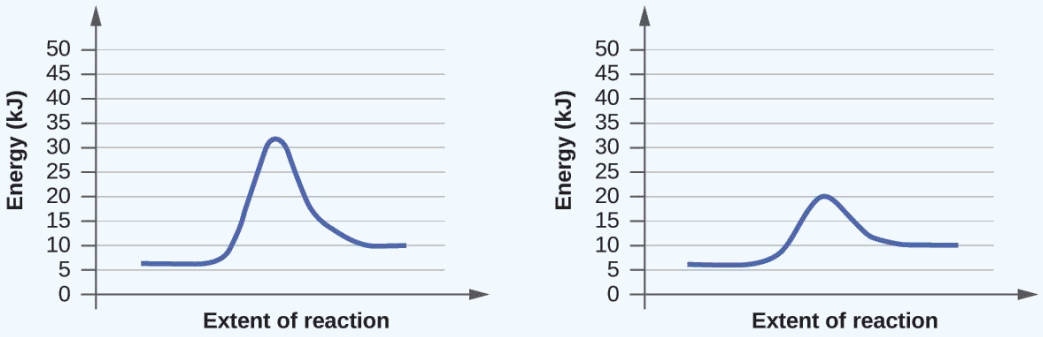


Figure **8.6.2**: This potential energy diagram shows the effect of a catalyst on the activation energy. The catalyst provides a different reaction path with a lower activation energy. As shown, the catalyzed pathway involves a two-step mechanism (note the presence of two transition states) and an intermediate species (represented by the valley between the two transitions states).

A graph is shown with the label, “Extent of reaction,” appearing in a right pointing arrow below the x-axis and the label, “Energy,” in an upward pointing arrow just left of the y-axis. Approximately one-fifth of the way up the y-axis, a very short, somewhat flattened portion of both a red and a blue curve are shown. This region is labeled “Reactants.” A red concave down curve extends upward to reach a maximum near the height of the y-axis. This curve is labeled, “Uncatalyzed pathway.” From the peak, the curve continues downward to a second horizontally flattened region at a height of about one-third the height of the y-axis. This flattened region is labeled, “Products.” A second curve is drawn in blue with the same flattened regions at the start and end of the curve. The height of this curve is about two-thirds the height of the first curve and just right of its maximum, the curve dips low, then rises back and continues a downward trend at a lower height, but similar to that of the red curve. This blue curve is labeled, “Catalyzed pathway.”

Example 8.6.1: Using Reaction Diagrams to Compare Catalyzed Reactions

The two reaction diagrams here represent the same reaction: one without a catalyst and one with a catalyst. Identify which diagram suggests the presence of a catalyst, and determine the activation energy for the catalyzed reaction:



In this figure, two graphs are shown. The x-axes are labeled, “Extent of reaction,” and the y-axes are labeled, “Energy (k J).” The y-axes are marked off from 0 to 50 in intervals of five. In a, a blue curve is shown. It begins with a horizontal segment at about 6. The curve then rises sharply near the middle to reach a maximum of about 32 and similarly falls to another horizontal segment at about 10. In b, the curve begins and ends similarly, but the maximum reached near the center of the graph is only 20.

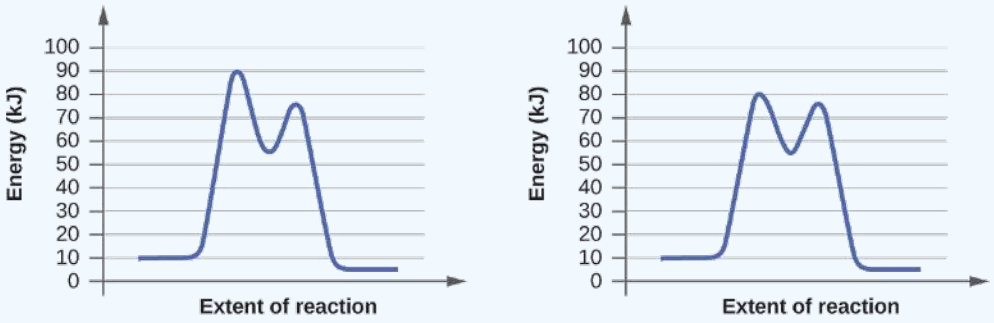
Solution

A catalyst does not affect the energy of reactant or product, so those aspects of the diagrams can be ignored; they are, as we would expect, identical in that respect. There is, however, a noticeable difference in the transition state, which is distinctly lower in diagram (b) than it is in (a). This indicates the use of a catalyst in diagram (b). The activation energy is the difference between the energy of the starting reagents and the transition state—a maximum on the reaction coordinate diagram. The reagents are at 6 kJ and the transition state is at 20 kJ, so the activation energy can be calculated as follows:

$$E_a = 20\ \text{kJ} - 6\ \text{kJ} = 14\ \text{kJ} \tag{8.6.1}$$

Exercise 8.6.1

Determine which of the two diagrams here (both for the same reaction) involves a catalyst, and identify the activation energy for the catalyzed reaction:



In this figure, two graphs are shown. The x-axes are labeled, “Extent of reaction,” and the y-axes are labeledc “Energy (k J).” The y-axes are marked off from 0 to 100 at intervals of 10. In a, a blue curve is shown. It begins with a horizontal segment at about 10. The curve then rises sharply near the middle to reach a maximum of about 91, then sharply falls to about 52, again rises sharply to about 73 and falls to another horizontal segment at about 5. In b, the curve begins and ends similarly, but the first peak reaches about 81, drops to about 55, then rises to about 77 before falling to the horizontal region at about 5.

Answer

Diagram (b) is a catalyzed reaction with an activation energy of about 70 kJ.

Homogeneous Catalysts

A homogeneous catalyst is present in the same phase as the reactants. It interacts with a reactant to form an intermediate substance, which then decomposes or reacts with another reactant in one or more steps to regenerate the original catalyst and form product. As an important illustration of homogeneous catalysis, consider the earth’s ozone layer. Ozone in the upper atmosphere, which protects the earth from ultraviolet radiation, is formed when oxygen molecules absorb ultraviolet light and undergo the reaction:

$$3\,O_2(g) \xrightarrow{h\nu} 2\,O_3(g) \tag{8.6.2}$$

Ozone is a relatively unstable molecule that decomposes to yield diatomic oxygen by the reverse of this equation. This decomposition reaction is consistent with the following mechanism:

$$\begin{aligned} O_3 &\longrightarrow O_2 + O \\ O + O_3 &\longrightarrow 2\,O_2 \end{aligned} \tag{8.6.3}$$

The presence of nitric oxide, NO, influences the rate of decomposition of ozone. Nitric oxide acts as a catalyst in the following mechanism:

$$\begin{aligned} NO(g) + O_3(g) &\longrightarrow NO_2(g) + O_2(g) \\ O_3(g) &\longrightarrow O_2(g) + O(g) \\ NO_2(g) + O(g) &\longrightarrow NO(g) + O_2(g) \end{aligned} \tag{8.6.4}$$

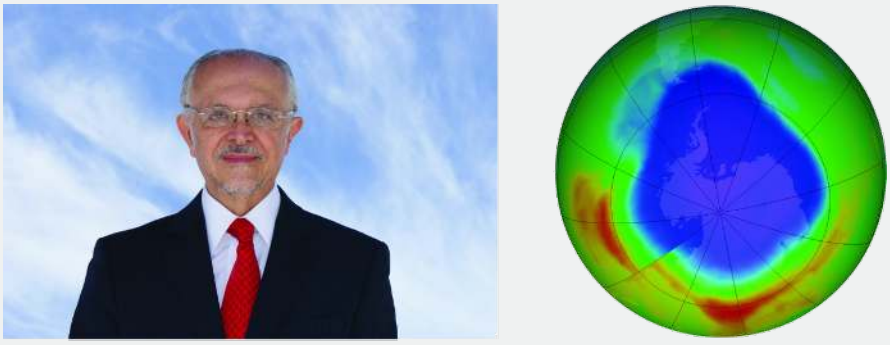
The overall chemical change for the catalyzed mechanism is the same as:

$$2\,O_3(g) \longrightarrow 3\,O_2(g) \tag{8.6.5}$$

The nitric oxide reacts and is regenerated in these reactions. It is not permanently used up; thus, it acts as a catalyst. The rate of decomposition of ozone is greater in the presence of nitric oxide because of the catalytic activity of NO. Certain compounds that contain chlorine also catalyze the decomposition of ozone.

Mario J. Molina

The 1995 Nobel Prize in Chemistry was shared by Paul J. Crutzen, Mario J. Molina (Figure 8.6.3), and F. Sherwood Rowland "for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone." Molina, a Mexican citizen, carried out the majority of his work at the Massachusetts Institute of Technology (MIT).



(a) (b)

Figure 8.6.3: (a) Mexican chemist Mario Molina (1943 –) shared the Nobel Prize in Chemistry in 1995 for his research on (b) the Antarctic ozone hole. (credit a: courtesy of Mario Molina; credit b: modification of work by NASA)

A photograph is shown of Mario Molina. To the right of the photo, an image of Earth's southern hemisphere is shown with a central circular region in purple with a radius of about half that of the entire hemisphere. Just outside this region is a narrow royal blue band, followed by an outer thin turquoise blue band. The majority of the outermost region is green. Two small bands of yellow are present in the lower regions of the image.

In 1974, Molina and Rowland published a paper in the journal *Nature* (one of the major peer-reviewed publications in the field of science) detailing the threat of chlorofluorocarbon gases to the stability of the ozone layer in earth's upper atmosphere. The ozone layer protects earth from solar radiation by absorbing ultraviolet light. As chemical reactions deplete the amount of ozone in the upper atmosphere, a measurable "hole" forms above Antarctica, and an increase in the amount of solar ultraviolet radiation— strongly linked to the prevalence of skin cancers—reaches earth's surface. The work of Molina and Rowland was instrumental in the adoption of the Montreal Protocol, an international treaty signed in 1987 that successfully began phasing out production of chemicals linked to ozone destruction.

Molina and Rowland demonstrated that chlorine atoms from human-made chemicals can catalyze ozone destruction in a process similar to that by which NO accelerates the depletion of ozone. Chlorine atoms are generated when chlorocarbons or chlorofluorocarbons—once widely used as refrigerants and propellants—are photochemically decomposed by ultraviolet light or react with hydroxyl radicals. A sample mechanism is shown here using methyl chloride:

\[\ce{CH3Cl + OH ⟶ Cl + other\: products} \nonumber \]

Chlorine radicals break down ozone and are regenerated by the following catalytic cycle:

$$\mathrm{Cl + O_3 \longrightarrow ClO + O_2}$$
$$\mathrm{ClO + O \longrightarrow Cl + O_2}$$
$$\mathrm{\textbf{overall Reaction: } O_3 + O \longrightarrow 2\,O_2}$$

A single monatomic chlorine can break down thousands of ozone molecules. Luckily, the majority of atmospheric chlorine exists as the catalytically inactive forms Cl_2 and $ClONO_2$.

Glucose-6-Phosphate Dehydrogenase Deficiency

Enzymes in the human body act as catalysts for important chemical reactions in cellular metabolism. As such, a deficiency of a particular enzyme can translate to a life-threatening disease. G6PD (glucose-6-phosphate dehydrogenase) deficiency, a genetic condition that results in a shortage of the enzyme glucose-6-phosphate dehydrogenase, is the most common enzyme deficiency in humans. This enzyme, shown in Figure 8.6.4, is the rate-limiting enzyme for the metabolic pathway that supplies NADPH to cells (FIgure 8.6.5).

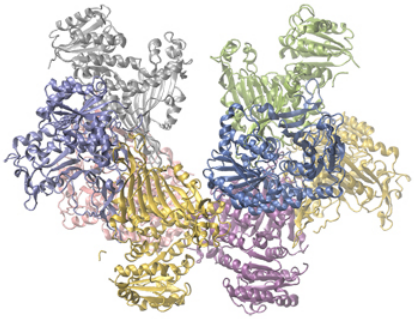


Figure **8.6.4:** Glucose-6-phosphate dehydrogenase is a rate-limiting enzyme for the metabolic pathway that supplies NADPH to cells.

A colorful model of the Glucose-6-phosphate dehydrogenase structure is shown. The molecule has two distinct lobes which are filled with spiraled ribbon-like regions of yellow, lavender, blue, silver, green, and pink.

A disruption in this pathway can lead to reduced glutathione in red blood cells; once all glutathione is consumed, enzymes and other proteins such as hemoglobin are susceptible to damage. For example, hemoglobin can be metabolized to bilirubin, which leads to jaundice, a condition that can become severe. People who suffer from G6PD deficiency must avoid certain foods and medicines containing chemicals that can trigger damage their glutathione-deficient red blood cells.

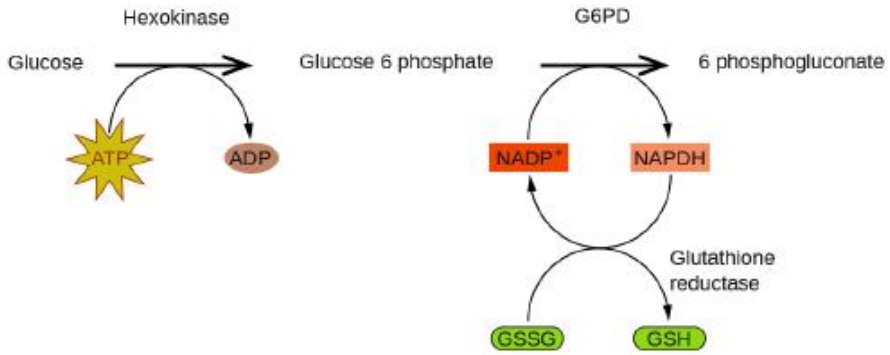


Figure **8.6.5**: In the mechanism for the pentose phosphate pathway, G6PD catalyzes the reaction that regulates NAPDH, a co-enzyme that regulates glutathione, an antioxidant that protects red blood cells and other cells from oxidative damage.

A reaction mechanism is diagrammed in this figure. At the left, the name Glucose is followed by a horizontal, right pointing arrow, labeled, “Hexokinase.” Below this arrow and to the left is a yellow star shape labeled, “A T P.” A curved arrow extends from this shape to the right pointing arrow, and down to the right to a small brown oval labeled, “A D P.” To the right of the horizontal arrow is the name Glucose 6 phosphate, which is followed by another horizontal, right pointing arrow which is labeled, “G 6 P D.” A small orange rectangle below and left of this arrow is labeled “N A D P superscript plus.” A curved arrow extends from this shape to the right pointing arrow, and down to the right to a small salmon-colored rectangle labeled “N A P D H.” A curved arrow extends from this shape below and to the left, back to the orange rectangle labeled, “N A D P superscript plus.” Another curved arrow extends from a green oval labeled “G S S G” below the orange rectangle, up to the arrow curving back to the orange rectangle. This last curved arrow continues on to the lower right to a second green oval labeled, “G S H.” The end of this curved arrow is labeled, “Glutathione reductase.” To the right of the rightmost horizontal arrow appears the name 6 phosphogluconate.

Heterogeneous Catalysts

A heterogeneous catalyst is a catalyst that is present in a different phase (usually a solid) than the reactants. Such catalysts generally function by furnishing an active surface upon which a reaction can occur. Gas and liquid phase reactions catalyzed by heterogeneous catalysts occur on the surface of the catalyst rather than within the gas or liquid phase.

Heterogeneous catalysis has at least four steps:

1. Adsorption of the reactant onto the surface of the catalyst
2. Activation of the adsorbed reactant
3. Reaction of the adsorbed reactant
4. Diffusion of the product from the surface into the gas or liquid phase (desorption).

Any one of these steps may be slow and thus may serve as the rate determining step. In general, however, in the presence of the catalyst, the overall rate of the reaction is faster than it would be if the reactants were in the gas or liquid phase.

Figure 8.6.6 illustrates the steps that chemists believe to occur in the reaction of compounds containing a carbon–carbon double bond with hydrogen on a nickel catalyst. Nickel is the catalyst used in the hydrogenation of polyunsaturated fats and oils (which contain several carbon–carbon double bonds) to produce saturated fats and oils (which contain only carbon–carbon single bonds).

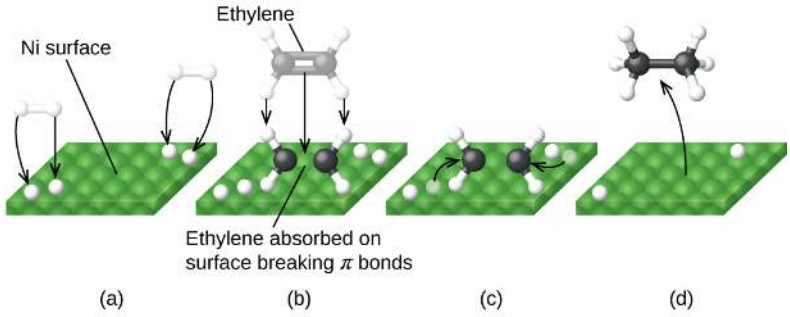


Figure 8.6.6: There are four steps in the catalysis of the reaction $C_2H_4 + H_2 \longrightarrow C_2H_6$ *by nickel. (a) Hydrogen is adsorbed on the surface, breaking the H–H bonds and forming Ni–H bonds. (b) Ethylene is adsorbed on the surface, breaking the π-bond and forming Ni–C bonds. (c) Atoms diffuse across the surface and form new C–H bonds when they collide. (d)* C_2H_6 *molecules escape from the nickel surface, since they are not strongly attracted to nickel.*

In this figure, four diagrams labeled a through d are shown. In each, a green square surface is shown in perspective to provide a three-dimensional appearance. In a, the label “N i surface” is placed above with a line segment extending to the green square. At the lower left and upper right, pairs of white spheres bonded tougher together appear as well as white spheres on the green surface. Black arrows are drawn from each of the white spheres above the surface to the white sphere on the green surface. In b, the white spheres are still present on the green surface. Near the center of this surface is a molecule with two central black spheres with a double bond indicated by two horizontal black rods between them. Above and below to the left and right, a total of four white spheres are connected to the black spheres with white rods. A line segment extends from this structure to the label, “Ethylene absorbed on surface breaking pi bonds.” Just above this is a nearly identical structure greyed out with three downward pointing arrows to the black and white structure to indicate downward motion. The label “Ethylene” at the top of the diagram is connected to the greyed out structure with a line segment. In c, the diagram is very similar to b except that the greyed out structure and labels are gone and one of the white spheres near the black and white structure in each pair on the green surface is greyed out. Arrows point from the greyed out white spheres to the double bond between the two black spheres. In d, only a single white sphere remains from each pair in the green surface. A curved arrow points from the middle of the green surface to a model above with two central black spheres with a single black rod indicating a single bond between them. Each of the black rods has three small white spheres bonded as indicated by white rods between the black spheres and the small white spheres. The four bonds around each black sphere are evenly distributed about the black spheres.

Other significant industrial processes that involve the use of heterogeneous catalysts include the preparation of sulfuric acid, the preparation of ammonia, the oxidation of ammonia to nitric acid, and the synthesis of methanol, CH_3OH. Heterogeneous catalysts are also used in the catalytic converters found on most gasoline-powered automobiles (Figure 8.6.7).

Automobile Catalytic Converters

Scientists developed catalytic converters to reduce the amount of toxic emissions produced by burning gasoline in internal combustion engines. Catalytic converters take advantage of all five factors that affect the speed of chemical reactions to ensure that exhaust emissions are as safe as possible.

By utilizing a carefully selected blend of catalytically active metals, it is possible to effect complete combustion of all carbon-containing compounds to carbon dioxide while also reducing the output of nitrogen oxides. This is particularly impressive when we consider that one step involves adding more oxygen to the molecule and the other involves removing the oxygen (Figure 8.6.6).

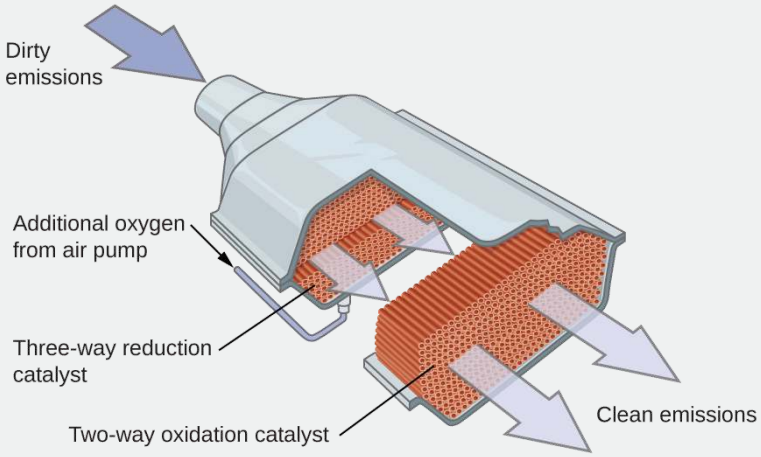


Figure 8.6.6: A catalytic converter allows for the combustion of all carbon-containing compounds to carbon dioxide, while at the same time reducing the output of nitrogen oxide and other pollutants in emissions from gasoline-burning engines.

An image is shown of a catalytic converter. At the upper left, a blue arrow pointing into a pipe that enters a larger, widened chamber is labeled, “Dirty emissions.” A small black arrow that points to the lower right is positioned along the upper left side of the widened region. This arrow is labeled, “Additional oxygen from air pump.” The image shows the converter with the upper surface removed, exposing a red-brown interior. The portion of the converter closest to the dirty emissions inlet shows small, round components in an interior layer. This layer is labeled “Three-way reduction catalyst.” The middle region shows closely packed small brown rods that are aligned parallel to the dirty emissions inlet pipe. The final quarter of the interior of the catalytic converter again shows a layer of closely packed small red brown circles. Two large light grey arrows extend from this layer to the open region at the lower right of the image to the label “Clean emissions.”

Most modern, three-way catalytic converters possess a surface impregnated with a platinum-rhodium catalyst, which catalyzes the conversion nitric oxide into dinitrogen and oxygen as well as the conversion of carbon monoxide and hydrocarbons such as octane into carbon dioxide and water vapor:

$$2\,NO_2(g) \longrightarrow N_2(g) + 2\,O_2(g)$$
$$[5pt]2\,CO(g) + O_2(g) \longrightarrow 2\,CO_2(g)$$
$$[5pt]2\,C_8H_{18}(g) + 25\,O_2(g) \longrightarrow 16\,CO_2(g) + 18\,H_2O(g)$$

In order to be as efficient as possible, most catalytic converters are preheated by an electric heater. This ensures that the metals in the catalyst are fully active even before the automobile exhaust is hot enough to maintain appropriate reaction temperatures.

Enzyme Structure and Function

The study of enzymes is an important interconnection between biology and chemistry. Enzymes are usually proteins (polypeptides) that help to control the rate of chemical reactions between biologically important compounds, particularly those that are involved in cellular metabolism. Different classes of enzymes perform a variety of functions, as shown in Table 8.6.1.

ATP hydrolysis.”" data-quail-id="131" data-mt-width="1016">

Table 8.6.1: Classes of Enzymes and Their Functions

Class	Function
oxidoreductases	redox reactions
transferases	transfer of functional groups
hydrolases	hydrolysis reactions
lyases	group elimination to form double bonds
isomerases	isomerization
ligases	bond formation with ATP hydrolysis

Enzyme molecules possess an active site, a part of the molecule with a shape that allows it to bond to a specific substrate (a reactant molecule), forming an enzyme-substrate complex as a reaction intermediate. There are two models that attempt to explain how this active site works. The most simplistic model is referred to as the lock-and-key hypothesis, which suggests that the molecular shapes of the active site and substrate are complementary, fitting together like a key in a lock. The induced fit hypothesis, on the other hand, suggests that the enzyme molecule is flexible and changes shape to accommodate a bond with the substrate. This is not to suggest that an enzyme's active site is completely malleable, however. Both the lock-and-key model and the induced fit model account for the fact that enzymes can only bind with specific substrates, since in general a particular enzyme only catalyzes a particular reaction (Figure 8.6.7).

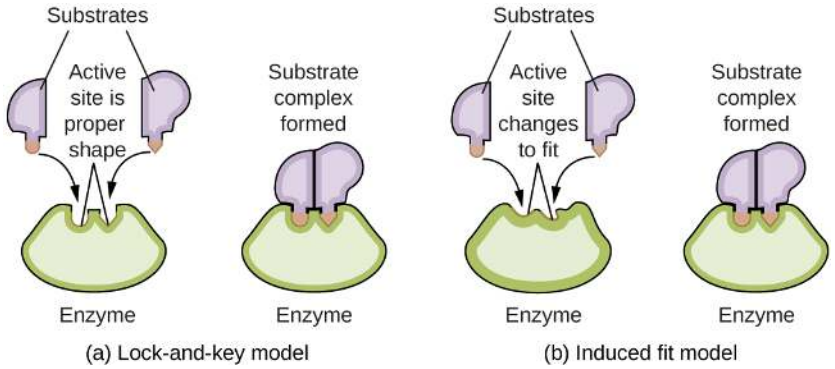


Figure 8.6.7: (a) According to the lock-and-key model, the shape of an enzyme's active site is a perfect fit for the substrate. (b) According to the induced fit model, the active site is somewhat flexible, and can change shape in order to bond with the substrate.

A diagram is shown of two possible interactions of an enzyme and a substrate. In a, which is labeled "Lock-and-key," two diagrams are shown. The first shows a green wedge-like shape with two small depressions in the upper surface of similar size, but the depression on the left has a curved shape, and the depression on the right has a pointed shape. This green shape is labeled "Enzyme." Just above this shape are two smaller, irregular, lavender shapes each with a projection from its lower surface. The lavender shape on the left has a curved projection which matches the shape of the depression on the left in the green shape below. This projection is shaded orange and has a curved arrow extending from in to the matching depression in the green shape below. Similarly, the lavender shape on the right has a projection with a pointed tip which matches the shape of the depression on the right in the green shape below. This projection is shaded orange and has a curved arrow extending from in to the matching depression in the green shape below. Two line segments extend from the depressions in the green shape to form an inverted V shape above the depressions. Above this and between the lavender shapes is the label, "Active site is proper shape." The label "Substrates" is at the very top of the diagram with line segments extending to the two lavender shapes. To the right of this diagram is a second diagram showing the lavender shapes positioned next to each other, fit snugly into the depressions in the green shape, which is labeled "Enzyme." Above this diagram is the label, "Substrate complex formed." In b, which is labeled "Induced fit," two diagrams are shown. The first shows a green wedge-like shape with two small depressions in the upper surface of similar size, but irregular shape. This green shape is labeled "Enzyme." Just above this shape are two smaller irregular lavender shapes each with a projection from its lower surface. The lavender shape on the left has a curved projection. This projection is shaded orange and has a curved arrow extending from it to the irregular depression just below it in the green shape below. Similarly, the lavender shape on the right has a projection with a pointed tip. This projection is shaded orange and has a curved arrow extending from it to the irregular depression just below it in the green shape below. Two line segments extend from the depressions in the green shape to form an inverted V shape above the depressions. Above this and between the lavender shapes is the label, "Active site changes to fit." The label, "Substrates" is at the very top of the diagram with line segments extending to the two lavender shapes. To the right of this diagram is a second diagram showing the purple shapes positioned next to each other, fit snugly into the depressions in the green shape, which is labeled "Enzyme." Above this diagram is the label "Substrate complex formed." The projections from the lavender shapes match the depression shapes in the green shape, resulting in a proper fit.

Summary

Catalysts affect the rate of a chemical reaction by altering its mechanism to provide a lower activation energy. Catalysts can be homogenous (in the same phase as the reactants) or heterogeneous (a different phase than the reactants).

Footnotes

1. "The Nobel Prize in Chemistry 1995," Nobel Prize.org, accessed February 18, 2015, Nobel Prizes Chemistry [www.nobelprize.org].

Glossary

heterogeneous catalyst

catalyst present in a different phase from the reactants, furnishing a surface at which a reaction can occur

homogeneous catalyst

catalyst present in the same phase as the reactants

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8.E: Kinetics (Exercises)

12.1: Chemical Reaction Rates

Q12.1.1

What is the difference between average rate, initial rate, and instantaneous rate?

Solution

First, a general reaction rate must be defined to know what any variation of a rate is. The reaction rate is defined as the measure of the change in concentration of the reactants or products per unit time. The rate of a chemical reaction is not a constant and rather changes continuously, and can be influenced by temperature. Rate of a reaction can be defined as the disappearance of any reactant or appearance of any product. Thus, an average rate is the average reaction rate over a given period of time in the reaction, the instantaneous rate is the reaction rate at a specific given moment during the reaction, and the initial rate is the instantaneous rate at the very start of the reaction (when the product begins to form).

The instantaneous rate of a reaction can be denoted as

$$\lim_{\Delta t \to 0} \frac{\Delta[concentration]}{\Delta t}$$

Q12.1.2

Ozone decomposes to oxygen according to the equation $2\,O_3(g) \longrightarrow 3\,O_2(g)$. Write the equation that relates the rate expressions for this reaction in terms of the disappearance of O_3 and the formation of oxygen.

Solution

For the general reaction, aA ---> bB, the rate of the reaction can be expressed in terms of the disappearance of A or the appearance of B over a certain time period as follows.

$$-\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t} \tag{8.E.1}$$

We want the rate of a reaction to be positive, but the change in the concentration of a reactant, A, will be negative because it is being used up to be transformed into product, B. Therefore, when expressing the rate of the reaction in terms of the change in the concentration of A, it is important to add a negative sign in front to ensure the overall rate positive.

Lastly, the rate must be normalized according to the stoichiometry of the reaction. In the decomposition of ozone to oxygen, two moles of ozone form three moles of oxygen gas. This means that the increase in oxygen gas will be 1.5 times as great as the decrease in ozone. Because the rate of the reaction should be able to describe both species, we divide the change in concentration by its stoichiometric coefficient in the balanced reaction equation to deal with this issue.

Therefore, the rate of the reaction of the decomposition of ozone into oxygen gas can be described as follows:

$$Rate = -\frac{\Delta[O3]}{2\Delta T} = \frac{\Delta[O2]}{3\Delta T} \tag{8.E.2}$$

Answer

$$Rate=-\frac{\Delta[O3]}{2\Delta T}=\frac{\Delta[O2]}{3\Delta T}\]

Q12.1.3

In the nuclear industry, chlorine trifluoride is used to prepare uranium hexafluoride, a volatile compound of uranium used in the separation of uranium isotopes. Chlorine trifluoride is prepared by the reaction $Cl_2(g) + 3\,F_2(g) \longrightarrow 2\,ClF_3(g)$. Write the equation that relates the rate expressions for this reaction in terms of the disappearance of Cl_2 and F_2 and the formation of ClF_3.

Solution

In this problem we are asked to write the equation that relates rate expressions in terms of disappearance of the reactants of the equation and in terms of the formation of the product. A reaction rate gives insight to how rate is affected as a function of concentration of the substances in the equation. Rates can often be expressed on graphs of concentration vs time expressed in change (Δ) of concentration and time and in a short enough time interval, the instantaneous rate can be approximated. If we were to analyze the reaction given, the graph would demonstrate that Cl_2 decreases, that F_2 decreases 3 times as quickly, and then ClF_3 increases at a rate doubles. The reactants are being used and converted to product so they decrease while products increase.

For this problem, we can apply the general formula of a rate to the specific aspects of a problem where the general form follows:

$$aA + bB \longrightarrow cC + dD$$

.

And the rate can then be written as $rate = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$. Here the negative signs are used to keep the convention of expressing rates as positive numbers.

In this specific case we use the stoichiometry to get the specific rates of disappearance and formation (back to what was said in the first paragraph). So, the problem just involves referring the to the equation and its balanced coefficients. Based upon the equation we see that Cl_2 is a reactant and has no coefficient, F_2 has a coefficient of 3 and is also used up, and then ClF_3 is a product that increases two-fold with a coefficient of 2. So, the rate here can be written as:

$$rate = -\frac{\Delta[Cl_2]}{\Delta t} = -\frac{1}{3}\frac{\Delta[F_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[ClF_3]}{\Delta t}$$

Answer

$$\text{rate} = +\frac{1}{2}\frac{\Delta[\text{ClF}_3]}{\Delta t} = -\frac{\Delta[\text{Cl}_2]}{\Delta t} = -\frac{1}{3}\frac{\Delta[\text{F}_2]}{\Delta t}$$

Q12.1.4

A study of the rate of dimerization of C_4H_6 gave the data shown in the table:

$$2\,\text{C}_4\text{H}_6 \longrightarrow \text{C}_8\text{H}_{12}$$

Time (s)	0	1600	3200	4800	6200
$[C_4H_6]$ (M)	1.00×10^{-2}	5.04×10^{-3}	3.37×10^{-3}	2.53×10^{-3}	2.08×10^{-3}

a. Determine the average rate of dimerization between 0 s and 1600 s, and between 1600 s and 3200 s.
b. Estimate the instantaneous rate of dimerization at 3200 s from a graph of time versus $[C_4H_6]$. What are the units of this rate?
c. Determine the average rate of formation of C_8H_{12} at 1600 s and the instantaneous rate of formation at 3200 s from the rates found in parts (a) and (b).

Solution

1.) The average rate of dimerization is the change in concentration of a reactant per unit time. In this case it would be:

$$rate\ of\ dimerization = -\frac{\Delta[C_4H_6]}{\Delta t}$$

Rate of dimerization between 0 s and 1600 s:

$$rate\ of\ dimerization = -\frac{5.04\times10^{-3}M - 1.00\times10^{-2}M}{1600s - 0s}$$

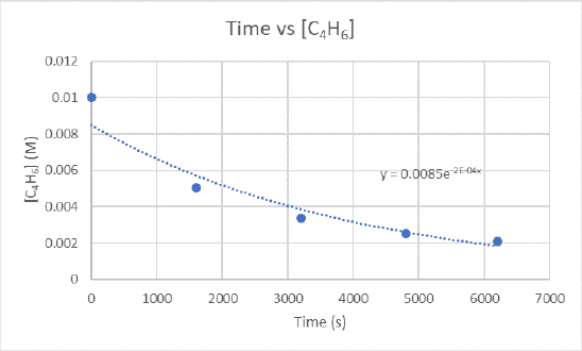
$$rate\ of\ dimerization = 3.10 \times 10^{-6}\frac{M}{s}$$

Rate of dimerization between 1600 s and 3200 s:

$$rate\ of\ dimerization = -\frac{3.37\times10^{-3}M - 5.04\times10^{-3}M}{3200s - 1600s}$$

$$rate\ of\ dimerization = 1.04 \times 10^{-6}\frac{M}{s}$$

2.) The instantaneous rate of dimerization at 3200 s can be found by graphing time versus $[C_4H_6]$.



Because you want to find the rate of dimerization at 3200 s, you need to find the slope between 1600 s and 3200 s and also 3200 s and 4800 s.

For the slope between 1600 s and 3200 s use the points (1600 s, 5.04 x 10^{-3} M) and (3200 s, 3.37 x 10^{-3} M)

$$\frac{3.37\times10^{-3}M-5.04\times10^{-3}M}{3200s-1600s}$$

$$\frac{-0.00167M}{1600s}$$

$$-1.04\times10^{-6}\frac{M}{s}$$

For the slope between 3200 s and 4800 s use the points (3200s, 3.37 x 10^{-3} M) and (4800s, 2.53 x 10^{-3} M)

$$\frac{2.53\times10^{-3}M-3.37\times10^{-3}M}{4800s-3200s}$$

$$\frac{-8.4\times10^{-4}M}{1600s}$$

$$-5.25\times10^{-7}\frac{M}{s}$$

Take the two slopes you just found and find the average of them to get the instantaneous rate of dimerization.

$$\frac{-1.04\times10^{-6}\frac{M}{s}+-5.25\times x10^{-7}\frac{M}{s}}{2}$$

$$\frac{-1.565\times10^{-6}\frac{M}{s}}{2}$$

$$-7.83\times10^{-7}\frac{M}{s}$$

The instantaneous rate of dimerization is $-7.83\times10^{-7}\frac{M}{s}$ and the units of this rate is $\frac{M}{s}$.

3.) The average rate of formation of C_8H_{12} at 1600 s and the instantaneous rate of formation at 3200 s can be found by using our answers from part a and b. If you look back up at the original equation, you could see that C_4H_6 and C_8H_{12} are related in a two to one ratio. For every two moles of C_4H_6 used, there is one mole of C_8H_{12} produced.

For this reaction, the average rate of dimerization and the average rate of formation can be linked through this equation:

$$\frac{-1}{2}\frac{\Delta[C_4H_6]}{\Delta t}=\frac{\Delta[C_8H_{12}]}{\Delta t}$$

Notice that reactant side is negative because the reactants are being used up in the reaction.

So, for the average rate of formation of C_8H_{12} at 1600 s, use the rate of dimerization between 0 s and 1600 s we found earlier and plug into the equation:

$$\frac{-1}{2}\times3.10\times10^{-6}\frac{M}{s}=\frac{\Delta[C_8H_{12}]}{\Delta t}$$

$$\frac{\Delta[C_8H_{12}]}{\Delta t}=1.55\times10^{-6}\frac{M}{s}$$

The average rate of formation for C_8H_{12} at 1600 s is $1.55\times10^{-6}\frac{M}{s}$. The rate of formation will be positive because products are being formed.

The instantaneous rate of formation for C_8H_{12} can be linked to the instantaneous rate of dimerization by this equation:

$$\frac{-1}{2}\frac{d[C_4H_6]}{dt}=\frac{d[C_8H_{12}]}{dt}$$

So, for the instantaneous rate of formation for C_8H_{12} at 3200 s, use the value of instantaneous rate of dimerization at 3200 s found earlier and plug into the equation:

$$\frac{-1}{2} \times -7.83 \times 10^{-7} \frac{M}{s} = \frac{d[C_8H_{12}]}{dt}$$

$$\frac{d[C_8H_{12}]}{dt} = -3.92 \times 10^{-7} \frac{M}{s}$$

The instantaneous rate of formation for C_8H_{12} at 3200 s is $-3.92 \times 10^{-7} \frac{M}{s}$

Answer

a. $3.10 \times 10^{-6} \frac{M}{s}$ and $1.04 \times 10^{-6} \frac{M}{s}$
b. $-7.83 \times 10^{-7} \frac{M}{s}$ and $\frac{M}{s}$
c. $-3.92 \times 10^{-7} \frac{M}{s}$

Q12.1.5

A study of the rate of the reaction represented as $2A \longrightarrow B$ gave the following data:

Time (s)	0.0	5.0	10.0	15.0	20.0	25.0	35.0
[A] (M)	1.00	0.952	0.625	0.465	0.370	0.308	0.230

a. Determine the average rate of disappearance of *A* between 0.0 s and 10.0 s, and between 10.0 s and 20.0 s.
b. Estimate the instantaneous rate of disappearance of *A* at 15.0 s from a graph of time versus [*A*]. What are the units of this rate?
c. Use the rates found in parts (a) and (b) to determine the average rate of formation of *B* between 0.00 s and 10.0 s, and the instantaneous rate of formation of *B* at 15.0 s.

Solution

Equations: $\frac{-\triangle A}{\triangle time}$ and Rate=$\frac{-\triangle A}{2\triangle time} = \frac{\triangle B}{time}$

Solve: 1.)The change in A from 0s to 10s is .625-1=-.375 so $\frac{-\triangle A}{\triangle time}$=.375/10= **0.0374 M/s**

Similarly, the change in A from 10 to 20 seconds is .370-.625=-.255 so $\frac{-\triangle A}{\triangle time}$=.255/20-10= **0.0255M/s**

2.) We can estimate the rate law graphing the points against different order equations to determine the right order.

Zero Order:

$$\frac{d[A]}{dt} = -k$$

$$\int_{A_\circ}^{A} d[A] = -k \int_0^t dt$$

$$[A] = -kt + [A_\circ]$$

First Order:

$$\frac{d[A]}{dt} = -k[A]$$

$$\int_{A_\circ}^{A} \frac{d[A]}{[A]} = -kdt$$

$$Ln(A) = -kt + Ln(A_\circ)$$

Second Order:

$$\frac{d[A]}{dt} = -k[A]^2$$

$$\int_{A_\circ}^{A} \frac{d[A]}{[A]^2} = -k\int_0^t dt$$

$$\frac{1}{[A]} = kt + \frac{1}{[A_\circ]}$$

Now that we have found the linear from of each order we will plot the points vs an [A] y-axis, a Ln(A) y-axis, and a 1/[A] y-axis. whichever of the plots has the most linear points will give us a good idea of the order and the slope will be the k value.



Here we notice that the second order is most linear so we conclude the Rate to be..

$$\frac{-d[A]}{2dt} = k[A]^2$$

At 15 seconds [A]=.465 and from the slope of the graph we find k=.116.so if we plug this data in and multiply both sides by 2 to get rid of the 2 in the denominator on the left side of the equation we find that the rate of disappearance of A is .05 M/s where the units are equivalent to [mol*L^{-1}*s^{-1}]

3.) Using the equation $\frac{-\triangle A}{2\triangle time} = \frac{\triangle B}{time}$ we divide the rates in part a and b in half to get .0188 M/s from 0 to 10 seconds and .025 M/s for the estimated instantaneous rate at 15s.

Answer

(a) average rate, 0 − 10 s = 0.0375 mol L^{-1} s^{-1}; average rate, 12 − 18 s = 0.0225 mol L^{-1} s^{-1}; (b) instantaneous rate, 15 s = 0.0500 mol L^{-1} s^{-1}; (c) average rate for B formation = 0.0188 mol L^{-1} s^{-1}; instantaneous rate for B formation = 0.0250 mol L^{-1} s^{-1}

Q12.1.6

Consider the following reaction in aqueous solution:

$$5\,Br^-(aq) + BrO_3^-(aq) + 6\,H^+(aq) \longrightarrow 3\,Br_2(aq) + 3\,H_2O(l)$$

If the rate of disappearance of $Br^-(aq)$ at a particular moment during the reaction is $3.5 \times 10^{-4}\ M\ s^{-1}$, what is the rate of appearance of $Br_2(aq)$ at that moment?

Solution

Step 1. Define the rate of the reaction.

Recall:

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

$rate = -\frac{\Delta[A]}{a\Delta t} = -\frac{\Delta[B]}{b\Delta t} = \frac{\Delta[C]}{c\Delta t} = \frac{\Delta[D]}{d\Delta t}$

So, for the reaction: $5Br^-(aq) + BrO_3^-(aq) + 6H^+ \rightarrow 3Br_2(aq) + 3H_2O(l)$

The rate would be: $rate = -\frac{\Delta[Br^-]}{5\Delta t} = -\frac{\Delta[BrO_3^-]}{\Delta t} = -\frac{\Delta[H^+]}{6\Delta t} = \frac{\Delta[Br_2]}{3\Delta t} = \frac{H_2O}{3\Delta t}$

Step 2. Since we are given the rate for the disappearance of Br^-(aq) is $3.5x10^-4Ms^{-1}$, and we want to find the rate of appearance of Br_2(aq). Therefore we set the two rates equal to each other.

$$rate = -\frac{\Delta[Br^-]}{5\Delta t} = \frac{\Delta[Br_2]}{3\Delta t}$$

And, $-\frac{\Delta[Br^-]}{\Delta t} = -3.5x10^{-4}Ms^{-1}$

So, $3.5x10^{-4}Ms^{-1} = \frac{5}{3}\frac{\Delta[Br_2]}{\Delta t}$

Step 3. Now solve the equation.

$$\frac{(3.5x10^{-4})(3)}{5} = \frac{\Delta[Br_2]}{\Delta t}$$

$$\frac{\Delta[Br_2]}{\Delta t} = 2.1x10^{-4}Ms^{-1}$$

Answer

$$\frac{\Delta[Br_2]}{\Delta t} = 2.1x10^{-4}Ms^{-1}$$

12.2: Factors Affecting Reaction Rates

Q12.2.1

Describe the effect of each of the following on the rate of the reaction of magnesium metal with a solution of hydrochloric acid: the molarity of the hydrochloric acid, the temperature of the solution, and the size of the pieces of magnesium.

Solution

Molarity of Hydrochloric Acid

- Reaction rates are affected by the frequency at which molecules collide. High Molarity=High Concentration which means more molecules are available to collide thus a faster reaction that one with a low molarity of HCl at a fixed volume.

Temperature of Solution

- Higher temperatures increase the rate of reaction because molecules move faster thus colliding more frequently
- increasing temperatures allows for more particles to move past activation energy barrier to start the reaction

Size of pieces of Magnesium

- reaction rate is dependent on solid reactant size; smaller pieces increases the chance of collision because they enable a greater surface area thus faster reaction rate

Q12.2.2

Go to the PhET Reactions & Rates interactive. Use the Single Collision tab to represent how the collision between monatomic oxygen (O) and carbon monoxide (CO) results in the breaking of one bond and the formation of another. Pull back on the red plunger to release the atom and observe the results. Then, click on “Reload Launcher” and change to “Angled shot” to see the difference.

a. What happens when the angle of the collision is changed?
b. Explain how this is relevant to rate of reaction.

Solution

According to the collision theory, there are many factors that cause a reaction to happen, with three of the factors being how often the molecules or atoms collide, the molecules' or atoms' orientations, and if there is sufficient energy for the reaction to happen. So, if the angle of the plunger is changed, the atom that is shot (a lone Oxygen atom in this case) will hit the other molecule (CO in this case) at a different spot and at a different angle, therefore changing the orientation and the number of proper collisions will most likely not cause for a reaction to happen. Thanks to the simulation, we can see that this is true: depending on the angle selected, the atom may take a long time to collide with the molecule and, when a collision does occur, it may not result in the breaking of the bond and the forming of the other (no reaction happens).

In this particular case, the rate of the reaction will decrease because, by changing the angle, the molecules or atoms won't collide with the correct orientation or as often with the correct orientation.

Q12.2.3

In the PhET Reactions & Rates interactive, use the “Many Collisions” tab to observe how multiple atoms and molecules interact under varying conditions. Select a molecule to pump into the chamber. Set the initial temperature and select the current amounts of each reactant. Select “Show bonds” under Options. How is the rate of the reaction affected by concentration and temperature?

S12.2.3

Based on the Collision Theory, a reaction will only occur if the molecules collide with proper orientation and with sufficient energy required for the reaction to occur. The minimum energy the molecules must collide with is called the activation energy (energy of transition state).

Increasing the concentration of reactants increases the probability that reactants will collide in the correct orientation since there are more reactants in the same volume of space. Therefore, increasing the concentration of reactants would increase the rate of the reaction. Decreasing the concentration of reactants would decrease the rate of reaction because the overall number of possible collisions would decrease.

Temperature is directly related the the kinetic energy of molecules and activation energy E_a is the minimum energy required for a reaction to occur and doesn't change for a reaction. Increasing the temperature increases the kinetic energy of the reactants meaning the reactants will move faster and collide with each other more frequently. Therefore, increasing the temperature increase the rate of the reaction. Decreasing the temperature decreases the rate of reaction since the molecules will have less kinetic energy, move slower, and therefore collide with each other less frequently.

Q12.2.4

In the PhET Reactions & Rates interactive, on the Many Collisions tab, set up a simulation with 15 molecules of A and 10 molecules of BC. Select “Show Bonds” under Options.

a. Leave the Initial Temperature at the default setting. Observe the reaction. Is the rate of reaction fast or slow?
b. Click “Pause” and then “Reset All,” and then enter 15 molecules of A and 10 molecules of BC once again. Select “Show Bonds” under Options. This time, increase the initial temperature until, on the graph, the total average energy line is completely above the potential energy curve. Describe what happens to the reaction.

Solution

a. On the simulation, we select the default setting and the reaction A+BC. In the default setting, we see frequent collisions, a low initial temperature, and a total average energy lower than the energy of activation. The collision theory states that the rate of a reaction is directly proportional to (the fraction of molecules with required orientation), (fractions of collisions with required energy), and (collision frequency). Although we see moving and frequently colliding reactants, the rate of the forward reaction is actually slow because it takes a long time for the products, AB and C, to start appearing. This is mainly because the fractions of collisions with required energy is low, coming from the average energy of the molecules being lower than the energy of activation.

b. The reaction proceeds at an even faster rate. Again, the collision theory states that the rate of a reaction is directly proportional to (the fraction of molecules with required orientation), (fractions of collisions with required energy), and (collision frequency). Because molecules have a higher amount of energy, they have more kinetic energy. With an increased kinetic energy, the molecules not only collide more but also increase in the fraction of collision. However, the forward reaction and the backward reaction both proceed at a fast rate, so both happen almost simultaneously. It takes a shorter time for both reactions to happen. With both of the reactions adding up together overall, there is eventually a state of equilibrium. The process at which equilibrium is reached, however, is faster. Therefore, the amount of products of A+BC stays the same after a while.

12.3: Rate Laws

Q12.3.1

How do the rate of a reaction and its rate constant differ?

S12.3.1

The rate of a reaction or reaction rate is the change in the concentration of either the reactant or the product over a period of time. If the concentrations change, the rate also changes.

Rate for A → B:

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

The rate constant (k) is a proportionality constant that relates the reaction rates to reactants. If the concentrations change, the rate constant does not change.

For a reaction with the general equation: $aA + bB \rightarrow cC + dD$

the experimentally determined rate law usually has the following form:

$$rate = k[A]^m[B]^n$$

Q12.3.2

Doubling the concentration of a reactant increases the rate of a reaction four times. With this knowledge, answer the following questions:

a. What is the order of the reaction with respect to that reactant?
b. Tripling the concentration of a different reactant increases the rate of a reaction three times. What is the order of the reaction with respect to that reactant?

Solution

(a) 2; (b) 1

Q12.3.3

Tripling the concentration of a reactant increases the rate of a reaction nine times. With this knowledge, answer the following questions:

a. What is the order of the reaction with respect to that reactant?
b. Increasing the concentration of a reactant by a factor of four increases the rate of a reaction four times. What is the order of the reaction with respect to that reactant?

Q12.3.4

How much and in what direction will each of the following affect the rate of the reaction: $\mathrm{CO}(g) + \mathrm{NO_2}(g) \longrightarrow \mathrm{CO_2}(g) + \mathrm{NO}(g)$ if the rate law for the reaction is $\text{rate} = k[\mathrm{NO_2}]^2$?

a. Decreasing the pressure of NO_2 from 0.50 atm to 0.250 atm.
b. Increasing the concentration of CO from 0.01 *M* to 0.03 *M*.

Solution

(a) The process reduces the rate by a factor of 4. (b) Since CO does not appear in the rate law, the rate is not affected.

Q12.3.5

How will each of the following affect the rate of the reaction: $\mathrm{CO}(g) + \mathrm{NO_2}(g) \longrightarrow \mathrm{CO_2}(g) + \mathrm{NO}(g)$ if the rate law for the reaction is $\text{rate} = k[\mathrm{NO_2}][\mathrm{CO}]$?

a. Increasing the pressure of NO_2 from 0.1 atm to 0.3 atm
b. Increasing the concentration of CO from 0.02 *M* to 0.06 *M*.

Q12.3.6

Regular flights of supersonic aircraft in the stratosphere are of concern because such aircraft produce nitric oxide, NO, as a byproduct in the exhaust of their engines. Nitric oxide reacts with ozone, and it has been suggested that this could contribute to

depletion of the ozone layer. The reaction $\mathbf{NO + O_3 \longrightarrow NO_2 + O_2}$ is first order with respect to both NO and O_3 with a rate constant of 2.20×10^7 L/mol/s. What is the instantaneous rate of disappearance of NO when [NO] = 3.3×10^{-6} *M* and [O_3] = 5.9×10^{-7} *M*?

Solution

4.3×10^{-5} mol/L/s

Q12.3.7

Radioactive phosphorus is used in the study of biochemical reaction mechanisms because phosphorus atoms are components of many biochemical molecules. The location of the phosphorus (and the location of the molecule it is bound in) can be detected from the electrons (beta particles) it produces:

$$\mathbf{^{32}_{15}P \longrightarrow {}^{32}_{16}S + e^-}$$

Rate = 4.85×10^{-2} $\mathbf{day^{-1}}$ $\mathbf{[^{32}P]}$

What is the instantaneous rate of production of electrons in a sample with a phosphorus concentration of 0.0033 *M*?

Q12.3.8

The rate constant for the radioactive decay of ^{14}C is 1.21×10^{-4} $year^{-1}$. The products of the decay are nitrogen atoms and electrons (beta particles):

$$\mathbf{^{6}_{14}C \longrightarrow {}^{6}_{14}N + e^-}$$

$$\mathbf{rate = \mathit{k}[^{6}_{14}C]}$$

What is the instantaneous rate of production of N atoms in a sample with a carbon-14 content of 6.5×10^{-9} *M*?

Solution

7.9×10^{-13} mol/L/year

Q12.3.9

What is the instantaneous rate of production of N atoms Q12.3.8 in a sample with a carbon-14 content of 1.5×10^{-9} *M*?

Q12.3.10

The decomposition of acetaldehyde is a second order reaction with a rate constant of 4.71×10^{-8} L/mol/s. What is the instantaneous rate of decomposition of acetaldehyde in a solution with a concentration of 5.55×10^{-4} *M*?

Q12.3.11

Alcohol is removed from the bloodstream by a series of metabolic reactions. The first reaction produces acetaldehyde; then other products are formed. The following data have been determined for the rate at which alcohol is removed from the blood of an average male, although individual rates can vary by 25–30%. Women metabolize alcohol a little more slowly than men:

[C_2H_5OH] (*M*)	4.4×10^{-2}	3.3×10^{-2}	2.2×10^{-2}
Rate (mol/L/h)	2.0×10^{-2}	2.0×10^{-2}	2.0×10^{-2}

Determine the rate equation, the rate constant, and the overall order for this reaction.

Solution

rate = k; $k = 2.0 \times 10^{-2}$ mol/L/h (about 0.9 g/L/h for the average male); The reaction is zero order.

Q12.3.12

Under certain conditions the decomposition of ammonia on a metal surface gives the following data:

$[NH_3]$ (M)	1.0×10^{-3}	2.0×10^{-3}	3.0×10^{-3}
Rate (mol/L/h^1)	1.5×10^{-6}	1.5×10^{-6}	1.5×10^{-6}

Determine the rate equation, the rate constant, and the overall order for this reaction.

Q12.3.13

Nitrosyl chloride, NOCl, decomposes to NO and Cl_2.

$$2\,NOCl(g) \longrightarrow 2\,NO(g) + Cl_2(g)$$

Determine the rate equation, the rate constant, and the overall order for this reaction from the following data:

[NOCl] (M)	0.10	0.20	0.30
Rate (mol/L/h)	8.0×10^{-10}	3.2×10^{-9}	7.2×10^{-9}

Solution

Before we can figure out the rate constant first we must first determine the basic rate equation and rate order. The basic rate equation for this reaction, where n is the rate order of NOCl and k is the rate constant, is

$$rate = k[NOCl]^n$$

since NOCl is the reactant in the reaction.

In order to figure out the order of the reaction we must find the order of [NOCl] as it is the only reactant in the reaction. To do this we must examine how the rate of the reaction changes as the concentration of NOCl changes.

As [NOCl] doubles in concentration from 0.10 M to 0.20 M the rate goes from 8.0 x 10^{-10} to 3.2 x 10^{-9}

(3.2 x 10^{-9}(mol/L/h))/(8.0 x 10^{-10}(mol/L/h)) = 4

so we conclude that as [NOCl] doubles, the rate goes up by 4. Since 2^2= 4 we can say that the order of [NOCl] is 2 so our updated rate law is

$$rate = k[NOCl]^2$$

Now that we have the order, we can substitute the first experimental values from the given table to find the rate constant, k

(8.0 x 10^{-10}(mol/L/h)) = k(0.10 M)^2 so

$$k = \frac{8.0 \times 10^{-10}}{(0.10\,M)^2} = 8 \times 10^{-8} M^{-1} sec^{-1}$$

We were able to find the units of k using rate order, when the rate order is 2 units of k are M^{-1} x sec^{-1}

So the rate equation is: rate = k[NOCl]^2, it is second order, and k = 8 x 10^{-8} M^{-1} x sec^{-1}

Overall rate law :

$$rate = \underbrace{(8 \times 10^{-8})}_{1/(M \times sec)} [NOCl]^2$$

Answer

rate = k[NOCl]^2; k = 8.0 × 10^{-8} L/mol/s; second order

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Q12.3.14

From the following data, determine the rate equation, the rate constant, and the order with respect to *A* for the reaction $A \longrightarrow 2C$.

[*A*] (*M*)	1.33×10^{-2}	2.66×10^{-2}	3.99×10^{-2}
Rate (mol/L/h)	3.80×10^{-7}	1.52×10^{-6}	3.42×10^{-6}

Solution

A. Using the experimental data, we can compare the effects of changing [A] on the rate of reaction by relating ratios of [A] to ratios of rates

$$\frac{2.66 \times 10^{-2}}{1.33 \times 10^{-2}} = 2$$

and

$$\frac{1.52 \times 10^{-6}}{3.8 \times 10^{-7}} = 4$$

B. From this we know that doubling the concentration of A will result in quadrupling the rate of reaction. The order of this reaction is 2.

C. We can now write the rate equation since we know the order:

$$rate = k[A]^2$$

D. By plugging in one set of experimental data into our rate equation we can solve for the rate constant, k:

$$3.8 \times 10^{-7} = k \times (1.33 \times 10^{-2})^2$$

$$k = \frac{3.8 \times 10^{-7}}{1.769 \times 10^{-4}}$$

$$k = .00215 M^{-1} s^{-1}$$

Answer

$k = .00215 M^{-1} s^{-1}$

2nd Order

Q12.3.15

Nitrogen(II) oxide reacts with chlorine according to the equation:

$$2\,NO(g) + Cl_2(g) \longrightarrow 2\,NOCl(g)$$

The following initial rates of reaction have been observed for certain reactant concentrations:

[NO] (mol/L^1)	[Cl_2] (mol/L)	Rate (mol/L/h)
0.50	0.50	1.14
1.00	0.50	4.56
1.00	1.00	9.12

What is the rate equation that describes the rate's dependence on the concentrations of NO and Cl_2? What is the rate constant? What are the orders with respect to each reactant?

Solution

For the general equation,

$aA + bB \rightarrow cC + dD$

The rate can be written as

$rate = k[A]^m[B]^n$ where k is the rate constant, and m and n are the reaction orders.

For our equation

$2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$

the $rate = k[NO]^m[Cl_2]^n$

Now, we need to find the reaction orders. Reaction orders can only be found through experimental values. We can compare two reactions where one of the reactants has the same concentration for both trials, and solve for the reaction order.

$\frac{rate_1}{rate_2} = \frac{[NO]_1^m[Cl_2]_1^n}{[NO]_2^m[Cl_2]_2^n}$

We can use the data in the table provided. If we plug in the values for rows 1 and 2, we see that the values for the concentration of Cl will cancel, leaving just the rates and the concentrations of NO.

$\frac{1.14}{4.56} = \frac{[0.5]^m}{[1.0]^m}$

We can now solve for m, and we find that m =2. This means that the reaction order for [NO] is 2.

Now we must find the value of n. To do so, we can use the same equation but with the values from rows 2 and 3. This time, the concentration of NO will cancel out.

$\frac{4.56}{9.12} = \frac{[0.5]^n}{[1.0]^n}$

When we solve for n, we find that n = 1. This means that the reaction order for $[Cl_2]$ is 1.

We are one step closer to finishing our rate equation.

$rate = k[NO]^2[Cl_2]$

Finally, we can solve for the rate constant. To do this, we can use one of the trials of the experiment, and plug in the values for the rate, and concentrations of reactants, then solve for k.

$1.14 mol/L/h = k[0.5 mol/L]^2[0.5 mol/L]$

$k = 9.12 L^2 mol^{-2} h^{-1}$

So, our final rate equation is:

$rate = (9.12 L^2 mol^{-2} h^{-1})[NO]^2[Cl_2]$

*A common mistake is forgetting units. Make sure to track your units throughout the process of determining your rate constant. Be careful because the units will change relative to the reaction order.

Answer

rate = $k[NO]^2[Cl]_2$; k = 9.12 L^2 mol^{-2} h^{-1}; second order in NO; first order in Cl_2

Q12.3.17

Hydrogen reacts with nitrogen monoxide to form dinitrogen monoxide (laughing gas) according to the equation:

$$H_2(g) + 2NO(g) \longrightarrow N_2O(g) + H_2O(g)$$

Determine the rate equation, the rate constant, and the orders with respect to each reactant from the following data:

[NO] (*M*)	0.30	0.60	0.60
[H_2] (*M*)	0.35	0.35	0.70
Rate (mol/L/s)	2.835×10^{-3}	1.134×10^{-2}	2.268×10^{-2}

Solution

Determine the rate equation, the rate constant, and the orders with respect to each reactant.

The rate constant and the orders can be determined through the differential rate law. The general form of the differential rate law is given below:

aA + bB + cC ==> products

$$\text{rate} = -\frac{d[A]}{dt} = k[A]^n[B]^m[C]^p$$

where A, B, and C are the concentrations of the reactants, k is the rate constant, and n,m, and p refer to the order of each reactant.

To find the orders of each reactant, we see that when [NO] doubles but $[H_2]$ doesn't change, the rate quadruples, meaning that [NO] is a second order reaction ($[NO]^2$). When $[H_2]$ doubles but [NO] doesn't change, the rate doubles, meaning that $[H_2]$ is a first order reaction. So the rate law would look something like this:

$$\text{Rate} = k[NO]^2[H_2]$$

We can use this rate law to determine the value of the rate constant. Plug in the data for reactant concentration and rate from one of the trials to solve for k the rate constant. In this case, we chose to use the data from trial 1 from the second column of the data table.

$$2.835\text{x}10^{-3} = k[0.3]^2[0.35]$$

$$k = .09\ M^{-2}/s^{-1}$$

Q12.3.18

For the reaction $A \longrightarrow B + C$, the following data were obtained at 30 °C:

[A] (*M*)	0.230	0.356	0.557
Rate (mol/L/s)	4.17×10^{-4}	9.99×10^{-4}	2.44×10^{-3}

a. What is the order of the reaction with respect to [*A*], and what is the rate equation?
b. What is the rate constant?

Solution

1. The rate equation for an n order reaction is given as $\frac{dr}{dt} = k[A]^n$. Where $[A]$ is the concentration in M, and $\frac{dr}{dt}$ is the rate in M/s.

We can then use each set of data points, plug its values into the rate equation and solve for n. Note you can use any of the data points as long as the concentration corresponds to its rate.

Rate equation 1: $4.17 \times 10^{-4} = k[0.230]^n$

Rate equation 2: $9.99 \times 10^{-4} = k[0.356]^n$

We divide Rate equation 1 by Rate equation 2 in order to cancel out k, the rate constant.

$$\frac{4.17\times10^{-4}}{9.99\times10^{-4}} = \frac{k[0.230]^n}{k[0.356]^n}$$

$$0.417 = 0.646^n$$

Now the only unknown we have is n. Using logarithm rules one can solve for it.

$$ln\ 0.417 = n \cdot ln\ 0.646$$

$$\frac{ln\ 0.417}{ln\ 0.646} = n = 2$$

The rate equation is second order with respect to A and is written as $\frac{dr}{dt} = k[A]^2$.

2. We can solve for k by plugging in any data point into our rate equation $\frac{dr}{dt} = k[A]^2$.

Using the first data points for instance $[A] = 0.230 \ \frac{mol}{L}$ and $\frac{dr}{dt} = 4.17 \times 10^{-4} \ \frac{mol}{L \cdot s}$] we get the equation $4.17 \times 10^{-4} \ \frac{mol}{L \cdot s} = k[0.230 \ \frac{mol}{L}]^2$

Which solves for $k = 7.88 \times 10^{-3} \frac{L}{mol \cdot s}$

Since we know this is a second order reaction the appropriate units for k can also be written as $\frac{1}{M \cdot s}$

Answer

(a) The rate equation is second order in A and is written as rate = $k[A]^2$. (b) $k = 7.88 \times 10^{-13}$ L mol^{-1} s^{-1}

Q12.3.19

For the reaction $Q \longrightarrow W + X$, the following data were obtained at 30 °C:

$[Q]_{initial}$ (M)	0.170	0.212	0.357
Rate (mol/L/s)	6.68×10^{-3}	1.04×10^{-2}	2.94×10^{-2}

a. What is the order of the reaction with respect to [Q], and what is the rate equation?
b. What is the rate constant?

Solution

What is the order of the reaction with respect to [Q], and what is the rate equation?

- Order reaction: 2 because when you use the ratio trial 3:2, it will look like this:
- $(\frac{2.94 * 10^{-2}}{1.04 * 10^{-2}}) = (\frac{0.357^x}{0.212^x})$
- $2.82 = 1.7^x$
- x = 2 so the order of reaction is 2
- Rate reaction equation: Rate=k[Q]^2

What is the rate constant?

- To find the rate constant (k) simply plug and calculate one of the trials into the rate equation
- 1.04 x 10^{-2}=k[0.212]^2
- k=0.231 $M^{-1}s^{-1}$

Answer

Order: 2

k=0.231 $M^{-1}s^{-1}$

Q12.3.20

The rate constant for the first-order decomposition at 45 °C of dinitrogen pentoxide, N_2O_5, dissolved in chloroform, $CHCl_3$, is 6.2×10^{-4} min^{-1}.

$$2\,N_2O_5 \longrightarrow 4\,NO_2 + O_2$$

What is the rate of the reaction when [N_2O_5] = 0.40 M?

Solution

Step 1: The first step is to write the rate law. We know the general formula for for a first-order rate law. It is as follows: Rate=k[A]

Step 2: We now plug in [N_2O_5] in for [A] in our general rate law. We also plug in our rate constant (k), which was given to us. Now our equation looks as follows:

Rate=(6.2x10^{-4} min^{-1})[N_2O_5]

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Step 3: We now plug in our given molarity. $[N_2O_5]$=0.4 M. Now our equation looks as follows:

Rate=($6.2x10^{-4}$ min^{-1})(0.4 M)

Step 4: We now solve our equation. Rate=($6.2x10^{-4}$ min^{-1})(0.4 M)= $2.48x10^{-4}$ M/min.
Step 5: Use significant figures and unit conversion to round $2.48x10^{-4}$ M/min to 2.5×10^{-4} (moles)$L^{-1}min^{-1}$

Answer

(a) 2.5×10^{-4} mol/L/min

Q12.3.21

The annual production of HNO_3 in 2013 was 60 million metric tons Most of that was prepared by the following sequence of reactions, each run in a separate reaction vessel.

a. $4\,NH_3(g) + 5\,O_2(g) \longrightarrow 4\,NO(g) + 6\,H_2O(g)$
b. $2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g)$
c. $3\,NO_2(g) + H_2O(l) \longrightarrow 2\,HNO_3(aq) + NO(g)$

The first reaction is run by burning ammonia in air over a platinum catalyst. This reaction is fast. The reaction in equation (c) is also fast. The second reaction limits the rate at which nitric acid can be prepared from ammonia. If equation (b) is second order in NO and first order in O_2, what is the rate of formation of NO_2 when the oxygen concentration is 0.50 *M* and the nitric oxide concentration is 0.75 *M*? The rate constant for the reaction is 5.8×10^{-6} $L^2/mol^2/s$.

Solution

To determine the rate law for an equation we need to look at its slow step. Since both equation a and c are fast, equation b can be considered the slow step of the reaction. The slow step is also considered the rate determining step of the system.

Hence, The rate determining step is the second step because it's the slow step.

rate of production of $NO_2 = k[A]^m[B]^n$

$rate = k[NO]^2[O_2]^1\ M/s$

$rate = (5.8 * 10^{-6})[0.75]^2[0.5]^1\ M/s$

$rate = 1.6 * 10^{-6}\ M/s$

Answer

$rate = 1.6 * 10^{-6}\ M/s$

Q12.3.22

The following data have been determined for the reaction:

$$I^- + OCl^- \longrightarrow IO^- + Cl^-$$

	1	2	3
$[I^-]_{initial}$ (*M*)	0.10	0.20	0.30
$[OCl^-]_{initial}$ (*M*)	0.050	0.050	0.010
Rate (mol/L/s)	3.05×10^{-4}	6.20×10^{-4}	1.83×10^{-4}

Determine the rate equation and the rate constant for this reaction.

Solution

Using the reactants, we can form the rate law of the reaction: $$ r=k[OCl^-]^n[I^-]^m \]

From there, we need to use the data to determine the order of both $[OCl^-]$ and $[I^-]$. In doing so, we need to compare r_1 to r_2 such that:

$$\frac{r_1}{r_2} = \frac{(0.10^m)(0.050^n)}{(0.20^m)(0.050^n)} = \frac{3.05 \times 10^{-4}}{6.20 \times 10^{-4}} \tag{8.E.3}$$

$$0.5^m = 0.5 \tag{8.E.4}$$

$$m = 1 \tag{8.E.5}$$

We can "cross out" the concentration of $[OCl^-]$ because it has the same concentration in both of the trials used.

Now that we know m ($[I^-]$) has a first order of 1.

We cannot "cross out" $[I^-]$ to find $[OCl^-]$ because no two trials have the same concentration. In order to solve for n we will plug in 1 for m.

$$\frac{r_1}{r_3} = \frac{(0.10^1)(0.050^n)}{(0.30^1)(0.010^n)} = \frac{3.05 \times 10^{-4}}{1.83 \times 10^{-4}} \tag{8.E.6}$$

$$\frac{1}{3}(5^n) = 1.6666667 \tag{8.E.7}$$

$$5^n = 5 \tag{8.E.8}$$

$$n = 1 \tag{8.E.9}$$

Since we know that orders of both n and m are equal to one, we can not substitute them into the rate law equation along with the respective concentrations (from either the first, second, or third reaction) and solve for the rate constant, k.

$$r = k[OCl^-]^n[I^-]^m \tag{8.E.10}$$

$$3.05 * 10^{-4} = k[0.05]^1[0.10]^1 \tag{8.E.11}$$

$$k = 6.1 * 10^{-2} \frac{L}{mol \times s} \tag{8.E.12}$$

Thus the overall rate law is: $$ r = (6.1 * 10^{-2} \frac {L}{mol \times s})[OCl^-][I^-] \]

The units for K depend on the overall order of the reaction. To find the overall order we add m and n together. By doing this we find an overall order of 2. This is why the units for K are $$ \frac {L}{mol \times s} \]

Answer

rate = $k[I^-][OCl^{-1}]$; k = 6.1 × 10^{-2} L mol $^{-1}$ s^{-1}

Q12.3.23

In the reaction

$$2NO + Cl_2 \rightarrow 2NOCl$$

the reactants and products are gases at the temperature of the reaction. The following rate data were measured for three experiments:

Initial p{NO}$	Initial $p\{Cl_2\}$	Initial rate
(atm)	(atm)	(moles of A consumed atm sec^{-1})
0.50	0.50	5.1 x 10^{-3}
1.0	1.0	4.0 x 10^{-2}
0.50	1.0	1.0 x 10^{-2}

a. From these data, write the rate equation for this gas reaction. What order is the reaction in NO, Cl_2, and overall?
b. Calculate the specific rate constant for this reaction.

Solution

a. The rate equation can be determined by designing experiments that measure the concentration(s) of one or more reactants or products as a function of time. For the reaction $A + B \rightarrow products$, for example, we need to determine *k* and the exponents *m* and *n* in the following equation:

$$rate = k[A]^m[B]^n$$

To do this, the initial concentration of B can be kept constant while varying the initial concentration of A and calculating the initial reaction rate. This information would deduce the reaction order with respect to A. The same process can be done to find the reaction order with respect to B.
In this particular example,

$$\frac{rate_2}{rate_3} = \frac{k[A_2]^m[B_2]^n}{k[A_3]^m[B_3]^n}$$

So taking the values from the table,

$$\frac{4.0 * 10^{-2}}{1.0 * 10^{-2}} = \frac{k[1.0]^m[1.0]^n}{k[0.5]^m[1.0]^n}$$

and by canceling like terms, you are left with

$$\frac{4.0 * 10^{-2}}{1.0 * 10^{-2}} = \frac{[1.0]^m}{[0.5]^m}$$

Now, solve for m

$4 = 2^m \Longrightarrow m = 2$ Because m=2, the reaction with respect to *NO* is 2. ***NO* is second order.**

You can repeat the same process to find n.

$$\frac{rate_3}{rate_1} = \frac{k[A_3]^m[B_3]^n}{k[A_1]^m[B_1]^n}$$

Taking the values from the table,

$$\frac{1.0 * 10^{-2}}{5.1 * 10^{-3}} = \frac{k[0.5]^m[1.0]^n}{k[0.5]^m[0.5]^n}$$

and by canceling like terms, you are left with

$$\frac{1.0 * 10^{-2}}{5.1 * 10^{-3}} = \frac{[1.0]^n}{[0.5]^n}$$

Now this time, solve for n

$2 = 2^n \implies n = 1$

Because n=1, the reaction with respect to Cl_2 is 1. Cl_2 **is first order.**

So the rate equation is

$$rate = k[NO]^2[Cl_2]^1$$

To find the overall rate order, you simply add the orders together. Second order + first order makes the **overall reaction third order.**

b. The rate constant is calculated by inserting the data from any row of the table into the experimentally determined rate law and solving for k. For a third order reaction, the units of k are $frac1atm^2 * sec$. Using Experiment 1,

$$rate = k[NO]^2[Cl_2]^1 \implies 5.1 * 10^{-3} \frac{atm}{sec} = k[0.5matm]^2[0.5atm]^1$$

$$k = 0.0408 \frac{1}{atm^2 * sec}$$

Answer

NO is second order.

Cl_2 is first order.

Overall reaction order is three.

b)

$k = 0.0408\ atm^{-2} * sec^{-1}$

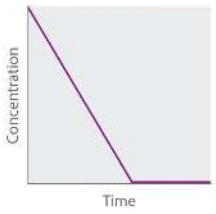
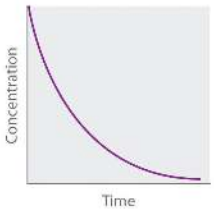
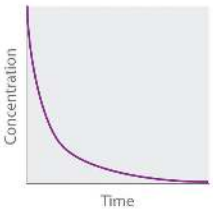
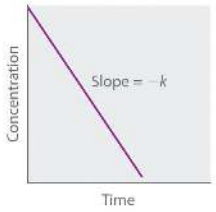
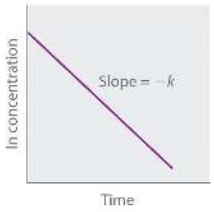
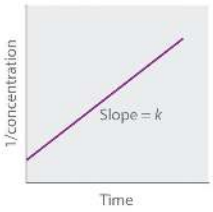
12.4: Integrated Rate Laws

Q12.4.1

Describe how graphical methods can be used to determine the order of a reaction and its rate constant from a series of data that includes the concentration of *A* at varying times.

Solution

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	Zeroth Order	First Order	Second Order
Differential rate law	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k$	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]$	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2$
Concentration vs. time			
Integrated rate law	$[A] = [A]_0 - kt$	$[A] = [A]_0 e^{-kt}$ or $\ln[A] = \ln[A]_0 - kt$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$
Straight-line plot to determine rate constant			
Relative rate vs. concentration	[A], *M* / Rate, M/s 1 / 1 2 / 1 3 / 1	[A], *M* / Rate, M/s 1 / 1 2 / 2 3 / 3	[A], *M* / Rate, M/s 1 / 1 2 / 4 3 / 9
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$
Units of *k*, rate constant	M/s	1/s	$M^{-1}\cdot s^{-1}$

To determine the order of a reaction when given the data series, one must graph the data how it is, graph it as natural log of [A], and graph it as 1/[A]. Whichever method yields a straight line will determine the order. Respective of the methods of graphing above, if a straight line is yielded by the first graphing method its a 0 order, if by the second method it's a 1st order, and the third graphing method its a 2nd order. When the order of the graph is known, a series of equations, given in the above image, can be used with the various points on the graph to determine the value of k. We can see that we need an initial value of A and a final value of A, and both of these would be given by the data.

Zeroth order when plotting initial concentrating versus final concentration you have a negative linear slope.

$$[A] = [A]_0 - kt$$

First order when plotting ln[initial concentration] versus ln[final concentration] you have a negative linear slope.

$$\ln[A] = \ln[A]_0 - kt$$

Second order when plotting the 1/[initial concentration] versus 1/[final concentration] you have a positive linear slope.

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

Q12.4.2

Use the data provided to graphically determine the order and rate constant of the following reaction: $SO_2Cl_2 \longrightarrow SO_2 + Cl_2$

Time (s)	0	5.00×10^3	1.00×10^4	1.50×10^4	2.50×10^4	3.00×10^4	4.00×10^4
$[SO_2Cl_2]$ (M)	0.100	0.0896	0.0802	0.0719	0.0577	0.0517	0.0415

Solution

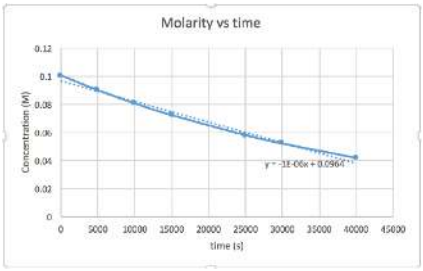
Use the data to graphically determine the order and rate constant of the following reaction.

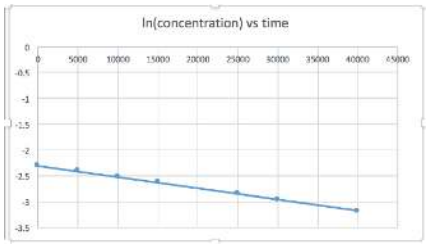
In order to determine the rate law for a reaction from a set of data consisting of concentration (or the values of some function of concentration) versus time, make three graphs of the data based on the integrated rate laws of each order reaction.

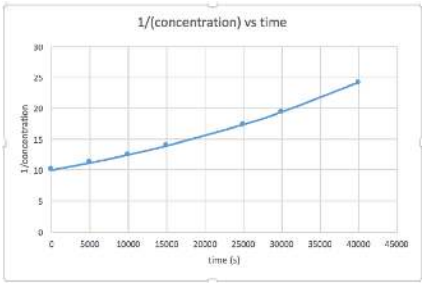
[concentration] versus time (linear for a zero order reaction) ln [concentration] versus time (linear for a 1st order reaction) 1 / [concentration] versus time (linear for a 2nd order reaction)

slope= -2.0 x 10^{-5}

k = 2.0 x 10^{-5}







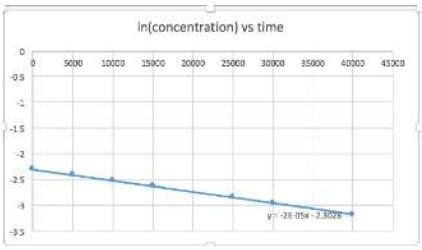
The graph that is linear indicates the order of the reaction. Then, you can find the correct rate equation:

zero order reaction	rate = k	(k = - slope of line)
1st order reaction	rate = k[A]	(k = - slope of line)
2nd order reaction	rate = $k[A]^2$	(k = slope of line)

In this graph, ln(concentration) vs time is linear, indicating that the **reaction is first order**.

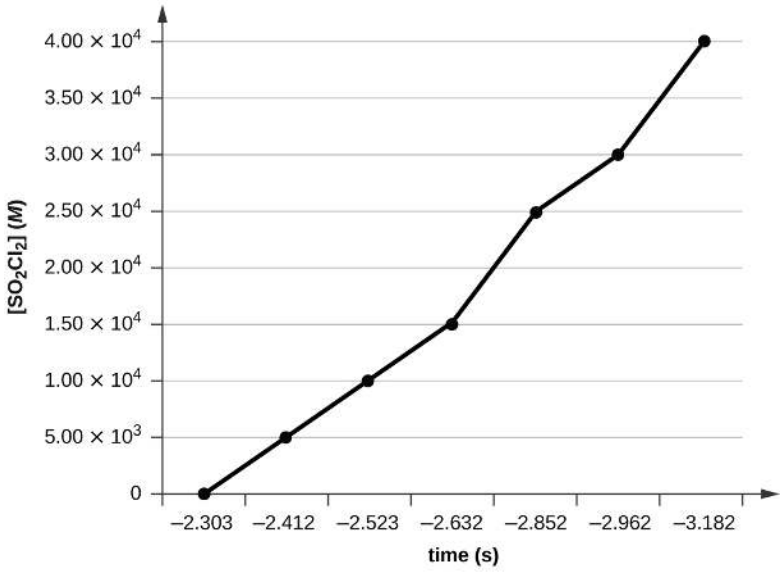
k=-slope of line

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Answer

Plotting a graph of $\ln[SO_2Cl_2]$ versus t reveals a linear trend; therefore we know this is a first-order reaction:



$k = -2.20 \times 10^5\ s^{-1}$

Q12.4.3

Use the data provided in a graphical method to determine the order and rate constant of the following reaction:

$$2P \longrightarrow Q + W$$

Time (s)	9.0	13.0	18.0	22.0	25.0
[P] (*M*)	1.077×10^{-3}	1.068×10^{-3}	1.055×10^{-3}	1.046×10^{-3}	1.039×10^{-3}

Solution

Add texts here. Do not delete this text first.

Q12.4.4

Pure ozone decomposes slowly to oxygen, $2\,O_3(g) \longrightarrow 3\,O_2(g)$. Use the data provided in a graphical method and determine the order and rate constant of the reaction.

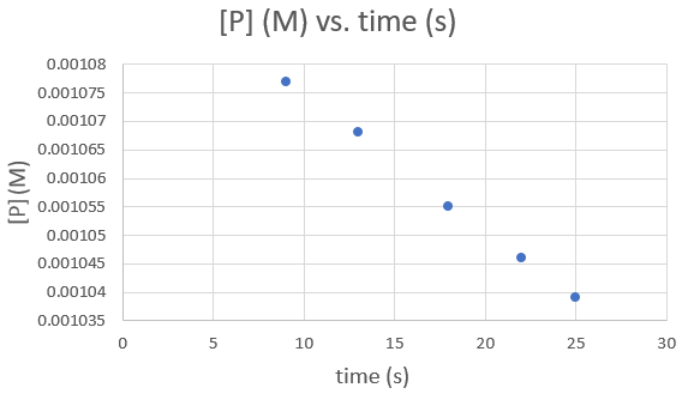
Time (h)	0	2.0×10^3	7.6×10^3	1.23×10^4	1.70×10^4	1.70×10^4
$[O_3]$ (*M*)	1.00×10^{-5}	4.98×10^{-6}	2.07×10^{-6}	1.39×10^{-6}	1.22×10^{-6}	1.05×10^{-6}

Solution

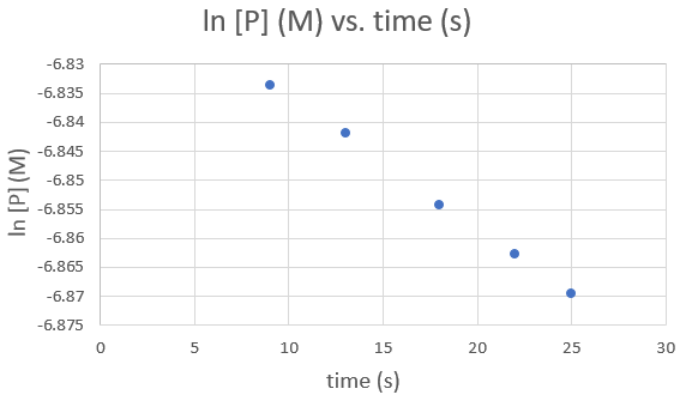
https://chem.libretexts.org/@go/page/242855

To determine the order and rate constant, you need to graph the data for zero order, first order, and second order by plotting concentration versus time- [A] vs. time, natural logarithm (ln) of [A] vs. time, and 1/[A] vs. time respectively. The order of the reaction is determined by identifying which of these three graphs produces a straight line. The rate constant *k* is represented by the slope of the graph. The graphs with their respective data values would be

Time (s)	9.0	13.0	18.0	22.0	25.0
[P] (*M*)	1.077 × 10−3	1.068 × 10−3	1.055 × 10−3	1.046 × 10−3	1.039 × 10−3

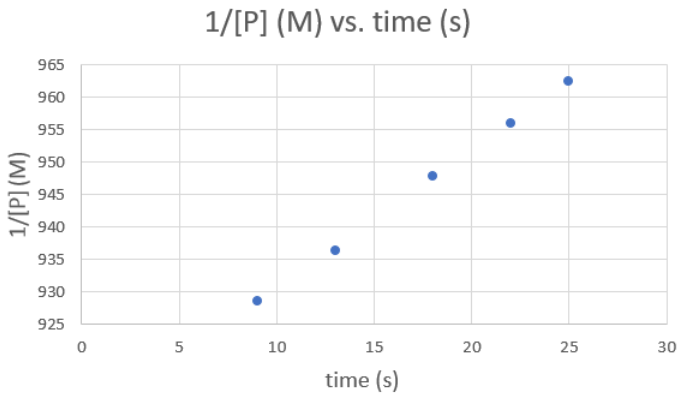


Time (s)	9.0	13.0	18.0	22.0	25.0
ln [P] (*M*)	-6.83358	-6.84197	-6.85421	-6.86278	-6.8695



Time (s)	9.0	13.0	18.0	22.0	25.0
1/[P] (*M*)	928.5051	936.3296	947.8673	956.0229	962.4639

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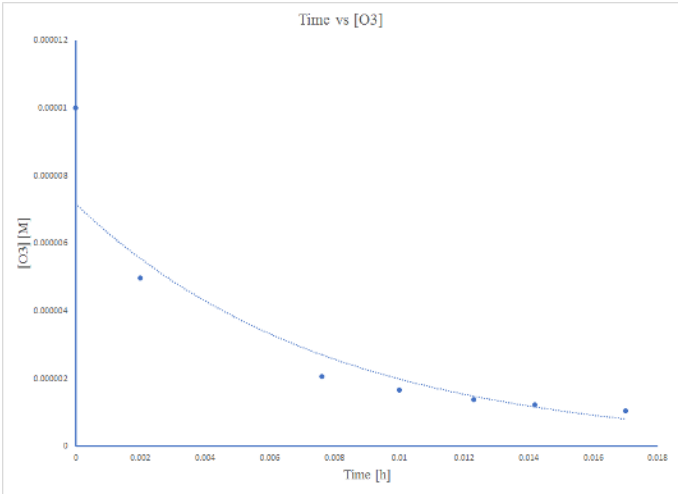
Since each graph yields a straight line **the order and rate constant of the reaction cannot be determined**.

To identify how the concentrations changes a function of time, requires solving the appropriate differential equation (i.e., the differential rate law).

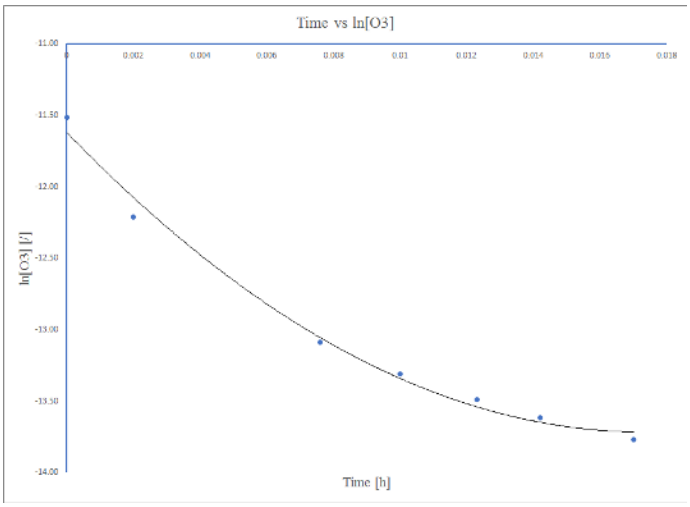
The zero-order rate law predicts in a linear decay of concentration with time

The 1st-order rate law predicts in an exponential decay of concentration with time

The 2nd-order rate law predicts in an reciprocal decay of concentration with time

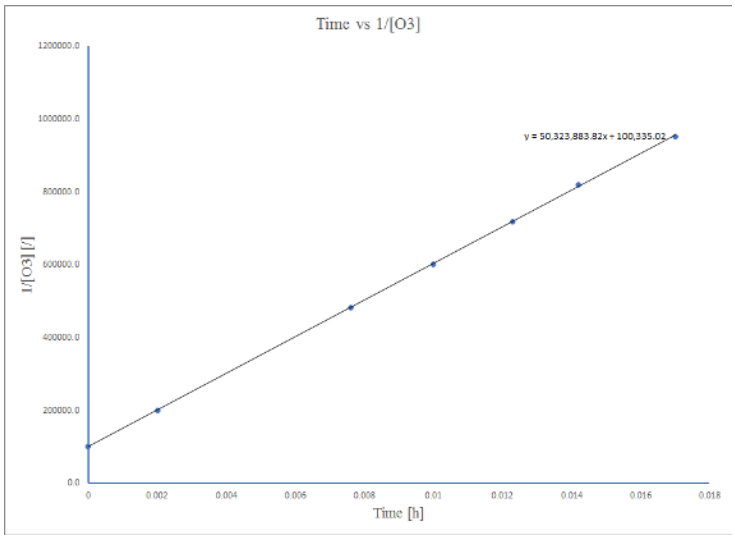


The plot is not linear, so the reaction is not zero order.



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The plot is not linear, so the reaction is not first order.



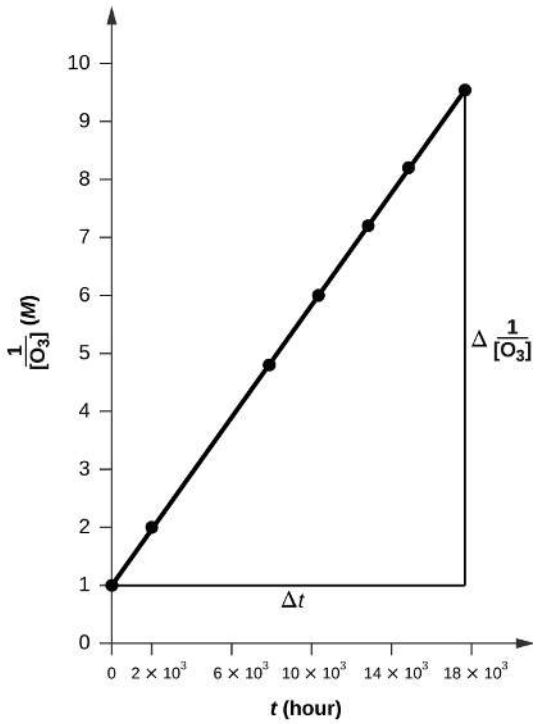
The plot is nicely linear, so the reaction is second order.

To a second order equation, $1/[A] = k*t+1/[A_0]$

Thus, the value of K is the slope of the graph Time vs $\frac{1}{O_3}$,

k = 50.3*10^6 L mol^{-1} h^{-1}

Answer



The plot is nicely linear, so the reaction is second order.

k = 50.1 L mol^{-1} h^{-1}

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Q12.4.5

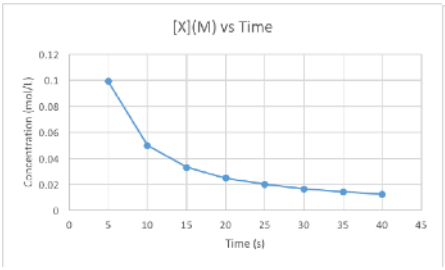
From the given data, use a graphical method to determine the order and rate constant of the following reaction:

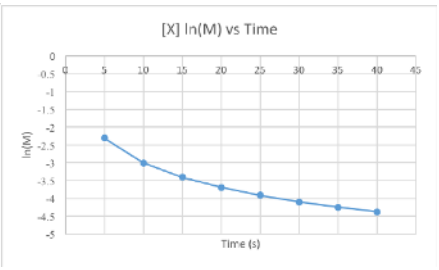
$$2X \longrightarrow Y + Z \tag{8.E.13}$$

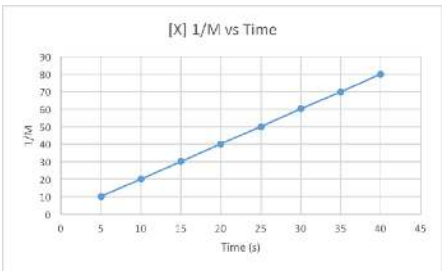
Time (s)	5.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0
[*X*] (*M*)	0.0990	0.0497	0.0332	0.0249	0.0200	0.0166	0.0143	0.0125

Solution

In order to determine the order of the reaction we need to plot the data using three different graphs. All three graphs will have time in seconds as the x-axis, but the y-axis is what will differ. One graph will plot concentration versus time, the second will plot natural log of concentration versus time, and the other will plot 1/concentration versus times. Whichever graph results in a line, we know that must be the order of the reaction. If we get a line using the first graph, it will be zero order, if it is a line for the second graph it will be first order, and if it is a line for the third graph it will be a second order reaction. Now lets plot the data to determine the order.







We can clearly see that the third graph, which plots 1/M versus time, is a straight line while the other two are slightly curved. Therefore, we can determine that the rate of this reaction is second order. This also tells us that the units of the rate constant which should be $M^{-2}s^{-1}$ for a second order reaction.

To determine the rate constant, called k, we simple need to figure out the slope of the third graph since that is the order of this reaction. To find the slope of the line, we take two points and subtract the y values and then divide them by the difference of the x values. This is how to do it:

Use the points (5, 10.101) and (40, 80).

Now use these to get the slop, aka the rate constant: (80-10.101)/(40-5) = 1.997 = k

So the rate constant for this second order reaction is 1.997 $M^{-1}s^{-1}$.

Q12.4.6

What is the half-life for the first-order decay of phosphorus-32? ($^{32}_{15}\mathrm{P} \longrightarrow {}^{32}_{16}\mathrm{S} + \mathrm{e}^-$) The rate constant for the decay is 4.85×10^{-2} day^{-1}.

Solution

This is a first order reaction, so we can use our half life equation below:

$$t_{1/2} = \frac{0.693}{k}$$

The rate constant is given to us in units per day. All we have to do, is to plug it into the equation.

$$t_{1/2} = \frac{0.693}{4.85 * 10^{-2}}$$

$$= 14.3\ days$$

A12.4.6

14.3 d

Q12.4.7

What is the half-life for the first-order decay of carbon-14? ($_{14}^{6}\mathrm{C} \longrightarrow {}_{14}^{7}\mathrm{N} + \mathrm{e}^{-}$) The rate constant for the decay is 1.21 × 10^{-4} $year^{-1}$.

Solution

To find the half life, we need to use the first-order half-life equation. All half life reactions undergo first order reactions.

The half-life equation for first order is

$$t_{1/2} = ln2/k$$

with k being the rate constant. The rate constant for carbon-14 was given as $1.21 \times 10^{-4} year^{-1}$.

Plug it in the equation.

$$t_{1/2} = ln2/(1.21 \times 10^{-4} year^{-1})$$

and solve for $t_{1/2}$.

When you calculate it, the half life for carbon-14 is 5.73*10^3

Answer

The half-life for carbon-14 is calculated to be 5.73*10^3

Q12.4.8

What is the half-life for the decomposition of NOCl when the concentration of NOCl is 0.15 *M*? The rate constant for this second-order reaction is 8.0 × 10^{-8} L/mol/s.

Solution

The half-life of a reaction, $t_{1/2}$, is the amount of time that is required for a reactant concentration to decrease by half compared to its initial concentration. When solving for the half-life of a reaction, we should first consider the order of reaction to determine it's rate law. In this case, we are told that this reaction is second-order, so we know that the integrated rate law is given as:

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

Isolating for time, we find that:

$$t_{1/2} = \frac{1}{k[A]_0}$$

Now it is just a matter of substituting the information we have been given to calculate $t_{1/2}$, where the rate constant, k, is equal to 8.0 × 10^{-8} L/mol/s and initial concentration, $[A]_0$, is equal to 0.15*M*:

$$t_{1/2} = \frac{1}{(8.0 \times 10^{-8})(0.15)} = 8.33 \times 10^{7} seconds$$

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Answer

8.33×10^7 s

Q12.4.9

What is the half-life for the decomposition of O_3 when the concentration of O_3 is 2.35×10^{-6} *M*? The rate constant for this second-order reaction is 50.4 L/mol/h.

Solution

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Since the reaction is second order, its half-life is

$$t_{\frac{1}{2}} = \frac{1}{k[\mathrm{A}]_0}$$

$$t_{1/2} = \frac{1}{(50.4 M^{-1}/h)[2.35 \times 10^{-6} M]}$$

So, half-life is 8443 hours.

Q12.4.10

The reaction of compound *A* to give compounds *C* and *D* was found to be second-order in *A*. The rate constant for the reaction was determined to be 2.42 L/mol/s. If the initial concentration is 0.500 mol/L, what is the value of $t_{1/2}$?

Solution

As mentioned in the question the reaction of compound *A* will result in the formation of compounds C and D. This reaction was found to be second-order in *A*. Therefore, we should use the second order equation for half-life which relates the rate constant and initial concentrations to the half-life:

$$t_{\frac{1}{2}} = \frac{1}{k[A]_0}$$

Since we were given *k* (rate constant) and Initial concentration of A, we have everything needed to calculate the half life of A.

$$k = 0.5 \frac{\frac{L}{mol}}{s}$$

$$[A]_0 = 2.42 \frac{mol}{L}$$

When we plug in the given information notice that the units cancel out to seconds.

$$t_{\frac{1}{2}} = \frac{1}{\frac{2.42 L mol^-}{s}[0.500 \frac{mol}{L}]} = 0.826 s$$

Answer

0.826 s

Q12.4.11

The half-life of a reaction of compound *A* to give compounds *D* and *E* is 8.50 minutes when the initial concentration of *A* is 0.150 mol/L. How long will it take for the concentration to drop to 0.0300 mol/L if the reaction is (a) first order with respect to *A* or (b) second order with respect to *A*?

Solution

Organize the given variables:

(half-life of A) $t_{1/2} = 8.50min$
(initial concentration of A) $[A]_0 = 0.150mol/L$
(target concentration of A) $[A] = 0.0300mol/L$

Find the the rate constant k, using the half-life formulas for each respective order. After finding k, use the integrated rate law respective to each order and the initial and target concentrations of A to find the time it took for the concentration to drop.

(a) first order with respect to A

(half-life) $t_{1/2} = \frac{ln(2)}{k} = \frac{0.693}{k}$
(rearranged for k) $k = \frac{0.693}{t_{1/2}}$
(plug in $t_{1/2}$ = 8.50 min) $k = \frac{0.693}{8.50min} = 0.0815min^{-1}$

(integrated rate law) $ln[A] = -kt + ln[A]_0$
(rearranged for t) $ln(\frac{[A]}{[A]_0}) = -kt$
$-ln(\frac{[A]}{[A]_0}) = kt$
$ln(\frac{[A]}{[A]_0})^{-1} = kt$
$ln(\frac{[A]_0}{[A]}) = kt$
$t = \frac{ln(\frac{[A]_0}{[A]})}{k}$
(plug in variables) $t = \frac{ln(\frac{0.150mol/L}{0.0300mol/L})}{0.0815min^{-1}} = \frac{ln(5.00)}{0.0815min^{-1}} = 19.7min$

(b) second order with respect to A

(half-life) $t_{1/2} = \frac{1}{k[A]_0}$
(rearranged for k) $k = \frac{1}{t_{1/2}[A]_0}$
(plug in variables) $k = \frac{1}{(8.50min)(0.150mol/L)} = \frac{1}{1.275min \cdot mol/L} = 0.784L/mol \cdot min$

(integrated rate law) $\frac{1}{[A]} = kt + \frac{1}{[A]_0}$
(rearranged for t) $\frac{1}{[A]} - \frac{1}{[A]_0} = kt$
$t = \frac{1}{k}(\frac{1}{[A]} - \frac{1}{[A]_0})$
(plug in variables) $t = \frac{1}{0.784L/mol \cdot min}(\frac{1}{0.0300mol/L} - \frac{1}{0.150mol/L}) = \frac{1}{0.784L/mol \cdot min}(\frac{80}{3}L/mol) = 34.0min$

Answer

a) 19.7 min

b) 34.0 min

Q12.4.12

Some bacteria are resistant to the antibiotic penicillin because they produce penicillinase, an enzyme with a molecular weight of 3 × 10^4 g/mol that converts penicillin into inactive molecules. Although the kinetics of enzyme-catalyzed reactions can be complex, at low concentrations this reaction can be described by a rate equation that is first order in the catalyst (penicillinase) and that also involves the concentration of penicillin. From the following data: 1.0 L of a solution containing 0.15 µg (0.15 × 10^{-6} g) of penicillinase, determine the order of the reaction with respect to penicillin and the value of the rate constant.

[Penicillin] (M)	Rate (mol/L/min)
2.0 × 10^{-6}	1.0 × 10^{-10}
3.0 × 10^{-6}	1.5 × 10^{-10}
4.0 × 10^{-6}	2.0 × 10^{-10}

Solution

The first step is to solve for the order or the reaction. This can be done by setting up two expressions which equate the rate to the rate constant times the molar concentration of penicillin raised to the power of it's order. Once we have both expressions set

up, we can divide them to cancel out k (rate constant) and use a basic logarithm to solve for the exponent, which is the order. It will look like this.

$$\text{rate(mol/L/min)}=k[M]^x$$

$$(1.0 \times 10^{-10})=k[2.0 \times 10^{-6}]^x$$

$$(1.5 \times 10^{-10})=k[3.0 \times 10^{-6}]^x$$

Dividing the two equations results in the expression:

$$(2/3)=(2/3)^x$$

*A single ratio equation can also be set up to solve for the reaction order:

*

$$\frac{rate_1}{rate_2} = \frac{k[Penicillin]_1^x}{k[Penicillin]_2^x}$$

*We then solve for x in a similar fashion.

*

$$\frac{1.0x10^{-10}}{1.5x10^{-10}} = \frac{[2.0x10^{-6}]^x}{[3.0x10^{-6}]^x}$$

We can now use the natural logarithm to solve for x, or simply and intuitively see that in order for the equation to work, **x must be equal to one. Thus, the reaction is of the first order.**

Now that we have the order of the reaction, we can proceed to solve for the value of the rate constant. Substituting x=1 into our first equation yields the expression:

$$(1 \times 10^{-10})=k[2.0 \times 10^{-6}]^1$$

$$k=(1 \times 10^{-10})/(2 \times 10^{-6})$$

$$k= (5 \times 10^{-5}) \text{ min}^{-1}$$

We have a unit of min^{-1} because we divided (mol/L/min) by molarity, which is in (mol/L), yielding a unit of min^{-1}.

We were given two important pieces of information to finish the problem. It is stated that the enzyme has a molecular weight of 3×10^4 g/mol, and that we have a one liter solution that contains (0.15×10^{-6}) g) of penicillinase. Dividing the amount of grams by the molecular weight yields **5×10^{-12} moles**.

$$(0.15 \times 10^{-6}) \text{ g} / (3 \times 10^4) \text{ g/mol} = (5 \times 10^{-12}) \text{ mol}$$

Now that we have the amount of moles, we can divide our rate constant by this value.

$$(5 \times 10^{-5}) \text{ min}^{-1} / (5 \times 10^{-12}) \text{ mol} = \mathbf{(1 \times 10^7) \text{ mol}^{-1} \text{ min}^{-1}}$$

Answer

The reaction is first order with $k = 1.0 \times 10^7 \text{ mol}^{-1} \text{ min}^{-1}$

Q12.4.13

Both technetium-99 and thallium-201 are used to image heart muscle in patients with suspected heart problems. The half-lives are 6 h and 73 h, respectively. What percent of the radioactivity would remain for each of the isotopes after 2 days (48 h)?

Solution

This problem is asking us for the percentage of radioactivity remaining after a certain time for both isotopes after 48 hours. We must identify an equation that will help us solve this and we can determine that we can determine this information using the first order equation.

This equation $Ln(N/N_o)$= -kt tells that the Natural log of the fraction remaining is equal to the rate constant times time. To determine the rate constant, we can also compute .693 over the half-life given in the information.

For Technetium-99 we can determine the rate constant by plugging into the second equation: .693/6 hrs= .1155 h^{-1}

Now that we have the rate constant we can plug in : $Ln(N/N_o)=-(.1155h^{-1})(48h)$ so $Ln(N/N_o)=-5.544$ and if we take the inverse of the natural log, we get $(N/N_o)=3.9x10^{-3}$ and if we multiply this by 100, we get .39% remaining.

We can do this same process for Thallium-201 and plugin: .693/73 hrs= .009493151 h^{-1} and when we plug this into the first order equation we get:

$Ln(N/N_o)=-(.009493h^{-1})(48h)$ so $Ln(N/N_o)=-.45567248$ and when we take the inverse of the natural log, we get $(N/N_o)=.6340$ and when multiplied by 100, we get 63.40% remaining which makes sense since its half-life is 73 hours and only 48 hours have passed, half of the amount has yet to be consumed.

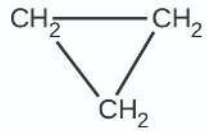
Answer

Technetium-99: 0.39%

Thallium-201: 63.40%

Q12.4.14

There are two molecules with the formula C_3H_6. Propene, $\mathbf{CH_3CH{=}CH_2}$, is the monomer of the polymer polypropylene, which is used for indoor-outdoor carpets. Cyclopropane is used as an anesthetic:



When heated to 499 °C, cyclopropane rearranges (isomerizes) and forms propene with a rate constant of 5.95×10^{-4} s^{-1}. What is the half-life of this reaction? What fraction of the cyclopropane remains after 0.75 h at 499 °C?

Solution

Use the equation

$$t_{1/2} = \frac{ln2}{k}$$

since this is a first-order reaction. You can tell that this is a **first order reaction** due to the units of measurement of the rate constant, which is s^{-1}. Different orders of reactions lead to different rate constants, and a rate constant of s^{-1} will always be first order.

Plug into the equation, and you get half life = 1164.95 seconds. To convert this to hours, we would divide this number by 3600 seconds/hour, to get **0.324 hours**.

Use the integrated first order rate law

$$ln\frac{[A]}{[A]_0} = -kt$$

. In this equation, $[A]_0$ represents the initial amount of compound present at time 0, while [A] represents the amount of compound that is left after the reaction has occurred. Therefore, the fraction

$$\frac{[A]}{[A]_0}$$

is equal to the fraction of cyclopropane that remains after a certain amount of time, in this case, 0.75 hours.

Substitute x for the fraction of

$$\frac{[A]}{[A]_0}$$

into the integrated rate law:

$$ln\frac{[A]}{[A]_0} = -kt$$

$$ln(x) = -5.95x10^{-4}(0.75)$$

$$x = e^{(-0.000595)(0.75)}$$

= 0.20058 = 20%.

So, the half life is 0.324 hours, and 20% of the cyclopropane will remain as 80% will have formed propene.

Answer

0.324 hours. ; 20% remains

Q12.4.16

Fluorine-18 is a radioactive isotope that decays by positron emission to form oxygen-18 with a half-life of 109.7 min. (A positron is a particle with the mass of an electron and a single unit of positive charge; the nuclear equation is $^{18}_{9}\mathrm{F} \longrightarrow {}^{18}_{8}\mathrm{O} + {}^{0}_{1}\mathrm{e}^{+}$.) Physicians use ^{18}F to study the brain by injecting a quantity of fluoro-substituted glucose into the blood of a patient. The glucose accumulates in the regions where the brain is active and needs nourishment.

a. What is the rate constant for the decomposition of fluorine-18?
b. If a sample of glucose containing radioactive fluorine-18 is injected into the blood, what percent of the radioactivity will remain after 5.59 h?
c. How long does it takFe for 99.99% of the ^{18}F to decay?

Solution

a) The nuclear decay of an isotope of an element is represented by the first order equation:

$$\ln(N/N0) = -kt$$

Where t is time, N0 is the initial amount of the substance, N is the amount of the substance after time t, and k is the rate constant. We can rearrange the equation and isolate k so that we could solve for the rate constant:

$$k = [-\ln(N/N0)] / t$$

We are given that fluorine-18 has a half-life of 109.7 minutes. Since we have the half-life, we can choose an arbitrary value for N_0 and use half of that value for N. In this case, we choose 100 for N_0 and 50 for N. Now we can plug in those values into the equation above and solve for k.

$$k = [-\ln(50/100)] / 109.7$$

$$k = 0.6931 / 109.7 = 0.006319\ \mathrm{min}^{-1}$$

The rate constant for this reaction is 0.006319 min^{-1}.

b) For this problem, we are able to use the same equation from part a:

$$\ln(N/N0) = -kt$$

However, this time we are given the amount of time elapsed instead of the half-life, and we are asked to determine the percent of fluorine-18 radioactivity remaining after that time. In this problem, we must plug in values for N0, k (determined from part a), and t.

But first, since we are given the elapsed time in hours, we must convert it into minutes:

$$5.59\ \text{hours} \times (60\ \text{minutes} / 1\ \text{hours}) = 335.4\ \text{minutes}$$

This gives us the value for t. We also have values for k (0.006319 min^{-1}) and N_0 (again an arbitrary number.) Now we can plug values into the original equation, giving us:

$$\ln(N/100) = -(0.006319)(335.4)$$

We solve this equation by taking the exponential of both sides:

$$e^{\ln(N/100)} = e^{-(0.006319)(335.4)}$$

where e^{ln} equals 1 and now we can just solve for N:

$$N/100 = e^{-(0.006319)(335.4)}$$

$$N = [e^{-(0.006319)(335.4)}] \times 100 = 12.0$$

Since 100 was used as the initial amount and 12.0 was determined as the remaining amount, 12.0 can be used as the percentage of remaining amount of radioactivity of fluorine-18. **Thus the percent of fluorine-18 radioactivity remaining after 5.59 hours is 12.0%.**

c) This part of the question is much like the previous two parts, but this time we are given the initial amount of radioactivity, the final amount of radioactivity and we are asked do determine how long it took for that amount of radioactivity to decay. We are able to use the same equation:

$$\ln(N/N0) = -kt$$

However, now we are given N and N_0 and we have already determined k from before. We are told that 99.99% of the radioactivity has decayed, so we can use 100 and 0.01 for N_0 and N respectively. We plug these values in to the equation, solve for t, and get

$$\ln(0.01/1000) = -0.006319t$$

$$-9.21 = -0.006319t$$

$$t = 1458 \text{ minutes}$$

Therefore, its takes 1458 minutes for 99.99% of the radioactivity to decay.

Answer

a) 0.006319 min^{-1}

b) 12.0%

c) 1458 minutes

Q12.4.17

Suppose that the half-life of steroids taken by an athlete is 42 days. Assuming that the steroids biodegrade by a first-order process, how long would it take for $\frac{1}{64}$ of the initial dose to remain in the athlete's body?

Solution

252 days

for first order reaction: $t_{1/2} = 0.693 / k$

$k = 0.693 / 42$

$k = 0.0165$

for first order reaction: $[A] = [A]_0 e^{-kt}$

1/64 initial means that: $[A] = 1/64 [A]_0$

therefore: $1/64 [A]_0 = [A]_0 e^{-0.0165t}$

$t = 252$ days

Q12.4.18

Recently, the skeleton of King Richard III was found under a parking lot in England. If tissue samples from the skeleton contain about 93.79% of the carbon-14 expected in living tissue, what year did King Richard III die? The half-life for carbon-14 is 5730 years.

Solution

In order to find out what year King Richard III died, set [A]/[A_0] (the percent of carbon-14 still contained) equal to $0.5^{\text{time(t)/half life } (t_{1/2})}$ or use the equation $N(t) = N_0e^{-rt.}$

Using the first equation:

$A/A_0 = 0.5^{t/t_{1/2}}$ plug in the given numbers $.9379 = 0.5^{t/5730}$ and solve for t.

$ln.9379 = (t/5730)(ln0.5)$ (using the rule of logs)

$-.0641 = (t/5730)(-.693)$

$-367.36 = -.693t$

$t = 530.1 years$

Using $N(t) = N_0e^{-rt}$ this problem is solved by the following:

$1/2 = e^{-5730r}$

$r = 0.000121$

Now that we know what r is, we can use this value in our original formula and solve for t, the amount of years that have passed.

This time, we use 93.78, the percent of the carbon-14 remaining as N(t) and 100 as the original, N_0.

$93.78 = 100e^{-0.000121t}$

$t = 530.7$ years

Another way of doing this is by using these two equations:

$\lambda = \frac{0.693}{t_{1/2}}$ and $\frac{n_t}{n_0} = -\lambda t$

n_t = concentration at time t (93.79)

n_0 = initial concentration (100)

First solve for lambda or the decay constant by plugging in the half life.

Then plug in lambda and the other numbers into the second equation, and solve for t- which should equal to 530.1 years as well.

If we want to find out what year King Richard III died, we take the current year, 2017, and subtract 530 years. Doing this, we find that King Richard III died in the year 1487.

Answer

King Richard III died in the year 1487

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Q12.4.19

Nitroglycerine is an extremely sensitive explosive. In a series of carefully controlled experiments, samples of the explosive were heated to 160 °C and their first-order decomposition studied. Determine the average rate constants for each experiment using the following data:

Initial $[C_3H_5N_3O_9]$ (M)	4.88	3.52	2.29	1.81	5.33	4.05	2.95	1.72
t (s)	300	300	300	300	180	180	180	180
% Decomposed	52.0	52.9	53.2	53.9	34.6	35.9	36.0	35.4

Solution

First we need to understand what the question is asking for: the average rate constant. The average rate constant is the variable "k" when discussing kinetics and it can be defined as the proportionality constant in the equation that expresses the relationship between the rate of a chemical reaction and the concentrations of the reacting substances. Knowing that we need to find K in this first order reaction, we can look to formulas that include "k," initial and final concentrations $[A]_o and [A]_t$, and half life time "t." Since this is a first order reaction, we can look to the first order equations, and doing that we find one that includes the variables given in the question:

$$\ln [A]_t = -kt + \ln [A]_o$$

For the first reaction, we have an initial concentration of 4.88 M, and a percentage decomposed. To find the final concentration, we must multiply the initial concentration by the percentage decomposed to know how much decomposed, and subtract that from the original to find out how much is left: 4.88M x 0.52= 2.54 M and 4.88M-2.54M=2.34M

Now, we have the variables we need, and we plug it into the equation above:

$\ln [A]_t = -kt + \ln [A]_o$

$\ln[2.34M] = -k(300s) + \ln[4.88M]$

k= $\frac{-(\ln[2.34M]-\ln[4.88M])}{300}$

$k = 2.45x10^{-3}$

Since it asks for the rate constant of each experiment, we now must do the same procedure for each data set to find the rate constant:

Second experiment

$\ln [A]_t = -kt + \ln [A]_o$

$\ln[1.66M] = -k(300s) + \ln[3.52M]$

k= $\frac{-(\ln[1.66M]-\ln[3.52M])}{300}$

$k = 2.51x10^{-3}$

Third experiment

$\ln [A]_t = -kt + \ln [A]_o$

$\ln[1.07M] = -k(300s) + \ln[2.29M]$

k= $\frac{-(\ln[1.07M]-\ln[2.29M])}{300}$

$k = 2.54x10^{-3}$

Fourth experiment

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$\ln [A]_t = -kt + \ln [A]_o$

$\ln[0.834M] = -k(300s) + \ln[1.81M]$

$k = \frac{-(\ln[0.834M] - \ln[1.81M])}{300}$

$k = 2.58x10^{-3}$

Fifth Experiment

$\ln [A]_t = -kt + \ln [A]_o$

$\ln[3.49M] = -k(180s) + \ln[5.33M]$

$k = \frac{-(\ln[3.49M] - \ln[5.33M])}{180}$

$k = 2.35x10^{-3}$

Sixth Experiment

$\ln [A]_t = -kt + \ln [A]_o$

$\ln[2.60M] = -k(180s) + \ln[4.05M]$

$k = \frac{-(\ln[2.60M] - \ln[4.05M])}{180}$

$k = 2.46x10^{-3}$

Seventh Experiment

$\ln [A]_t = -kt + \ln [A]_o$

$\ln[1.89M] = -k(180s) + \ln[2.95M]$

$k = \frac{-(\ln[1.89M] - \ln[2.95M])}{180}$

$k = 2.47x10^{-3}$

Eighth experiment

$\ln [A]_t = -kt + \ln [A]_o$

$\ln[1.11M] = -k(180s) + \ln[1.72M]$

$k = \frac{-(\ln[1.11M] - \ln[1.72M])}{180}$

$k = 2.43x10^{-3}$

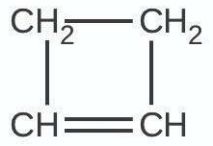
Answer

$[A]_0$ (M)	$k \times 10^3$ (s^{-1})
4.88	2.45
3.52	2.51
2.29	2.54
1.81	2.58
5.33	2.35
4.05	2.44
2.95	2.47
1.72	2.43

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Q12.4.20

For the past 10 years, the unsaturated hydrocarbon 1,3-butadiene ($\mathbf{CH_2{=}CH{-}CH{=}CH_2}$) has ranked 38th among the top 50 industrial chemicals. It is used primarily for the manufacture of synthetic rubber. An isomer exists also as cyclobutene:



The isomerization of cyclobutene to butadiene is first-order and the rate constant has been measured as 2.0×10^{-4} s^{-1} at 150 °C in a 0.53-L flask. Determine the partial pressure of cyclobutene and its concentration after 30.0 minutes if an isomerization reaction is carried out at 150 °C with an initial pressure of 55 torr.

Solution

Since this is a first order reaction, the integrated rate law is: $[A_t] = [A_0]e^{-kt}$

Partial Pressure: Use the integrated rate law to find the partial pressure at 30 minutes:

Use A_0 = 55 torr, t = 30 min, and k = $2.0 * 10^{-4} s^{-1}$ to solve the integrated rate law equation:

$[A_{30}] = (55torr) * e^{-(2.0x10^{-4}\frac{1}{sec})(30min \cdot \frac{60sec}{1min})}$

Solve this equation to get:

$[A_{30}] = (55torr) * e^{-0.36}$

$A_{30}]$ = 38.37 torr.

Initial Concentration: Find the initial concentration using the ideal gas law.

The ideal gas law is given by $PV = nRT \rightarrow n = \frac{PV}{RT}$. Use this form of the gas law to solve for the initial concentration n.

Use V = 0.53L, R = 0.08206 $\frac{L*atm}{mol*L}$, T = 423.15 K, and P = $\frac{1atm}{760}$ = 0.07237 atm .

Solve the ideal gas equation using these values:

$n = \frac{(55torr)(0.53L)}{(0.08206\frac{L*atm}{mol*K})(423.15K)} = 0.00110$ moles cyclobutene.

Now find the initial concentration of cyclobutene A_0 using the equation $[A_0] = \frac{n}{V}$:

$A_0 = \frac{n}{V} = \frac{0.00110moles}{0.53L} = 0.00208M$

Concentration at 30 minutes: Find the concentration of cyclobutene at 30 minutes by using the integrated rate law given above, using time t = 30 minutes, or 1800 seconds.

$[A_{30}] = (0.00208M)e^{-0.36} = 0.00145M$

So at 30 minutes, the cyclobutene concentration is 0.00145 M, and the partial pressure is 38.37 torr.

Answer

Partial Pressure: 38.37 torr.

Concentration: 0.00145 M

12.5: Collision Theory

Q12.5.1

Chemical reactions occur when reactants collide. What are two factors that may prevent a collision from producing a chemical reaction?

Solution

The two factors that may prevent a collision from producing a chemical reaction are:

1. **Kinetic energy of the molecule**

In order for chemical reactions to occur, molecules require enough velocity to overcome the minimum activation energy needed to break the old bonds and form new bonds with other molecules. At higher temperatures, the molecules possess the minimum amount of kinetic energy needed which ensures the collisions will be energetic enough to lead to a reaction.

2. **The orientation of molecules during the collision**

Two molecules have to collide in the right orientation in order for the reaction to occur. Molecules have to orient properly for another molecule to collide at the right activation state.

Q12.5.2

When every collision between reactants leads to a reaction, what determines the rate at which the reaction occurs?

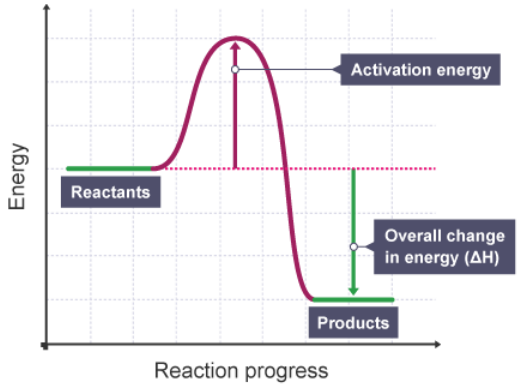
Solution

There has to be contact between reactants for a reaction to occur. The more the reactants collide, the more often reactions can occur. Factors that determine reaction rates include concentration of reactants, temperature, physical states of reactants, surface area, and the use of a catalyst. The reaction rate usually increases as the concentration of a reactant increases. Increasing the temperature increases the average kinetic energy of molecules, causing them to collide more frequently, which increases the reaction rate. When two reactants are in the same fluid phase, their particles collide more frequently, which increases the reaction rate. If the surface area of a reactant is increased, more particles are exposed to the other reactant therefore more collisions occur and the rate of reaction increases. A catalyst participates in a chemical reaction and increases the reaction rate without changing itself.

Q12.5.3

What is the activation energy of a reaction, and how is this energy related to the activated complex of the reaction?

Solution



Activation energy is the energy barrier that must be overcome in order for a reaction to occur. To get the molecules into a state that allows them to break and form bonds, the molecules must be contorted (deformed, or bent) into an unstable state called the transition state. The transition state is a high-energy state, and some amount of energy – the activation energy – must be added in order for the molecule reach it. Because the transition state is unstable, reactant molecules don't stay there long, but quickly proceed to the next step of the chemical reaction.The activated complex is the highest energy of the transition state of the reaction.

Q12.5.5

Describe how graphical methods can be used to determine the activation energy of a reaction from a series of data that includes the rate of reaction at varying temperatures.

Solution

This method is based on the **Arrhenius equation** which can be used to show the effect of a change of temperature on the **rate constant**, and therefore on the rate of reaction.

The rate constant is different from reaction rat in that the reaction rate is the measure of how fast or slow a chemical reaction takes place while a rate constant is a constant that shows the relationship between the reaction rate and the concentrations of the reactants or products.

For example, for the reaction $A + B \rightarrow C$, the rate law would be:

$$rate = k[A]^a[B]^b$$

k = rate constant

[A] = concentration of reactant A

a = order of reaction with respect to A

[B] = concentration of reactant B

b = order of reaction with respect to B

However, the rate constant remains constant only if you are changing the concentration of the reactants. If you change the temperature or the catalyst of the reaction, the rate constant will change and this is demonstrated by the Arrhenius equation:

$$k = Ae^{\frac{-E_a}{RT}}$$

$$ln\left(\frac{k_1}{k_2}\right) = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

k = rate constant

A = frequency factor

E_a = activation energy

e = exponential function, e^x

R = gas constant

T = temperature (K)

In other words, the activation energy of a reaction, E_a, from a series of data that includes the rate of reaction, k, at varying temperatures can be determined by graphing it on a plot of $\ln k$ versus $\frac{1}{T}$. You can then use the slope of the graph you have plotted to solve for E_a by setting the slope equal to $\frac{-E_a}{R}$.

Q12.5.6

How does an increase in temperature affect rate of reaction? Explain this effect in terms of the collision theory of the reaction rate.

S12.5.6

Collision theory states that the rates of chemical reactions depend on the fraction of molecules with the correct orientation, fraction of collisions with required energy, and the collision frequency. Because the fraction of collisions with required energy is a function of temperature, as temperature increases, the fraction of collisions with required energy also increases. The kinetic energy of reactants also increases with temperature which means molecules will collide more often increasing collisions frequency. With increased fraction of collisions with required energy and collisions frequency, the rate of chemical reaction increases. We see mathematically, from the Arrhenius equation, that temperature and the rate constant are related.

$$k = Ae^{\frac{E_a}{RT}} \tag{8.E.14}$$

where k is the rate constant, A is a specific constant, R is 8.3145 J/K, Ea is the reaction-specific activation energy in J, and T is temperature in K. We see from the equation that k is very sensitive to changes in the temperature.

Q12.5.7

The rate of a certain reaction doubles for every 10 °C rise in temperature.

a. How much faster does the reaction proceed at 45 °C than at 25 °C?
b. How much faster does the reaction proceed at 95 °C than at 25 °C?

Solution

By finding the difference in temperature, 45 °C - 25 °C, we get 20 °C. Since the rate of the reaction doubles every 10 °C increase in temperature and the rate of the reaction experienced a 20 °C increase in temperature, we see that the reaction rate doubled twice ($2^2 = 4$). As a result, the **reaction proceeds four times faster**.

Following the same process as in part a, we get the difference in temperature to be 70 °C. Since the rate of the reaction doubles every 10 °C increase in temperature and the system experienced a 70 °C change, we see that the reaction doubled seven times ($2^7 = 128$). We can see the **reaction proceeds 128 times faster**.

(a) 4-times faster (b) 128-times faster

Q12.5.8

In an experiment, a sample of $NaClO_3$ was 90% decomposed in 48 min. Approximately how long would this decomposition have taken if the sample had been heated 20 °C higher?

S12.5.8

First off, it is important to recognize that this decomposition reaction is a **first-order reaction**, which can be written as follows: $2NaClO_3 \rightarrow 2NaCl + 3O_2$

Understanding this, it is important to be able to then be able to recognize which equation would be most useful given the initial conditions presented by the question. Since we are dealing with time, percentage of material left, and temperature, the only viable equation that could relate all of this would be the Arrhenius Equation, which is written as follows: $\ln(\frac{k_2}{k_1}) = \frac{Ea}{R}(\frac{1}{t_1} - \frac{1}{t_2})$

However, this problem does not give us enough information such as what the activation energy is or the initial temperature in order to mathematically solve this problem. Additionally, the problem tells us to approximate how long the decomposition would take, which means we are asked to answer this question conceptually based on our knowledge of thermodynamics and reaction rates. As a general rule of thumb, we know that for every 10˚C rise in temperature the rate of reaction doubles. Since the question tells us that there is a 20˚C rise in temperature we can deduce that the reaction rate doubles twice, as per the general rule mentioned before. This means **the overall reaction rate for this decomposition would quadruple**, or would be 4 times faster than the reaction rate at the initial temperature.

We can gut check this answer by recalling how an increase in the average kinetic energy (temperature) decreases the time it takes for the reaction to take place and increase the reaction rate. Thus, if we increase the temperature we should have a faster reaction rate.

Q12.5.9

The rate constant at 325 °C for the decomposition reaction $C_4H_8 \longrightarrow 2\,C_2H_4$ is 6.1×10^{-8} s^{-1}, and the activation energy is 261 kJ per mole of C_4H_8. Determine the frequency factor for the reaction.

Solution

S12.5.9

Using the Arrhenius equation allows me to find the frequency factor, A.

$k=Ae^{-Ea/RT}$

k, Ea, R, and T are all known values. k, Ea, and T are given in the problem as $6.1x10^{-8}$, 261 kJ, and 598 K, respectively.

So, plugging them into the equation gives:

$6.1x10^{-8}\ s^{-1}=Ae^{(-261000\ J)/(8.3145\ J/mol)(598\ K)}$

Take $e^{(-261000\ J)/(8.3145\ J/mol)(598)}$ and get 1.59×10^{-23}. Divide k, 6.1×10^{-8}, by 1.59×10^{-23} and get A=$3.9 \times 10^{15} s^{-1}$

A12.5.9

$3.9 \times 10^{15}\ s^{-1}$

Q12.5.10

The rate constant for the decomposition of acetaldehyde (CH_3CHO), to methane (CH_4), and carbon monoxide (CO), in the gas phase is 1.1×10^{-2} L/mol/s at 703 K and 4.95 L/mol/s at 865 K. Determine the activation energy for this decomposition.

S12.5.10

The equation for relating the rate constant and activation energy of a reaction is the Arrhenius equation:

$$k = Ae^{-\frac{E_a}{RT}} \tag{8.E.15}$$

When given two rate constants at two different temperatures but for the same reaction, the Arrhenius equation can be rewritten as:

$$ln(\frac{k_2}{k_1}) = \frac{E_a}{R}(\frac{1}{T_1} - \frac{1}{T_2}) \tag{8.E.16}$$

In this problem, all the variables are given except for the E_a (activation energy).

$k_1 = 1.1 \times 10^{-2}$ L/mol/s

$T_1 = 703$ K

$k_2 = 4.95$ L/mol/s

$T_2 = 865$ K

R = 8.314 J/(mol K) (Ideal Gas Constant)

Now plug in all these values into the equation, and solve for E_a.

$$ln(\frac{4.95 \frac{L}{mol \times s}}{1.1 \times 10^{-2} \frac{L}{mol \times s}}) = \frac{E_a}{8.314 \times 10^{-3} \frac{kJ}{mol \times K}}(\frac{1}{703} - \frac{1}{865}) \tag{8.E.17}$$

$E_a = 190$ kJ (2 sig figs)

Q12.5.11

An elevated level of the enzyme alkaline phosphatase (ALP) in the serum is an indication of possible liver or bone disorder. The level of serum ALP is so low that it is very difficult to measure directly. However, ALP catalyzes a number of reactions, and its relative concentration can be determined by measuring the rate of one of these reactions under controlled conditions. One such reaction is the conversion of p-nitrophenyl phosphate (PNPP) to p-nitrophenoxide ion (PNP) and phosphate ion. Control of temperature during the test is very important; the rate of the reaction increases 1.47 times if the temperature changes from 30 °C to 37 °C. What is the activation energy for the ALP–catalyzed conversion of PNPP to PNP and phosphate?

Solution

43.0 kJ/mol

Q12.5.12

In terms of collision theory, to which of the following is the rate of a chemical reaction proportional?

a. the change in free energy per second
b. the change in temperature per second
c. the number of collisions per second
d. the number of product molecules

Q12.5.13

Hydrogen iodide, HI, decomposes in the gas phase to produce hydrogen, H_2, and iodine, I_2. The value of the rate constant, k, for the reaction was measured at several different temperatures and the data are shown here:

Temperature (K)	k (M^{-1} s^{-1})
555	6.23×10^{-7}
575	2.42×10^{-6}
645	1.44×10^{-4}
700	2.01×10^{-3}

What is the value of the activation energy (in kJ/mol) for this reaction?

Solution

177 kJ/mol

Q12.5.14

The element Co exists in two oxidation states, Co(II) and Co(III), and the ions form many complexes. The rate at which one of the complexes of Co(III) was reduced by Fe(II) in water was measured. Determine the activation energy of the reaction from the following data:

T (K)	k (s^{-1})
293	0.054
298	0.100

Q12.5.15

The hydrolysis of the sugar sucrose to the sugars glucose and fructose,

$$\mathbf{C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6}$$

follows a first-order rate equation for the disappearance of sucrose: Rate = $k[C_{12}H_{22}O_{11}]$ (The products of the reaction, glucose and fructose, have the same molecular formulas but differ in the arrangement of the atoms in their molecules.)

a. In neutral solution, $k = 2.1 \times 10^{-11}$ s^{-1} at 27 °C and 8.5×10^{-11} s^{-1} at 37 °C. Determine the activation energy, the frequency factor, and the rate constant for this equation at 47 °C (assuming the kinetics remain consistent with the Arrhenius equation at this temperature).
b. When a solution of sucrose with an initial concentration of 0.150 M reaches equilibrium, the concentration of sucrose is 1.65×10^{-7} M. How long will it take the solution to reach equilibrium at 27 °C in the absence of a catalyst? Because the concentration of sucrose at equilibrium is so low, assume that the reaction is irreversible.
c. Why does assuming that the reaction is irreversible simplify the calculation in part (b)?

Solution

$E_a = 108$ kJ

$A = 2.0 \times 10^8$ s^{-1}

$k = 3.2 \times 10^{-10}$ s^{-1}

(b) 1.81×10^8 h or 7.6×10^6 day. (c) Assuming that the reaction is irreversible simplifies the calculation because we do not have to account for any reactant that, having been converted to product, returns to the original state.

Q12.5.16

Use the PhET Reactions & Rates interactive simulation to simulate a system. On the “Single collision” tab of the simulation applet, enable the “Energy view” by clicking the “+” icon. Select the first $A + BC \longrightarrow AB + C$ reaction (A is yellow, B is purple, and C is navy blue). Using the “straight shot” default option, try launching the *A* atom with varying amounts of energy. What changes when the Total Energy line at launch is below the transition state of the Potential Energy line? Why? What happens when it is above the transition state? Why?

Q12.5.17

Use the PhET Reactions & Rates interactive simulation to simulate a system. On the “Single collision” tab of the simulation applet, enable the “Energy view” by clicking the “+” icon. Select the first $A + BC \longrightarrow AB + C$ reaction (A is yellow, B is purple, and C is navy blue). Using the “angled shot” option, try launching the *A* atom with varying angles, but with more Total energy than the transition state. What happens when the *A* atom hits the *BC* molecule from different directions? Why?

Solution

The *A* atom has enough energy to react with *BC*; however, the different angles at which it bounces off of *BC* without reacting indicate that the orientation of the molecule is an important part of the reaction kinetics and determines whether a reaction will occur.

12.6: Reaction Mechanisms

Q12.6.1

Why are elementary reactions involving three or more reactants very uncommon?

Q12.6.2

In general, can we predict the effect of doubling the concentration of *A* on the rate of the overall reaction $A + B \longrightarrow C$? Can we predict the effect if the reaction is known to be an elementary reaction?

Solution

Add texts here. Do not delete this text first.

No. In general, for the overall reaction, we cannot predict the effect of changing the concentration without knowing the rate equation. Yes. If the reaction is an elementary reaction, then doubling the concentration of *A* doubles the rate.

Q12.6.3

Phosgene, $COCl_2$, one of the poison gases used during World War I, is formed from chlorine and carbon monoxide. The mechanism is thought to proceed by:

step 1:	$Cl + CO \rightarrow COCl$
step 2:	$COCl + Cl_2 \rightarrow COCl_2 + Cl$

a. Write the overall reaction equation.
b. Identify any reaction intermediates.
c. Identify any intermediates.

Q12.6.4

Define these terms:

a. unimolecular reaction
b. bimolecular reaction
c. elementary reaction
d. overall reaction

Q12.6.5

What is the rate equation for the elementary termolecular reaction $A + 2B \longrightarrow \text{products}$? For $3A \longrightarrow \text{products}$?

Solution

Add texts here. Do not delete this text first.

We are given that both of these reactions are elementary termolecular. The molecularity of a reaction refers to the number of reactant particles that react together with the proper and energy and orientation. Termolecular reactions have three atoms to collide simultaneously. As it is termolecular, and there are no additional reactants aside from the three given in each reaction, there are no intermediate reactions. The rate law for elementary reactions is determined by the stoichiometry of the reaction without needed experimental data.

The basic rate form for the elementary step is what follows:

$rate = k \cdot reactant\ 1^{i} \cdot reactant\ 2^{ii} \cdot ...$ Where i and ii are the stochiometric coefficient from reactant 1 and 2 respectively.

For: $3A \rightarrow products$

$k \cdot A^3 = rate$

For: $A + 2B \rightarrow products$

$k \cdot [A] \cdot [B]^2 = rate$

Note that the order of these reactions are both three.

Answer

Add texts here. Do not delete this text first.

Rate = $k[A][B]^2$; Rate = $k[A]^3$

Q12.6.6

Given the following reactions and the corresponding rate laws, in which of the reactions might the elementary reaction and the overall reaction be the same?

(a) $Cl_2 + CO \longrightarrow Cl_2CO$

$\text{rate} = k[Cl_2]^{3/2}[CO]$

(b) $PCl_3 + Cl_2 \longrightarrow PCl_5$

$\text{rate} = k[PCl_3][Cl_2]$

(c) $2\,NO + H_2 \longrightarrow N_2 + H_2O$

$\text{rate} = k[NO][H_2]$

(d) $2\,NO + O_2 \longrightarrow 2\,NO_2$

$\text{rate} = k[NO]^2[O_2]$

(e) $NO + O_3 \longrightarrow NO_2 + O_2$

$\text{rate} = k[NO][O_3]$

Solution

Add texts here. Do not delete this text first.

An elementary reaction is a chemical reaction in which the reactants directly form products in a single step. In another words, the rate law for the overall reaction is same as experimentally found rate law. Out of 5 options, option (b),(d), and (e) are such reactions

Q12.6.7

Write the rate equation for each of the following elementary reactions:

a. $O_3 \xrightarrow{sunlight} O_2 + O$
b. $O_3 + Cl \longrightarrow O_2 + ClO$
c. $ClO + O \longrightarrow Cl + O_2$
d. $O_3 + NO \longrightarrow NO_2 + O_2$
e. $NO_2 + O \longrightarrow NO + O_2$

Solution

Add texts here. Do not delete this text first.

Rate equations are **dependent on the reactants and not the products.**

The rate law of a reaction can be found using a rate constant (which is found experimentally), and the initial concentrations of reactants.

A general solution for the equation

$aA + bB \rightarrow cC + dD$

is $rate = k[A]^m[B]^n$ where m and n are reaction orders.

However, reaction orders are found experimentally, and since we do not have experimental data for these reactions, we can disregard that part of the equation.

To find the rate laws, all we have to do is plug the reactants into the rate formula. This is only due to the case that these are elementary reactions. Further reading on elementary reactions can be found on Libre Texts.

a. $O_3 \longrightarrow O_2 + O$

To write this reaction's rate equation, only focus on the reactant(s) and its/their concentration and multiplying that by a rate constant, "k".

$$\text{Rate} = k[O_3]$$

b. $O_3 + Cl \longrightarrow O_2 + ClO$

To write this reaction's rate equation, only focus on the reactant(s) and its/their concentration and multiplying that by a rate constant, "k".

$$\text{Rate} = k[O_3][Cl]$$

c. $ClO + O \longrightarrow Cl + O_2$

To write this reaction's rate equation, only focus on the reactant(s) and its/their concentration and multiplying that by a rate constant, "k".

$$\text{Rate} = k[ClO][O]$$

d. $O_3 + NO \longrightarrow NO_2 + O_2$

To write this reaction's rate equation, only focus on the reactant(s) and its/their concentration and multiplying that by a rate constant, "k".

$$\text{Rate} = k[O_3][NO]$$

e. $NO_2 + O \longrightarrow NO + O_2$

To write this reaction's rate equation, only focus on the reactant(s) and its/their concentration and multiplying that by a rate constant, "k".

$$\text{Rate} = k[NO_2][O]$$

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Answer

Add texts here. Do not delete this text first.

(a) Rate$_1$ = k[O_3]; (b) Rate$_2$ = k[O_3][Cl]; (c) Rate$_3$ = k[ClO][O]; (d) Rate$_2$ = k[O_3][NO]; (e) Rate$_3$ = k[NO_2][O]

Q12.6.8

Nitrogen(II) oxide, NO, reacts with hydrogen, H_2, according to the following equation:

$$2\,NO + 2\,H_2 \longrightarrow N_2 + 2\,H_2O$$

What would the rate law be if the mechanism for this reaction were:

$$2\,NO + H_2 \longrightarrow N_2 + H_2O_2 \text{ (slow)}$$

$$H_2O_2 + H_2 \longrightarrow 2\,H_2O \text{ (fast)}$$

The rate law of the mechanism is determined by the slow step of the reaction. Since the slow step is an elementary step, the rate law can be drawn from the coefficients of the chemical equation. So therefore, the rate law is as follows: rate=k$[NO]^2[H_2]$. Since both NO and H_2 are reactants in the overall reaction (therefore are not intermediates in the reaction), no further steps have to be done to determine the rate law.

Q12.6.9

Consider the reaction

$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$ (occurs under light)

The mechanism is a chain reaction involving Cl atoms and CH_3 radicals. Which of the following steps does not terminate this chain reaction?

a. $CH_3 + Cl \rightarrow CH_3CI$
b. $CH_3 + HCl \rightarrow CH_4 + Cl$
c. $CH_3 + CH_3 \rightarrow C_2H_2$
d. $Cl + Cl \rightarrow Cl_2$

Solution

Add texts here. Do not delete this text first.

Chain reactions involve reactions that create products necessary for more reactions to occur. In this case, a reaction step will continue the chain reaction if a radical is generated. Radicals are highly reactive particles, so more reactions in the chain will take place as long as they are present. The chlorine is considered a free radical as it has an unpaired electron; for this reason it is very reactive and propagates a chain reaction. It does so by taking an electron from a stable molecule and making that molecule reactive, and that molecule goes on to react with stable species, and in that manner a long series of "chain" reactions are initiated. A chlorine radical will continue the chain by completing the following reaction:

$$Cl\cdot + CH_4 \rightarrow CH_3\cdot + HCl$$

The CH_3 generated by this reaction can then react with other species, continuing to propagate the chain reaction.

Option 1 is incorrect because the only species it produces is CH_3Cl, a product in the overall reaction that is unreactive. This terminates the chain reaction because it fails to produce any Cl or CH_3 radicals that are necessary for further propagating the overall reaction.

Option 2 is the correct answer because it produces a Cl radical. This Cl radical can continue the chain by colliding with CH_4 molecules.

Option 3 is incorrect because it fails to produce a radical capable of continuing the chain.

Option 4 is incorrect because it produces Cl_2, a molecule that does not react unless additional light is supplied. Therefore, this step breaks the chain.

Answer

Add texts here. Do not delete this text first.

Answer: Option 2: $CH_3 + HCl \rightarrow CH_4 + Cl$

Q12.6.10

Experiments were conducted to study the rate of the reaction represented by this equation.

$$2\,NO(g) + 2\,H_2(g) \longrightarrow N_2(g) + 2\,H_2O(g)$$

Initial concentrations and rates of reaction are given here.

Experiment	Initial Concentration [NO] (mol/L)	Initial Concentration, [H_2] (mol/L)	Initial Rate of Formation of N_2 (mol/L min)
1	0.0060	0.0010	1.8×10^{-4}
2	0.0060	0.0020	3.6×10^{-4}
3	0.0010	0.0060	0.30×10^{-4}
4	0.0020	0.0060	1.2×10^{-4}

Consider the following questions:

a. Determine the order for each of the reactants, NO and H_2, from the data given and show your reasoning.
b. Write the overall rate law for the reaction.
c. Calculate the value of the rate constant, *k*, for the reaction. Include units.
d. For experiment 2, calculate the concentration of NO remaining when exactly one-half of the original amount of H_2 had been consumed.
e. The following sequence of elementary steps is a proposed mechanism for the reaction.

Step 1: $NO + NO \rightleftharpoons N_2O_2$

Step 2: $N_2O_2 + H_2 \rightleftharpoons H_2O + N_2O$

Step 3: $N_2O + H_2 \rightleftharpoons N_2 + H_2O$

Based on the data presented, which of these is the rate determining step? Show that the mechanism is consistent with the observed rate law for the reaction and the overall stoichiometry of the reaction.

S12.6.10

1. i) Find the order for [NO] by using experiment 3 and 4 where [H_2] is constant

Notice that [NO] doubles from experiment 3 to 4 and the rate quadruples. So the order for [NO] is **2**

ii) Find the order for [H_2] by using experiment 1 and 2 where [NO] is constant

Notice that [H_2] doubles from experiment 1 to 2 and the rate doubles as well. So the order for [H_2] is **1**

2. Put in the order for each product as the exponents for the corresponding reactant.

$$rate = k[NO]^2[H_2]$$

3. Put in the concentrations and the rate from one of the experiments into the rate law and solve for k. (Here, experiement 1 is used but any of them will work)

$$rate = k[NO]^2[H_2]\ .00018 = k[.006]^2[.001]\ k = 5000M^{-2}s^{-1}$$

4. Plug in values for experiment 2 into the rate law equation and solve for the concentration of NO

$$.00036 = 5000[NO]^2[.001]\ [NO]^2 = 7.2x10^{-5}\ [NO] = .0085M$$

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5. Write the rate laws for each step and then see which matches the rate law we found in question 2. The rate determining step (the slow step) is the one that gives the rate for the overall reaction. Because of this, only those concentrations will influence the overall reaction, contrary to what we would believe if we just looked at the overall reaction.

Step 1: $NO + NO \rightleftharpoons N_2O_2$

$rate = k_1[NO]^2$ This rate law is not the same as the one we calculate in question 2 so this **can not** be the rate determining step

Step 2: $N_2O_2 + H_2 \rightleftharpoons N_2O + N_2O$

$rate = k_2[N_2O_2][H_2]$

Since N_2O_2 is an intermediate you must replace it in the rate law equation. Intermediates can not be in the rate law because they do not appear in the overall reaction. Here you can take the reverse of equation 1 (k_{-1}) and substitute the other side (the reactants of equation 1) for the intermediate in the rate law equation.

$$rate_1 = rate_{-1}$$

$$k_1[NO]^2 = k_{-1}[N_2O_2]$$

$$[N_2O_2] = \frac{k_1[NO]^2}{k_{-1}}$$

$rate = \frac{k_2k_1[NO]^2[H_2]}{k_{-1}}$

Overall: $rate = k[NO]^2[H_2]$ This **is the same** so it is the rate determining step.

So $N_2O_2 + H_2 \rightleftharpoons N_2O + N_2O$ is the rate determining step step.

Answer

Add texts here. Do not delete this text first.

(a) NO: 2

$\mathbf{H_2}$: 1

(b) Rate = k $[NO]^2[H_2]$;

(c) $k = 5.0 \times 10^3$ mol^{-2} L^{-2} min^{-1};

(d) 0.0050 mol/L;

(e) Step II is the rate-determining step.

Q12.6.11

The reaction of CO with Cl_2 gives phosgene ($COCl_2$), a nerve gas that was used in World War I. Use the mechanism shown here to complete the following exercises:

- $Cl_2(g) \rightleftharpoons 2\,Cl(g)$ (fast, k_1 represents the forward rate constant, k_{-1} the reverse rate constant)
- $CO(g) + Cl(g) \longrightarrow COCl(g)$ (slow, k_2 the rate constant)
- $COCl(g) + Cl(g) \longrightarrow COCl_2(g)$ (fast, k_3 the rate constant)

a. Write the overall reaction.
b. Identify all intermediates.
c. Write the rate law for each elementary reaction.
d. Write the overall rate law expression.

Solution

Add texts here. Do not delete this text first.

1. To write the overall reaction you have to identify the intermediates and leave them out. The easiest way to do this is to write out all the products and reactants and cross out anything that is on both sides.

$$Cl_2(g) + CO(g) + \cancel{2Cl(g)} + \cancel{COCl(g)} \Rightarrow \cancel{2Cl(g)} + \cancel{COCl(g)} + COCl_2(g)$$

In this you will cross out the 2Cl(g) molecules and the COCl(g). What is left after that is the overall reaction.

$Cl_2(g) + CO(g) \Rightarrow + COCl_2(g)$

2. For part two you will just list the intermediates that you crossed out.

Cl and COCl are intermediates

3. Each rate law will be the rate equal to the rate constant times the concentrations of the reactants

reaction 1

(forward) rate=$k_1[Cl_2]$ (reverse) rate=$k_{-1}[Cl]$

reaction 2

rate=$k_2[CO][Cl]$

Reaction 3

rate=$k_3[COCl][Cl]$

4. The overall rate law is based off the slowest step (step #2), since it is the rate determining step, but Cl is present in that rate law so we have to replace it with an equivalent that does not contain an intermediate. To do this you use the equilibrium since the rates are the same you can set up the rate laws of the forward and reverse equal to each other.

$k_1[Cl_2] = k_{-1}[Cl]$

$[Cl]= k_1[Cl_2]/k_{-1}$

rate=$k_2[CO]k_1[Cl_2]/k_{-1}$

rate=$k^{\circ}[CO][Cl_2]$

Steps to replacing and intermediate

1. Set the forward and reverse reaction equal to each other using separate constants
2. Solve for the intermediate using algebra
3. Plug into the rate determining formula
4. All the k's will be condensed into a K prime constant

12.7: Catalysis

Q12.7.1

Account for the increase in reaction rate brought about by a catalyst.

Q12.7.2

Compare the functions of homogeneous and heterogeneous catalysts.

Q12.7.3

Consider this scenario and answer the following questions: Chlorine atoms resulting from decomposition of chlorofluoromethanes, such as CCl_2F_2, catalyze the decomposition of ozone in the atmosphere. One simplified mechanism for the decomposition is:

$$\begin{aligned} O_3 &\xrightarrow{sunlight} O_2 + O \\ O_3 + Cl &\longrightarrow O_2 + ClO \\ ClO + O &\longrightarrow Cl + O_2 \end{aligned}$$

a. Explain why chlorine atoms are catalysts in the gas-phase transformation:

$$2\,O_3 \longrightarrow 3\,O_2$$

b. Nitric oxide is also involved in the decomposition of ozone by the mechanism:

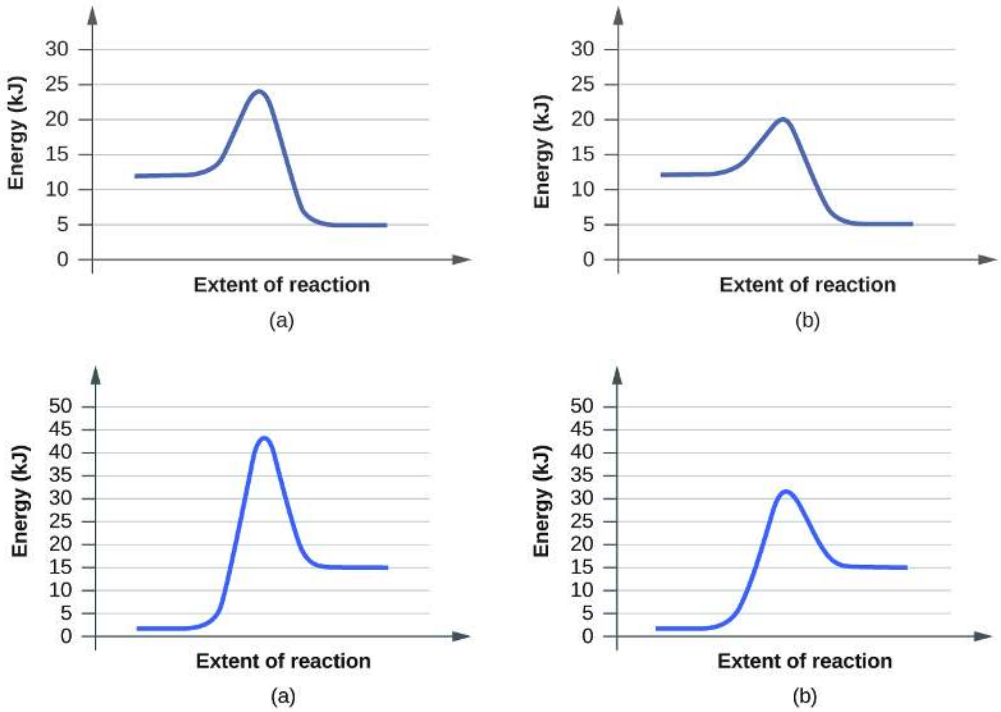
$$O_3 \xrightarrow{sunlight} O_2 + O$$
$$O_3 + NO \longrightarrow NO_2 + O_2$$
$$NO_2 + O \longrightarrow NO + O_2$$

Is NO a catalyst for the decomposition? Explain your answer.

Q12.7.4

For each of the following pairs of reaction diagrams, identify which of the pair is catalyzed:

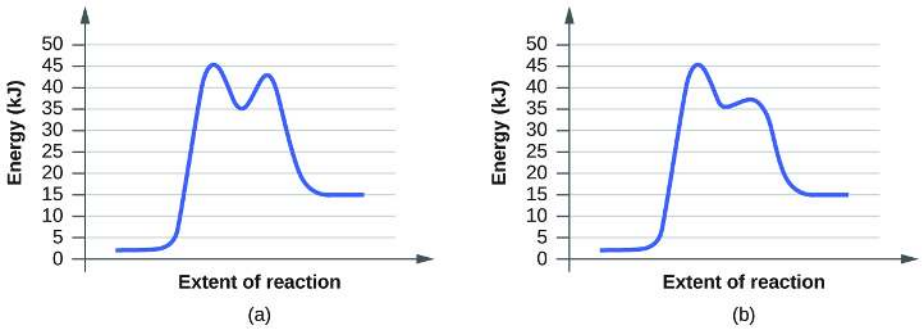
(a)



Q12.7.5

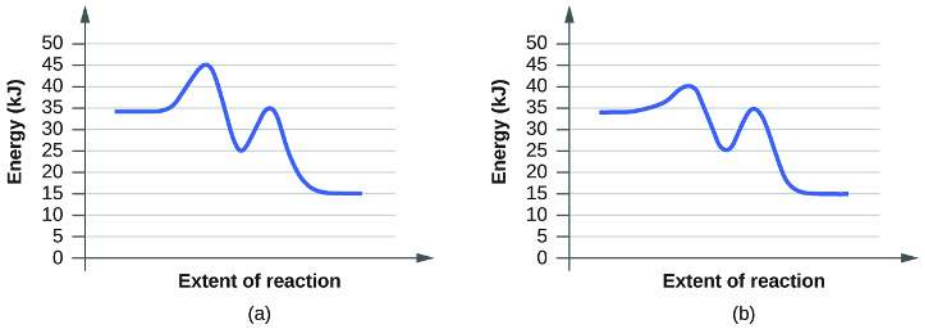
For each of the following pairs of reaction diagrams, identify which of the pairs is catalyzed:

(a)



(b)

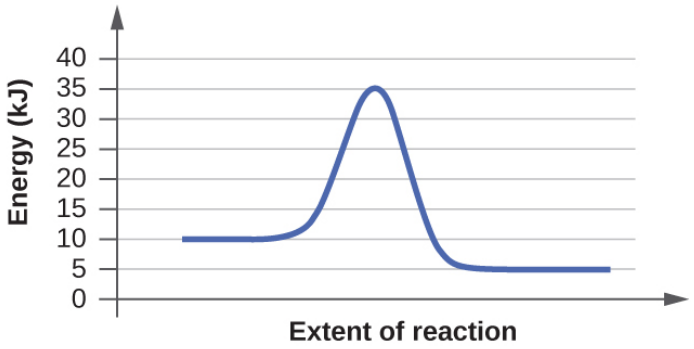
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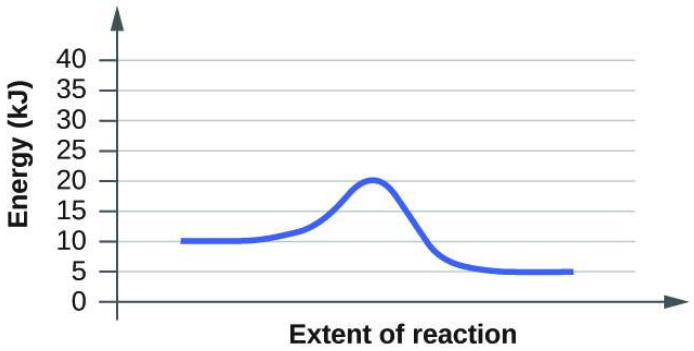
Q12.7.6

For each of the following reaction diagrams, estimate the activation energy (E_a) of the reaction:

(a)



(b)

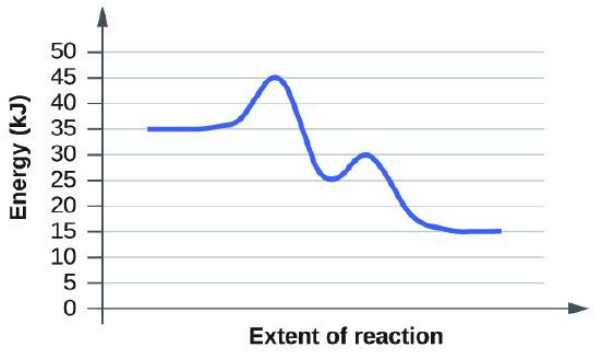


Q12.7.7

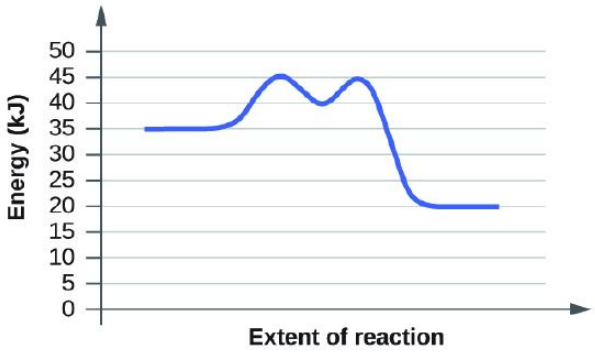
For each of the following reaction diagrams, estimate the activation energy (E_a) of the reaction:

(a)

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(b)



Q12.7.8

1. Based on the diagrams in Question Q12.7.6, which of the reactions has the fastest rate? Which has the slowest rate?
2. Based on the diagrams in Question Q12.7.7, which of the reactions has the fastest rate? Which has the slowest rate?

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CHAPTER OVERVIEW

9: Acid-Base Equilibria

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General Chemistry

This chapter will illustrate the chemistry of acid-base reactions and equilibria, and provide you with tools for quantifying the concentrations of acids and bases in solutions.

9.1: Brønsted-Lowry Acids and Bases

9.2: pH and pOH

9.3: Relative Strengths of Acids and Bases

9.4: Polyprotic Acids

9.5: Buffers

9.6: Acid-Base Titrations

9.E: Acid-Base Equilibria (Exercises)

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9.1: Brønsted-Lowry Acids and Bases

Learning Objectives

- Identify acids, bases, and conjugate acid-base pairs according to the Brønsted-Lowry definition
- Write equations for acid and base ionization reactions
- Use the ion-product constant for water to calculate hydronium and hydroxide ion concentrations
- Describe the acid-base behavior of amphiprotic substances

Acids and bases have been known for a long time. When Robert Boyle characterized them in 1680, he noted that acids dissolve many substances, change the color of certain natural dyes (for example, they change litmus from blue to red), and lose these characteristic properties after coming into contact with alkalis (bases). In the eighteenth century, it was recognized that acids have a sour taste, react with limestone to liberate a gaseous substance (now known to be CO_2), and interact with alkalis to form neutral substances. In 1815, Humphry Davy contributed greatly to the development of the modern acid-base concept by demonstrating that hydrogen is the essential constituent of acids. Around that same time, Joseph Louis Gay-Lussac concluded that acids are substances that can neutralize bases and that these two classes of substances can be defined only in terms of each other. The significance of hydrogen was reemphasized in 1884 when Svante Arrhenius defined an acid as a compound that dissolves in water to yield hydrogen cations (now recognized to be hydronium ions) and a base as a compound that dissolves in water to yield hydroxide anions.

In an earlier chapter on chemical reactions, we defined acids and bases as Arrhenius did: We identified an acid as a compound that dissolves in water to yield hydronium ions (H_3O^+) and a base as a compound that dissolves in water to yield hydroxide ions (OH^-). This definition is not wrong; it is simply limited.

Later, we extended the definition of an acid or a base using the more general definition proposed in 1923 by the Danish chemist Johannes Brønsted and the English chemist Thomas Lowry. Their definition centers on the proton, H^+. A proton is what remains when a normal hydrogen atom, ^1_1H, loses an electron. A compound that donates a proton to another compound is called a Brønsted-Lowry acid, and a compound that accepts a proton is called a Brønsted-Lowry base. An acid-base reaction is the transfer of a proton from a proton donor (acid) to a proton acceptor (base). In a subsequent chapter of this text we will introduce the most general model of acid-base behavior introduced by the American chemist G. N. Lewis.

Acids may be compounds such as HCl or H_2SO_4, organic acids like acetic acid (CH_3COOH) or ascorbic acid (vitamin C), or H_2O. Anions (such as HSO_4^-, $H_2PO_4^-$, HS^-, and HCO_3^-) and cations (such as H_3O^+, NH_4^+, and $[Al(H_2O)_6]^{3+}$) may also act as acids. Bases fall into the same three categories. Bases may be neutral molecules (such as H_2O, NH_3, and CH_3NH_2), anions (such as OH^-, HS^-, HCO_3^-, CO_3^{2-}, F^-, and PO_4^{3-}), or cations (such as $[Al(H_2O)_5OH]^{2+}$). The most familiar bases are ionic compounds such as $NaOH$ and $Ca(OH)_2$, which contain the hydroxide ion, OH^-. The hydroxide ion in these compounds accepts a proton from acids to form water:

$$H^+ + OH^- \rightarrow H_2O \tag{9.1.1}$$

We call the product that remains after an acid donates a proton the conjugate base of the acid. This species is a base because it can accept a proton (to re-form the acid):

$$\text{acid} \rightleftharpoons \text{proton} + \text{conjugate base} \tag{9.1.2}$$

$$HF \rightleftharpoons H^+ + F^- \tag{9.1.3}$$

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \tag{9.1.4}$$

$$H_2O \rightleftharpoons H^+ + OH^- \tag{9.1.5}$$

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-} \tag{9.1.6}$$

$$NH_4^+ \rightleftharpoons H^+ + NH_3 \tag{9.1.7}$$

We call the product that results when a base accepts a proton the base's conjugate acid. This species is an acid because it can give up a proton (and thus re-form the base):

$$\text{base} + \text{proton} \rightleftharpoons \text{conjugate acid} \tag{9.1.8}$$

$$OH^- + H^+ \rightleftharpoons H_2O \tag{9.1.9}$$

$$H_2O + H^+ \rightleftharpoons H_3O^+ \tag{9.1.10}$$

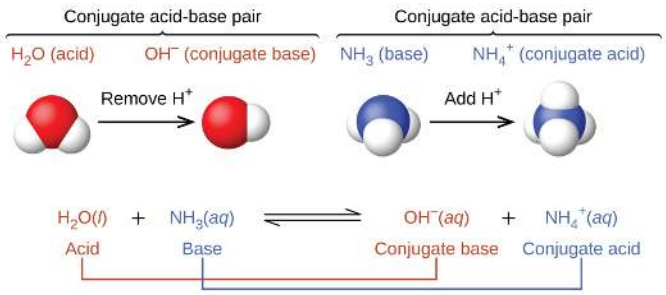
$$NH_3 + H^+ \rightleftharpoons NH_4^+ \tag{9.1.11}$$

$$S^{2-} + H^+ \rightleftharpoons HS^- \tag{9.1.12}$$

$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^- \tag{9.1.13}$$

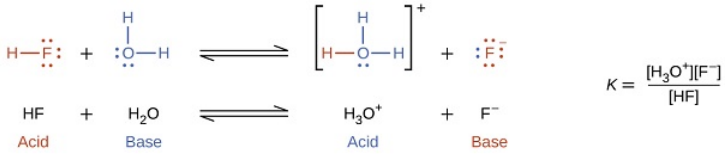
$$F^- + H^+ \rightleftharpoons HF \tag{9.1.14}$$

In these two sets of equations, the behaviors of acids as proton donors and bases as proton acceptors are represented in isolation. In reality, all acid-base reactions involve the transfer of protons between acids and bases. For example, consider the acid-base reaction that takes place when ammonia is dissolved in water. A water molecule (functioning as an acid) transfers a proton to an ammonia molecule (functioning as a base), yielding the conjugate base of water, OH^-, and the conjugate acid of ammonia, NH_4^+:



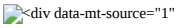
This figure has three parts in two rows. In the first row, two diagrams of acid-base pairs are shown. On the left, a space filling model of H subscript 2 O is shown with a red O atom at the center and two smaller white H atoms attached in a bent shape. Above this model is the label “H subscript 2 O (acid)” in purple. An arrow points right, which is labeled “Remove H superscript plus.” To the right is another space filling model with a single red O atom to which a single smaller white H atom is attached. The label in purple above this model reads, “O H superscript negative (conjugate base).” Above both of these red and white models is an upward pointing bracket that is labeled “Conjugate acid-base pair.” To the right is a space filling model with a central blue N atom to which three smaller white H atoms are attached in a triangular pyramid arrangement. A label in green above reads “N H subscript 3 (base).” An arrow labeled “Add H superscript plus” points right. To the right of the arrow is another space filling model with a blue central N atom and four smaller white H atoms in a tetrahedral arrangement. The green label above reads “N H subscript 3 superscript plus (conjugate acid).” Above both of these blue and white models is an upward pointing bracket that is labeled “Conjugate acid-base pair.” The second row of the figure shows the chemical reaction, H subscript 2 O (l) is shown in purple, and is labeled below in purple as “acid,” plus N H subscript 3 (a q) in green, labeled below in green as “base,” followed by a double sided arrow arrow and O H superscript negative (a q) in purple, labeled in purple as “conjugate base,” plus N H subscript 4 superscript plus (a q)” in green, which is labeled in green as “conjugate acid.” The acid on the left side of the equation is connected to the conjugate base on the right with a purple line. Similarly, the base on the left is connected to the conjugate acid on the right side.

The reaction between a Brønsted-Lowry acid and water is called acid ionization. For example, when hydrogen fluoride dissolves in water and ionizes, protons are transferred from hydrogen fluoride molecules to water molecules, yielding hydronium ions and fluoride ions:

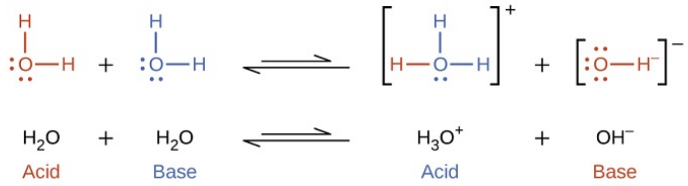


This figure has two rows. In both rows, a chemical reaction is shown. In the first, structural formulas are provided. In this model, in purple, an H atom is connected to an F atom with a single bond. The F atom has pairs of electron dots at the top, right, and bottom. This is followed by a plus sign, which is followed in green by an O atom which has H atoms singly bonded above and to the right. The O atom has pairs of electron dots on its left and lower sides. A double arrow follows. To the right, in brackets is a structure with a central O atom in green, with green H atoms singly bonded above and to the right. A pair of green electron dots is on the lower side of the O atom. To the left of the green O atom, a purple H atom is singly bonded. This is followed by a plus sign and an F atom in purple with pairs of electron dots above, right, below, and to the left. This atom also has a superscript negative sign. The reaction is written in symbolic form below. H F is labeled in purple below as “Acid subscript 1.” This is followed by plus H subscript 2 O, which is labeled in green below as “Base subscript 2.” A double sided arrow follows. To the right is H subscript 3 O superscript plus, which is labeled in green as below in as “Acid subscript 2.” This is followed by plus and F surrounded by 4 pairs of dots and superscript negative. The label below in purple reads, “Base subscript 1.” To the right of the reactions is the formula, K subscript a equals left bracket H subscript 3 O superscript plus right bracket left bracket F superscript negative right bracket all over left bracket H F right bracket.

When we add a base to water, a base ionization reaction occurs in which protons are transferred from water molecules to base molecules. For example, adding pyridine to water yields hydroxide ions and pyridinium ions:



Notice that both these ionization reactions are represented as equilibrium processes. The relative extent to which these acid and base ionization reactions proceed is an important topic treated in a later section of this chapter. In the preceding paragraphs we saw that water can function as either an acid or a base, depending on the nature of the solute dissolved in it. In fact, in pure water or in any aqueous solution, water acts both as an acid and a base. A very small fraction of water molecules donate protons to other water molecules to form hydronium ions and hydroxide ions:



This figure has two rows. In both rows, a chemical reaction is shown. In the first, structural formulas are provided. In this model, in purple, O atom which has H atoms singly bonded above and to the right. The O atom has pairs of electron dots on its left and lower sides. This is followed by a plus sign, which is followed in green by an O atom which has H atoms singly bonded above and to the right. The O atom has pairs of electron dots on its left and lower sides. A double arrow follows. To the right, in brackets is a structure with a central O atom in green, with green H atoms singly bonded above and to the right. A pair of green electron dots is on the lower side of the O atom. To the left of the green O atom, a purple H atom is singly bonded. Outside the brackets to the right is a superscript plus. This is followed by a plus sign and an O atom in purple with pairs of electron dots above, left, and below. An H atom is singly bonded to the right. This atom has a superscript negative sign. The reaction is written in symbolic form below. H subscript 2 O is labeled in purple below as “Acid subscript 1.” This is followed by plus H subscript 2 O, which is labeled in green below as “Base subscript 2.” A double sided arrow follows. To the right is H subscript 3 O superscript plus, which is labeled in green as below in as “Acid subscript 2.” This is followed by plus and O with pairs of dots above, below, and to the left with a singly bonded H on the right with a superscript negative. The label below in purple reads, “ Base subscript 1.”

This type of reaction, in which a substance ionizes when one molecule of the substance reacts with another molecule of the same substance, is referred to as **autoionization**. Pure water undergoes autoionization to a very slight extent. Only about two out of every 10^9 molecules in a sample of pure water are ionized at 25 °C. The equilibrium constant for the ionization of water is called the ion-product constant for water (K_w):

$$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)} \quad K_w = [H_3O^+][OH^-] \tag{9.1.15}$$

The slight ionization of pure water is reflected in the small value of the equilibrium constant; at 25 °C, Kw has a value of 1.0×10^{-14}. The process is endothermic, and so the extent of ionization and the resulting concentrations of hydronium ion and

hydroxide ion increase with temperature. For example, at 100 °C, the value for K_w is approximately 5.1×10^{-13}, roughly 50-times larger than the value at 25 °C.

Example 9.1.1: Ion Concentrations in Pure Water

What are the hydronium ion concentration and the hydroxide ion concentration in pure water at 25 °C?

Solution

The autoionization of water yields the same number of hydronium and hydroxide ions. Therefore, in pure water, $[H_3O^+] = [OH^-]$. At 25 °C:

$$K_w = [H_3O^+][OH^-] = [H_3O^+]^2 = [OH^-]^2 = 1.0 \times 10^{-14}$$

So:

$$[H_3O^+] = [OH^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}\ M$$

The hydronium ion concentration and the hydroxide ion concentration are the same, and we find that both equal $1.0 \times 10^{-7}\ M$.

Exercise 9.1.1

The ion product of water at 80 °C is 2.4×10^{-13}. What are the concentrations of hydronium and hydroxide ions in pure water at 80 °C?

Answer

$[H_3O^+] = [OH^-] = 4.9 \times 10^{-7}\ M$

It is important to realize that the autoionization equilibrium for water is established in all aqueous solutions. Adding an acid or base to water will not change the position of the equilibrium. Example 14.12 demonstrates the quantitative aspects of this relation between hydronium and hydroxide ion concentrations.

Example 9.1.2: The Inverse Proportionality of $[H_3O^+]$ and $[OH^-]$

The Inverse Proportionality of $[H_3O^+]$ and $[OH^-]$ A solution of carbon dioxide in water has a hydronium ion concentration of $2.0 \times 10^{-6}\ M$. What is the concentration of hydroxide ion at 25 °C?

Solution

We know the value of the ion-product constant for water at 25 °C:

$$2\,H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + OH^-{}_{(aq)}$$

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

Thus, we can calculate the missing equilibrium concentration.

Rearrangement of the K_w expression yields that $[OH^-]$ is directly proportional to the inverse of $[H_3O^+]$:

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-6}} = 5.0 \times 10^{-9}$$

The hydroxide ion concentration in water is reduced to $5.0 \times 10^{-9}\ M$ as the hydrogen ion concentration increases to $2.0 \times 10^{-6}\ M$. This is expected from Le Chatelier's principle; the autoionization reaction shifts to the left to reduce the stress of the increased hydronium ion concentration and the $[OH^-]$ is reduced relative to that in pure water.

A check of these concentrations confirms that our arithmetic is correct:

$$K_w = [H_3O^+][OH^-]$$
$$= (2.0 \times 10^{-6})(5.0 \times 10^{-9})$$
$$= 1.0 \times 10^{-14}$$

? Exercise 9.1.2

What is the hydronium ion concentration in an aqueous solution with a hydroxide ion concentration of 0.001 M at 25 °C?

Answer

$$[H_3O^+] = 1 \times 10^{-11} M$$

Amphiprotic Species

Like water, many molecules and ions may either gain or lose a proton under the appropriate conditions. Such species are said to be amphiprotic. Another term used to describe such species is amphoteric, which is a more general term for a species that may act either as an acid or a base by any definition (not just the Brønsted-Lowry one). Consider for example the bicarbonate ion, which may either donate or accept a proton as shown here:

$$HCO^-{}_{3(aq)} + H_2O_{(l)} \rightleftharpoons CO^{2-}{}_{3(aq)} + H_3O^+{}_{(aq)} \quad (9.1.16)$$

$$HCO^-{}_{3(aq)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)} + OH^-{}_{(aq)} \quad (9.1.17)$$

✓ Example 9.1.3: The Acid-Base Behavior of an Amphoteric Substance

Write separate equations representing the reaction of HSO_3^-

a. as an acid with OH^-
b. as a base with HI

Solution

a. $HSO_3^-(aq) + OH^-(aq) \rightleftharpoons SO_3{}^{2-}(aq) + H_2O_{(l)}$
b. $HSO_3^-(aq) + HI(aq) \rightleftharpoons H_2SO_3(aq) + I^-(aq)$

? Exercise 9.1.3

Write separate equations representing the reaction of $H_2PO_4^-$

a. as a base with HBr
b. as an acid with OH^-

Answer a

$$H_2PO_4^-(aq) + HBr(aq) \rightleftharpoons H_3PO_4(aq) + Br^-(aq)$$

Answer b

$$H_2PO_4^-(aq) + OH^-(aq) \rightleftharpoons HPO_4{}^{2-}(aq) + H_2O_{(l)}$$

Summary

A compound that can donate a proton (a hydrogen ion) to another compound is called a Brønsted-Lowry acid. The compound that accepts the proton is called a Brønsted-Lowry base. The species remaining after a Brønsted-Lowry acid has lost a proton is the conjugate base of the acid. The species formed when a Brønsted-Lowry base gains a proton is the conjugate acid of the base. Thus, an acid-base reaction occurs when a proton is transferred from an acid to a base, with formation of the conjugate base of the reactant acid and formation of the conjugate acid of the reactant base. Amphiprotic species can act as both proton donors and

proton acceptors. Water is the most important amphiprotic species. It can form both the hydronium ion, H_3O^+, and the hydroxide ion, OH^- when it undergoes autoionization:

$$2\,H_2O_{(l)} \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

The ion product of water, K_w is the equilibrium constant for the autoionization reaction:

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25°C$$

Key Equations

- $$K_w = [H_3O^+][OH^-\,] = 1.0 \times 10^{-14} \text{ (at 25 °C)}$$

Glossary

acid ionization
reaction involving the transfer of a proton from an acid to water, yielding hydronium ions and the conjugate base of the acid

amphiprotic
species that may either gain or lose a proton in a reaction

amphoteric
species that can act as either an acid or a base

autoionization
reaction between identical species yielding ionic products; for water, this reaction involves transfer of protons to yield hydronium and hydroxide ions

base ionization
reaction involving the transfer of a proton from water to a base, yielding hydroxide ions and the conjugate acid of the base

Brønsted-Lowry acid
proton donor

Brønsted-Lowry base
proton acceptor

conjugate acid
substance formed when a base gains a proton

conjugate base
substance formed when an acid loses a proton

ion-product constant for water (K_w)
equilibrium constant for the autoionization of water

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9.2: pH and pOH

Learning Objectives

- Explain the characterization of aqueous solutions as acidic, basic, or neutral
- Express hydronium and hydroxide ion concentrations on the pH and pOH scales
- Perform calculations relating pH and pOH

As discussed earlier, hydronium and hydroxide ions are present both in pure water and in all aqueous solutions, and their concentrations are inversely proportional as determined by the ion product of water (K_w). The concentrations of these ions in a solution are often critical determinants of the solution's properties and the chemical behaviors of its other solutes, and specific vocabulary has been developed to describe these concentrations in relative terms. A solution is neutral if it contains equal concentrations of hydronium and hydroxide ions; acidic if it contains a greater concentration of hydronium ions than hydroxide ions; and basic if it contains a lesser concentration of hydronium ions than hydroxide ions.

A common means of expressing quantities, the values of which may span many orders of magnitude, is to use a logarithmic scale. One such scale that is very popular for chemical concentrations and equilibrium constants is based on the p-function, defined as shown where "X" is the quantity of interest and "log" is the base-10 logarithm:

$$\mathrm{pX} = -\log \mathrm{X} \tag{9.2.1}$$

The pH of a solution is therefore defined as shown here, where $[H_3O^+]$ is the molar concentration of hydronium ion in the solution:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] \tag{9.2.2}$$

Rearranging this equation to isolate the hydronium ion molarity yields the equivalent expression:

$$[\mathrm{H_3O^+}] = 10^{-\mathrm{pH}} \tag{9.2.3}$$

Likewise, the hydroxide ion molarity may be expressed as a p-function, or pOH:

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] \tag{9.2.4}$$

or

$$[\mathrm{OH^-}] = 10^{-\mathrm{pOH}} \tag{9.2.5}$$

Finally, the relation between these two ion concentration expressed as p-functions is easily derived from the K_w expression:

$$K_\mathrm{w} = [\mathrm{H_3O^+}][\mathrm{OH^-}] \tag{9.2.6}$$

$$-\log K_\mathrm{w} = -\log([\mathrm{H_3O^+}][\mathrm{OH^-}]) = -\log[\mathrm{H_3O^+}] + -\log[\mathrm{OH^-}] \tag{9.2.7}$$

$$\mathrm{p}K_\mathrm{w} = \mathrm{pH} + \mathrm{pOH} \tag{9.2.8}$$

At 25 °C, the value of K_w is 1.0×10^{-14}, and so:

$$14.00 = \mathrm{pH} + \mathrm{pOH} \tag{9.2.9}$$

The hydronium ion molarity in pure water (or any neutral solution) is $1.0 \times 10^{-7}\ M$ at 25 °C. The pH and pOH of a neutral solution at this temperature are therefore:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = -\log(1.0 \times 10^{-7}) = 7.00 \tag{9.2.10}$$

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] = -\log(1.0 \times 10^{-7}) = 7.00 \tag{9.2.11}$$

And so, at this temperature, acidic solutions are those with hydronium ion molarities greater than $1.0 \times 10^{-7}\ M$ and hydroxide ion molarities less than $1.0 \times 10^{-7}\ M$ (corresponding to pH values less than 7.00 and pOH values greater than 7.00). Basic solutions are those with hydronium ion molarities less than $1.0 \times 10^{-7}\ M$ and hydroxide ion molarities greater than $1.0 \times 10^{-7}\ M$ (corresponding to pH values greater than 7.00 and pOH values less than 7.00).

When $pH = 7$ Solutions are not Neutral

Since the autoionization constant K_w is temperature dependent, these correlations between pH values and the acidic/neutral/basic adjectives will be different at temperatures other than 25 °C. For example, the hydronium molarity of pure water at 80 °C is 4.9×10^{-7} *M*, which corresponds to pH and pOH values of:

$$\begin{aligned} pH &= -\log[H_3O^+] \\ &= -\log(4.9 \times 10^{-7}) \\ &= 6.31 \end{aligned}$$

$$\begin{aligned} pOH &= -\log[OH^-] \\ &= -\log(4.9 \times 10^{-7}) \\ &= 6.31 \end{aligned}$$

At this temperature, then, neutral solutions exhibit pH = pOH = 6.31, acidic solutions exhibit pH less than 6.31 and pOH greater than 6.31, whereas basic solutions exhibit pH greater than 6.31 and pOH less than 6.31. This distinction can be important when studying certain processes that occur at nonstandard temperatures, such as enzyme reactions in warm-blooded organisms. Unless otherwise noted, references to pH values are presumed to be those at standard temperature (25 °C) (Table 9.2.1).

Table 9.2.1: Summary of Relations for Acidic, Basic and Neutral Solutions

Classification	Relative Ion Concentrations	pH at 25 °C
acidic	$[H_3O^+] > [OH^-]$	pH < 7
neutral	$[H_3O^+] = [OH^-]$	pH = 7
basic	$[H_3O^+] < [OH^-]$	pH > 7

Figure 9.2.1 shows the relationships between $[H_3O^+]$, $[OH^-]$, pH, and pOH, and gives values for these properties at standard temperatures for some common substances.

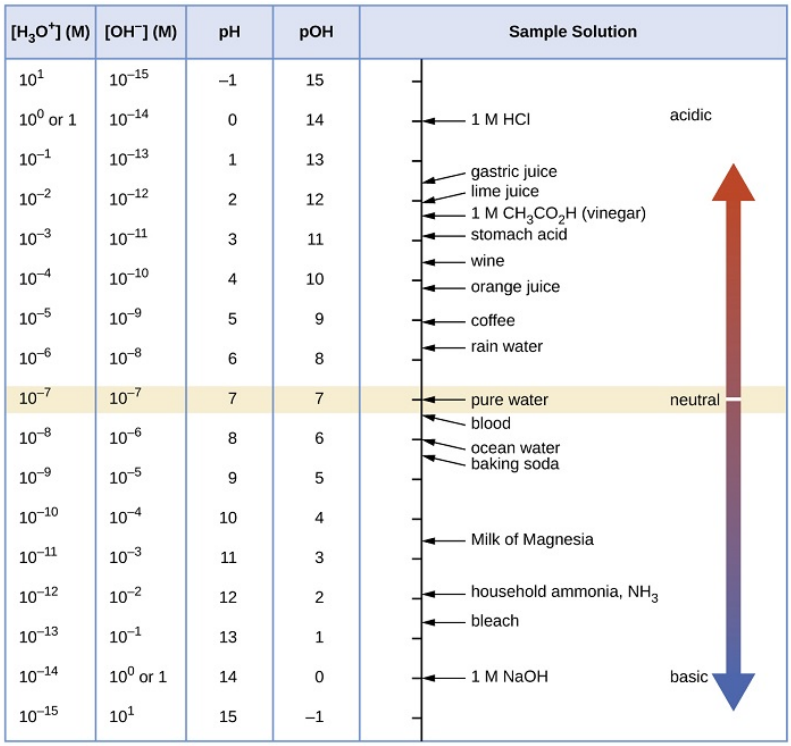


Figure **9.2.1**: The pH and pOH scales represent concentrations of $[H_3O^+]$ and OH^-, respectively. The pH and pOH values of some common substances at standard temperature (25 °C) are shown in this chart.

A table is provided with 5 columns. The first column is labeled “left bracket H subscript 3 O superscript plus right bracket (M).” Powers of ten are listed in the column beginning at 10 superscript 1, including 10 superscript 0 or 1, 10 superscript negative 1, decreasing by single powers of 10 to 10 superscript negative 15. The second column is labeled “left bracket O H superscript negative right bracket (M).” Powers of ten are listed in the column beginning at 10 superscript negative 15, increasing by single powers of 10 to including 10 superscript 0 or 1, and 10 superscript 1. The third column is labeled “p H.” Values listed in this column are integers beginning at negative 1, increasing by ones up to 14. The fourth column is labeled “p O H.” Values in this column are integers beginning at 15, decreasing by ones up to negative 1. The fifth column is labeled “Sample Solution.” A vertical line at the left of the column has tick marks corresponding to each p H level in the table. Substances are listed next to this line segment with line segments connecting them to the line to show approximate p H and p O H values. 1 M H C l is listed at a p H of 0. Gastric juices are listed at a p H of about 1.5. Lime juice is listed at a p H of about 2, followed by 1 M C H subscript 3 C O subscript 2 H, followed by stomach acid at a p H value of nearly 3. Wine is listed around 3.5. Coffee is listed just past 5. Pure water is listed at a p H of 7. Pure blood is just beyond 7. Milk of Magnesia is listed just past a p H of 10.5. Household ammonia is listed just before a pH of 12. 1 M N a O H is listed at a p H of 0. To the right of this labeled arrow is an arrow that points up and down through the height of the column. A beige strip passes through the table and to this double headed arrow at p H 7. To the left of the double headed arrow in this beige strip is the label “neutral.” A narrow beige strip runs through the arrow. Just above and below this region, the arrow is purple. It gradually turns to a bright red as it extends upward. At the top of the arrow, near the head of the arrow is the label “acidic.” Similarly, the lower region changes color from purple to blue moving to the bottom of the column. The head at this end of the arrow is labeled “basic.”

Example 9.2.1: Calculation of pH from $[H_3O^+]$

What is the pH of stomach acid, a solution of HCl with a hydronium ion concentration of $1.2 \times 10^{-3}\ M$?

Solution

$$\begin{aligned} pH &= -\log[H_3O^+] \\ &= -\log(1.2 \times 10^{-3}) \\ &= -(-2.92) \\ &= 2.92 \end{aligned}$$

? Exercise 9.2.1

Water exposed to air contains carbonic acid, H_2CO_3, due to the reaction between carbon dioxide and water:

$$CO_2\,(aq) + H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq)$$

Air-saturated water has a hydronium ion concentration caused by the dissolved CO_2 of $2.0 \times 10^{-6}\ M$, about 20-times larger than that of pure water. Calculate the pH of the solution at 25 °C.

Answer

5.70

✓ Example 9.2.2: Calculation of Hydronium Ion Concentration from pH

Calculate the hydronium ion concentration of blood, the pH of which is 7.3 (slightly alkaline).

Solution

$$pH = -\log[H_3O^+] = 7.3$$

$$\log[H_3O^+] = -7.3$$

$$[H_3O^+] = 10^{-7.3}$$

or

$$[H_3O^+] = \text{antilog of} - 7.3$$

$$[H_3O^+] = 5 \times 10^{-8}\ M$$

(On a calculator take the antilog, or the "inverse" log, of −7.3, or calculate $10^{-7.3}$.)

? Exercise 9.2.2

Calculate the hydronium ion concentration of a solution with a pH of −1.07.

Answer

12 M

Environmental Science

Normal rainwater has a pH between 5 and 6 due to the presence of dissolved CO_2 which forms carbonic acid:

$$H_2O\,(l) + CO_2\,(g) \longrightarrow H_2CO_3\,(aq) \tag{9.2.12}$$

$$H_2CO_3\,(aq) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq) \tag{9.2.13}$$

Acid rain is rainwater that has a pH of less than 5, due to a variety of nonmetal oxides, including CO_2, SO_2, SO_3, NO, and NO_2 being dissolved in the water and reacting with it to form not only carbonic acid, but sulfuric acid and nitric acid. The formation and subsequent ionization of sulfuric acid are shown here:

$$H_2O\,(l) + SO_3\,(g) \longrightarrow H_2SO_4\,(aq) \tag{9.2.14}$$

$$H_2SO_4\,(aq) \longrightarrow H^+\,(aq) + HSO_4^-\,(aq) \tag{9.2.15}$$

Carbon dioxide is naturally present in the atmosphere because we and most other organisms produce it as a waste product of metabolism. Carbon dioxide is also formed when fires release carbon stored in vegetation or when we burn wood or fossil fuels. Sulfur trioxide in the atmosphere is naturally produced by volcanic activity, but it also stems from burning fossil fuels, which have traces of sulfur, and from the process of "roasting" ores of metal sulfides in metal-refining processes. Oxides of nitrogen are

formed in internal combustion engines where the high temperatures make it possible for the nitrogen and oxygen in air to chemically combine.

Acid rain is a particular problem in industrial areas where the products of combustion and smelting are released into the air without being stripped of sulfur and nitrogen oxides. In North America and Europe until the 1980s, it was responsible for the destruction of forests and freshwater lakes, when the acidity of the rain actually killed trees, damaged soil, and made lakes uninhabitable for all but the most acid-tolerant species. Acid rain also corrodes statuary and building facades that are made of marble and limestone (Figure **9.2.2**). Regulations limiting the amount of sulfur and nitrogen oxides that can be released into the atmosphere by industry and automobiles have reduced the severity of acid damage to both natural and manmade environments in North America and Europe. It is now a growing problem in industrial areas of China and India.



(a) (b)

Figure **9.2.2**: (a) Acid rain makes trees more susceptible to drought and insect infestation, and depletes nutrients in the soil. (b) It also is corrodes statues that are carved from marble or limestone. (credit a: modification of work by Chris M Morris; credit b: modification of work by "Eden, Janine and Jim"/Flickr)

Two photos are shown. Photograph a on the left shows the upper portion of trees against a bright blue sky. The tops of several trees at the center of the photograph have bare branches and appear to be dead. Image b shows a statue of a man that appears to from the revolutionary war era in either marble or limestone.

✔ Example **9.2.3**: Calculation of pOH

What are the pOH and the pH of a 0.0125-M solution of potassium hydroxide, KOH?

Solution

Potassium hydroxide is a highly soluble ionic compound and completely dissociates when dissolved in dilute solution, yielding $[OH^-] = 0.0125$ M:

$$\mathbf{pOH} = -\log[\mathbf{OH}^-] = -\log 0.0125$$

$$= -(-1.903) = 1.903$$

The pH can be found from the $\mathbf{pOH}$:

$$\mathbf{pH} + \mathbf{pOH} = 14.00$$

$$\mathbf{pH} = 14.00 - \mathbf{pOH} = 14.00 - 1.903 = 12.10$$

? Exercise **9.2.3**

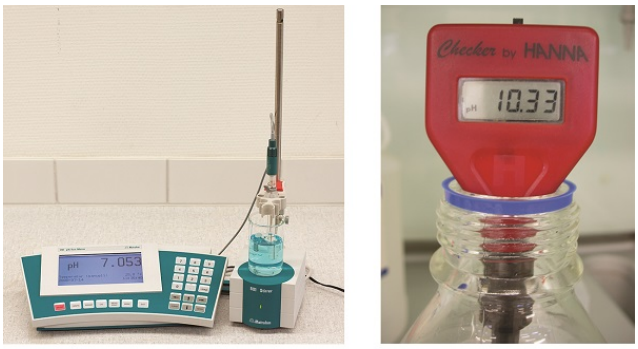
The hydronium ion concentration of vinegar is approximately $4 \times 10^{-3}\ M$. What are the corresponding values of pOH and pH?

Answer

pOH = 11.6,

pH = 14.00 - pOH = 2.4

The acidity of a solution is typically assessed experimentally by measurement of its pH. The pOH of a solution is not usually measured, as it is easily calculated from an experimentally determined pH value. The pH of a solution can be directly measured using a pH meter (Figure **9.2.3**).



(a) (b)

Figure 9.2.3: (a) A research-grade pH meter used in a laboratory can have a resolution of 0.001 pH units, an accuracy of ± 0.002 pH units, and may cost in excess of $1000. (b) A portable pH meter has lower resolution (0.01 pH units), lower accuracy (± 0.2 pH units), and a far lower price tag. (credit b: modification of work by Jacopo Werther)

This figure contains two images. The first, image a, is of an analytical digital p H meter on a laboratory counter. The second, image b, is of a portable hand held digital p H meter.

The pH of a solution may also be visually estimated using colored indicators (Figure 9.2.3).



(a) (b)

Figure 9.2.4: (a) A universal indicator assumes a different color in solutions of different pH values. Thus, it can be added to a solution to determine the pH of the solution. The eight vials each contain a universal indicator and 0.1-M solutions of progressively weaker acids: HCl (pH = l), CH_3CO_2H (pH = 3), and NH_4Cl (pH = 5), deionized water, a neutral substance (pH = 7); and 0.1-M solutions of the progressively stronger bases: KCl (pH = 7), aniline, $C_6H_5NH_2$ (pH = 9), NH_3 (pH = 11), and NaOH (pH = 13). (b) pH paper contains a mixture of indicators that give different colors in solutions of differing pH values. (credit: modification of work by Sahar Atwa).

This figure contains two images. The first shows a variety of colors of solutions in labeled beakers. A red solution in a beaker is labeled “0.10 M H C l.” An orange solution is labeled “0.10 M C H subscript 3 C O O H.” A yellow-orange solution is labeled “0.1 M N H subscript 4 C l.” A yellow solution is labeled “deionized water.” A second solution beaker is labeled “0.10 M K C l.” A green solution is labeled “0.10 M aniline.” A blue solution is labeled “0.10 M N H subscript 4 C l (a q).” A final beaker containing a dark blue solution is labeled “0.10 M N a O H.” Image b shows pHydrion paper that is used for measuring pH in the range of p H from 1 to 12. The color scale for identifying p H based on color is shown along with several of the test strips used to evaluate p H.

Summary

The concentration of hydronium ion in a solution of an acid in water is greater than $1.0 \times 10^{-7}\ M$ at 25 °C. The concentration of hydroxide ion in a solution of a base in water is greater than $1.0 \times 10^{-7}\ M$ at 25 °C. The concentration of H_3O^+ in a solution can be expressed as the pH of the solution; $\mathbf{pH = -\log H_3O^+}$. The concentration of OH^- can be expressed as the pOH of the solution: $\mathbf{pOH = -\log[OH^-]}$. In pure water, pH = 7.00 and pOH = 7.00

Key Equations

- $\mathbf{pH = -\log[H_3O^+]}$
- $\mathbf{pOH = -\log[OH^-]}$
- $[H_3O^+] = 10^{-pH}$
- $[OH^-] = 10^{-pOH}$
- pH + pOH = pK_w = 14.00 at 25 °C

Glossary

acidic

describes a solution in which $[H_3O^+] > [OH^-]$

basic

describes a solution in which $[H_3O^+] < [OH^-]$

neutral

describes a solution in which $[H_3O^+] = [OH^-]$

pH

logarithmic measure of the concentration of hydronium ions in a solution

pOH

logarithmic measure of the concentration of hydroxide ions in a solution

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9.3: Relative Strengths of Acids and Bases

Learning Objectives

- Assess the relative strengths of acids and bases according to their ionization constants
- Rationalize trends in acid–base strength in relation to molecular structure
- Carry out equilibrium calculations for weak acid–base systems

We can rank the strengths of acids by the extent to which they ionize in aqueous solution. The reaction of an acid with water is given by the general expression:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq)$$

Water is the base that reacts with the acid HA, $\mathrm{A^-}$ is the conjugate base of the acid HA, and the hydronium ion is the conjugate acid of water. A strong acid yields 100% (or very nearly so) of $\mathrm{H_3O^+}$ and $\mathrm{A^-}$ when the acid ionizes in water; Figure 9.3.1 lists several strong acids. A weak acid gives small amounts of $\mathrm{H_3O^+}$ and $\mathrm{A^-}$.

Figure 9.3.1: Some of the common strong acids and bases are listed here.

Six Strong Acids		Six Strong Bases	
$\mathrm{HClO_4}$	perchloric acid	LiOH	lithium hydroxide
HCl	hydrochloric acid	NaOH	sodium hydroxide
HBr	hydrobromic acid	KOH	potassium hydroxide
HI	hydroiodic acid	$\mathrm{Ca(OH)_2}$	calcium hydroxide
$\mathrm{HNO_3}$	nitric acid	$\mathrm{Sr(OH)_2}$	strontium hydroxide
$\mathrm{H_2SO_4}$	sulfuric acid	$\mathrm{Ba(OH)_2}$	barium hydroxide

The relative strengths of acids may be determined by measuring their equilibrium constants in aqueous solutions. In solutions of the same concentration, stronger acids ionize to a greater extent, and so yield higher concentrations of hydronium ions than do weaker acids. The equilibrium constant for an acid is called the acid-ionization constant, K_a. For the reaction of an acid HA:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq)$$

we write the equation for the ionization constant as:

$$K_a = \frac{[H3O+][A-]}{[HA]}$$

where the concentrations are those at equilibrium. As noted in the section on equilibrium constants, although water is a reactant in the reaction, it is the solvent as well, so its activity has a value of 1, which does not change the value of K_a.

Note

It is a common error to claim that the molar concentration of the solvent is in some way involved in the equilibrium law. This error is a result of a misunderstanding of solution thermodynamics. For example, it is often claimed that $K_a = K_{eq}[H_2O]$ for aqueous solutions. This equation is incorrect because it is an erroneous interpretation of the correct equation $K_a = K_{eq}(a_{H_2O})$. Because $a_{H_2O} = 1$ for a dilute solution, $K_a = K_{eq}(1)$, or $K_a = K_{eq}$.

The larger the K_a of an acid, the larger the concentration of H_3O^+ and A^- relative to the concentration of the nonionized acid, HA. Thus a stronger acid has a larger ionization constant than does a weaker acid. The ionization constants increase as the strengths of the acids increase.

The following data on acid-ionization constants indicate the order of acid strength: $CH_3CO_2H < HNO_2 < HSO_4^-$

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq) \qquad K_a = 1.8 \times 10^{-5}$$
$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq) \qquad K_a = 4.6 \times 10^{-4}$$
$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq) \qquad K_a = 1.2 \times 10^{-2}$$

Another measure of the strength of an acid is its *percent ionization*. The percent ionization of a weak acid is the ratio of the concentration of the ionized acid to the initial acid concentration, times 100:

$$\%\ \text{ionization} = \frac{[H3O+]_{eq}}{[HA]_0} \times 100\% \tag{9.3.1}$$

Because the ratio includes the initial concentration, the percent ionization for a solution of a given weak acid varies depending on the original concentration of the acid, and actually decreases with increasing acid concentration.

Example 9.3.1: Calculation of Percent Ionization from pH

Calculate the percent ionization of a 0.125-*M* solution of nitrous acid (a weak acid), with a pH of 2.09.

Solution

The percent ionization for an acid is:

$$\frac{[H3O+]_{eq}}{[HNO2]_0} \times 100$$

The chemical equation for the dissociation of the nitrous acid is:

$$HNO_2(aq) + H_2O(l) \rightleftharpoons NO_2^-(aq) + H_3O^+(aq).$$

Since $10^{-pH} = [H_3O^+]$, we find that $10^{-2.09} = 8.1 \times 10^{-3}\ M$, so that percent ionization (Equation 9.3.1) is:

$$\frac{8.1 \times 10^{-3}}{0.125} \times 100 = 6.5\%$$

Remember, the logarithm 2.09 indicates a hydronium ion concentration with only two significant figures.

Exercise 9.3.1

Calculate the percent ionization of a 0.10 *M* solution of acetic acid with a pH of 2.89.

Answer

1.3% ionized

We can rank the strengths of bases by their tendency to form hydroxide ions in aqueous solution. The reaction of a Brønsted-Lowry base with water is given by:

$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq)$$

Water is the acid that reacts with the base, HB^+ is the conjugate acid of the base B, and the hydroxide ion is the conjugate base of water. A strong base yields 100% (or very nearly so) of OH^- and HB^+ when it reacts with water; Figure 9.3.1 lists several strong bases. A weak base yields a small proportion of hydroxide ions. Soluble ionic hydroxides such as NaOH are considered strong bases because they dissociate completely when dissolved in water.

As we did with acids, we can measure the relative strengths of bases by measuring their base-ionization constant (K_b) in aqueous solutions. In solutions of the same concentration, stronger bases ionize to a greater extent, and so yield higher hydroxide ion concentrations than do weaker bases. A stronger base has a larger ionization constant than does a weaker base. For the reaction of a base, **B**:

$$\mathrm{B}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{HB^+}(aq) + \mathrm{OH^-}(aq),$$

we write the equation for the ionization constant as:

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

where the concentrations are those at equilibrium. Again, we do not see water in the equation because water is the solvent and has an activity of 1. The chemical reactions and ionization constants of the three bases shown are:

$$\mathrm{NO_2^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{HNO_2}(aq) + \mathrm{OH^-}(aq) \qquad K_b = 2.17 \times 10^{-11}$$
$$\mathrm{CH_3CO_2^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{CH_3CO_2H}(aq) + \mathrm{OH^-}(aq) \qquad K_b = 5.6 \times 10^{-10}$$
$$\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq) \qquad K_b = 1.8 \times 10^{-5}$$

A table of ionization constants of weak bases appears in Table E2. As with acids, percent ionization can be measured for basic solutions, but will vary depending on the base ionization constant and the initial concentration of the solution.

Consider the ionization reactions for a conjugate acid-base pair, $\mathrm{HA} - \mathrm{A^-}$:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq)$$

with $K_a = \frac{[H3O+][A-]}{[HA]}$.

$$\mathrm{A^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{OH^-}(aq) + \mathrm{HA}(aq)$$

with $K_b = \frac{[HA][OH]}{[A-]}$.

Adding these two chemical equations yields the equation for the autoionization for water:

$$\cancel{\mathrm{HA}(aq)} + \mathrm{H_2O}(l) + \cancel{\mathrm{A^-}(aq)} + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \cancel{\mathrm{A^-}(aq)} + \mathrm{OH^-}(aq) + \cancel{\mathrm{HA}(aq)}$$
$$2\,\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{OH^-}(aq)$$

As shown in the previous chapter on equilibrium, the K expression for a chemical equation derived from adding two or more other equations is the mathematical product of the other equations' K expressions. Multiplying the mass-action expressions together and cancelling common terms, we see that:

$$K_a \times K_b = \frac{[H3O+][A-]}{[HA]} \times \frac{[HA][OH-]}{[A-]} = [\mathrm{H_3O^+}][\mathrm{OH^-}] = K_w$$

For example, the acid ionization constant of acetic acid (CH_3COOH) is 1.8×10^{-5}, and the base ionization constant of its conjugate base, acetate ion ($\mathrm{CH_3COO^-}$), is 5.6×10^{-10}. The product of these two constants is indeed equal to K_w:

$$K_a \times K_b = (1.8 \times 10^{-5}) \times (5.6 \times 10^{-10}) = 1.0 \times 10^{-14} = K_w$$

The extent to which an acid, **HA**, donates protons to water molecules depends on the strength of the conjugate base, $\mathrm{A^-}$, of the acid. If $\mathrm{A^-}$ is a strong base, any protons that are donated to water molecules are recaptured by $\mathrm{A^-}$. Thus there is relatively little $\mathrm{A^-}$ and $\mathrm{H_3O^+}$ in solution, and the acid, **HA**, is weak. If $\mathrm{A^-}$ is a weak base, water binds the protons more strongly, and the solution contains primarily $\mathrm{A^-}$ and $\mathrm{H_3O^+}$—the acid is strong. Strong acids form very weak conjugate bases, and weak acids form stronger conjugate bases (Figure **9.3.2**).

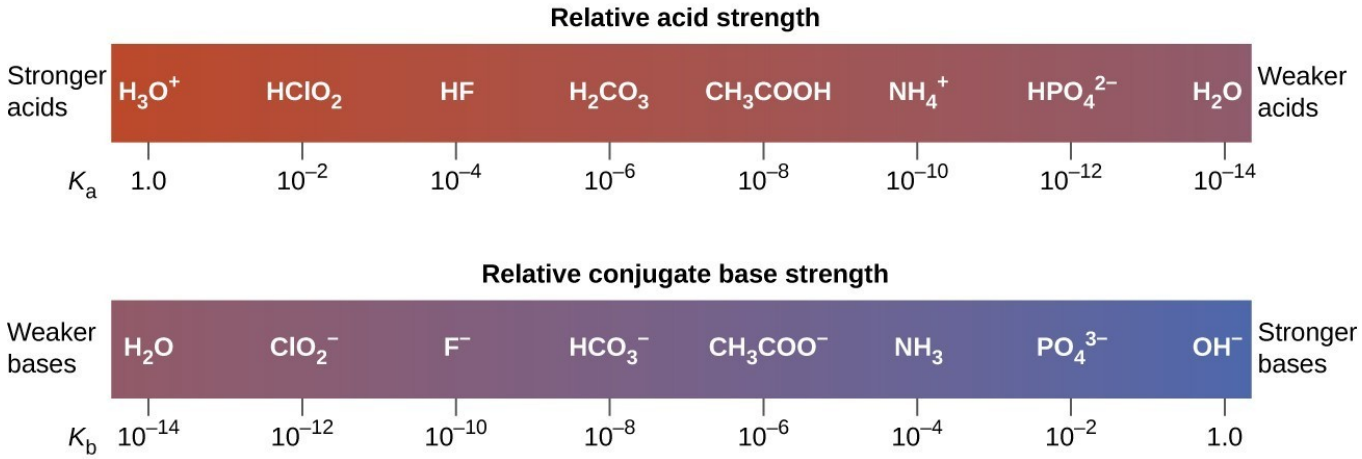


Figure **9.3.2**: This diagram shows the relative strengths of conjugate acid-base pairs, as indicated by their ionization constants in aqueous solution.

Figure **9.3.3** lists a series of acids and bases in order of the decreasing strengths of the acids and the corresponding increasing strengths of the bases. The acid and base in a given row are conjugate to each other.

The first six acids in Figure **9.3.3** are the most common strong acids. These acids are completely dissociated in aqueous solution. The conjugate bases of these acids are weaker bases than water. When one of these acids dissolves in water, their protons are completely transferred to water, the stronger base.

Those acids that lie between the hydronium ion and water in Figure **9.3.3** form conjugate bases that can compete with water for possession of a proton. Both hydronium ions and nonionized acid molecules are present in equilibrium in a solution of one of these acids. Compounds that are weaker acids than water (those found below water in the column of acids) in Figure **9.3.3** exhibit no observable acidic behavior when dissolved in water. Their conjugate bases are stronger than the hydroxide ion, and if any conjugate base were formed, it would react with water to re-form the acid.

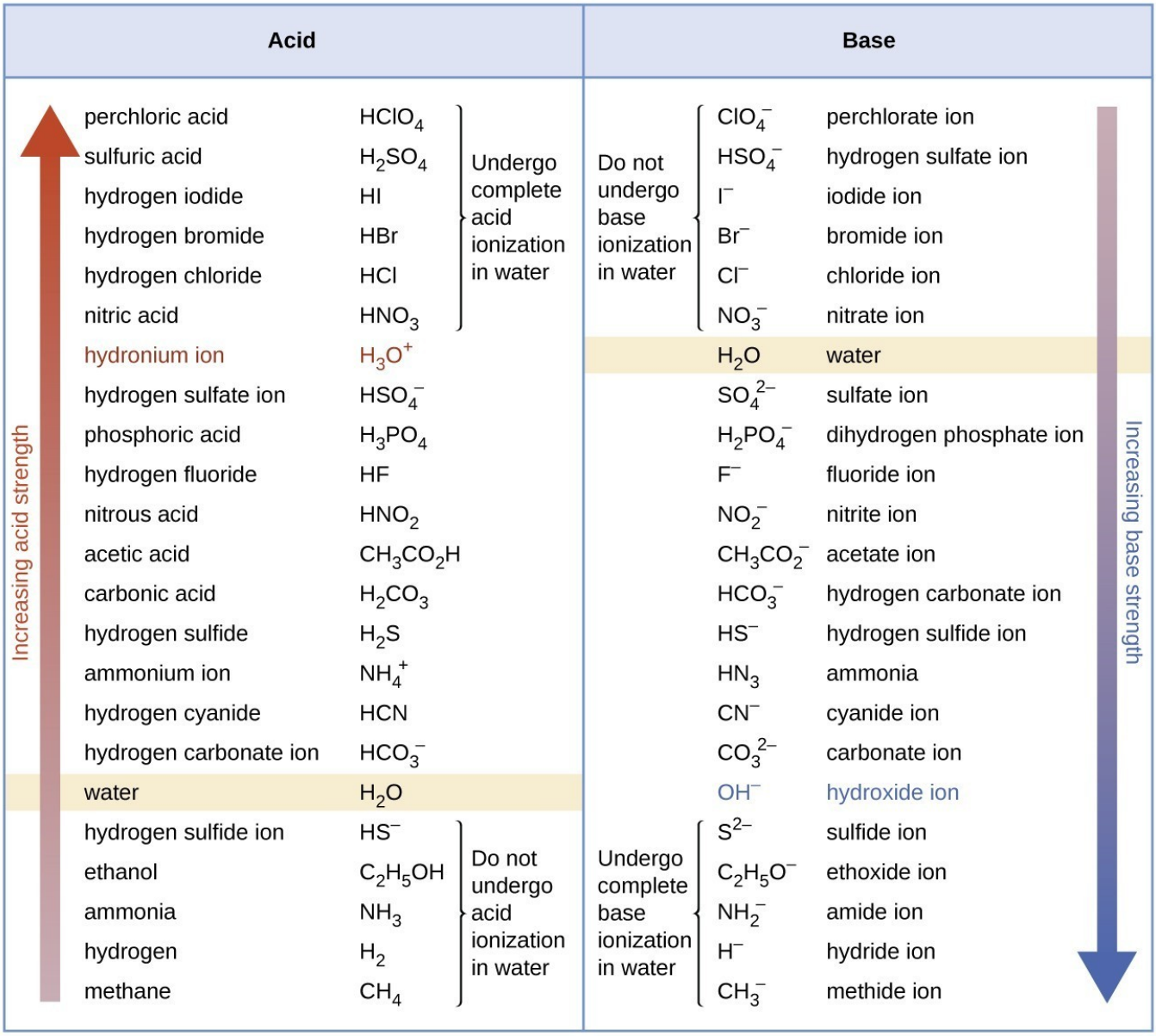


Figure **9.3.3**: The chart shows the relative strengths of conjugate acid-base pairs.

The extent to which a base forms hydroxide ion in aqueous solution depends on the strength of the base relative to that of the hydroxide ion, as shown in the last column in Figure **9.3.3**. A strong base, such as one of those lying below hydroxide ion, accepts protons from water to yield 100% of the conjugate acid and hydroxide ion. Those bases lying between water and hydroxide ion accept protons from water, but a mixture of the hydroxide ion and the base results. Bases that are weaker than water (those that lie above water in the column of bases) show no observable basic behavior in aqueous solution.

✔ Example **9.3.2**: The Product $K_a \times K_b = K_w$

Use the K_b for the nitrite ion, NO_2^-, to calculate the K_a for its conjugate acid.

Solution

K_b for NO_2^- is given in this section as 2.17×10^{-11}. The conjugate acid of NO_2^- is HNO_2; K_a for HNO_2 can be calculated using the relationship:

$$K_a \times K_b = 1.0 \times 10^{-14} = K_w$$

Solving for K_a, we get:

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{2.17 \times 10^{-11}} = 4.6 \times 10^{-4}$$

This answer can be verified by finding the K_a for HNO_2 in Table E1

? Exercise 9.3.2

We can determine the relative acid strengths of NH_4^+ and HCN by comparing their ionization constants. The ionization constant of HCN is given in Table E1 as 4.9×10^{-10}. The ionization constant of NH_4^+ is not listed, but the ionization constant of its conjugate base, NH_3, is listed as 1.8×10^{-5}. Determine the ionization constant of NH_4^+, and decide which is the stronger acid, HCN or NH_4^+.

Answer

NH_4^+ is the slightly stronger acid (K_a for $NH_4^+ = 5.6 \times 10^{-10}$).

The Ionization of Weak Acids and Weak Bases

Many acids and bases are weak; that is, they do not ionize fully in aqueous solution. A solution of a weak acid in water is a mixture of the nonionized acid, hydronium ion, and the conjugate base of the acid, with the nonionized acid present in the greatest concentration. Thus, a weak acid increases the hydronium ion concentration in an aqueous solution (but not as much as the same amount of a strong acid).

Acetic acid (CH_3CO_2H) is a weak acid. When we add acetic acid to water, it ionizes to a small extent according to the equation:

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$

giving an equilibrium mixture with most of the acid present in the nonionized (molecular) form. This equilibrium, like other equilibria, is dynamic; acetic acid molecules donate hydrogen ions to water molecules and form hydronium ions and acetate ions at the same rate that hydronium ions donate hydrogen ions to acetate ions to reform acetic acid molecules and water molecules. We can tell by measuring the pH of an aqueous solution of known concentration that only a fraction of the weak acid is ionized at any moment (Figure 9.3.4). The remaining weak acid is present in the nonionized form.

For acetic acid, at equilibrium:

$$K_a = \frac{[H3O+][CH3CO2-]}{[CH3CO2H]} = 1.8 \times 10^{-5}$$



Figure **9.3.4**: pH paper indicates that a 0.l-M solution of **HCl** (beaker on left) has a pH of 1. The acid is fully ionized and $[H_3O^+]$ = 0.1 M. A 0.1-M solution of CH_3CO_2H (beaker on right) has a pH of 3 ($[H_3O^+]$ = 0.001 M) because the weak acid CH_3CO_2H is only partially ionized. In this solution, $[H_3O^+] < [CH_3CO_2H]$. (credit: modification of work by Sahar Atwa)

This image shows two bottles containing clear colorless solutions. Each bottle contains a single p H indicator strip. The strip in the bottle on the left is red, and a similar red strip is placed on a filter paper circle in front of the bottle on surface on which the bottles are resting. Similarly, the second bottle on the right contains and orange strip and an orange strip is placed in front of it on a filter paper circle. Between the two bottles is a pack of p Hydrion papers with a p H color scale on its cover.

Table **9.3.1**: Ionization Constants of Some Weak Acids

Ionization Reaction	K_a at 25 °C
$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$	1.2×10^{-2}
$HF + H_2O \rightleftharpoons H_3O^+ + F^-$	3.5×10^{-4}
$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$	4.6×10^{-4}
$HNCO + H_2O \rightleftharpoons H_3O^+ + NCO^-$	2×10^{-4}
$HCO_2H + H_2O \rightleftharpoons H_3O^+ + HCO_2^-$	1.8×10^{-4}
$CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-$	1.8×10^{-5}
$HClO + H_2O \rightleftharpoons H_3O^+ + ClO^-$	2.9×10^{-8}
$HBrO + H_2O \rightleftharpoons H_3O^+ + BrO^-$	2.8×10^{-9}
$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$	4.9×10^{-10}

Table **9.3.1** gives the ionization constants for several weak acids; additional ionization constants can be found in Table E1.

At equilibrium, a solution of a weak base in water is a mixture of the nonionized base, the conjugate acid of the weak base, and hydroxide ion with the nonionized base present in the greatest concentration. Thus, a weak base increases the hydroxide ion concentration in an aqueous solution (but not as much as the same amount of a strong base).

For example, a solution of the weak base trimethylamine, $(CH_3)_3N$, in water reacts according to the equation:

$$(CH_3)_3N(aq) + H_2O(l) \rightleftharpoons (CH_3)_3NH^+(aq) + OH^-(aq)$$

This gives an equilibrium mixture with most of the base present as the nonionized amine. This equilibrium is analogous to that described for weak acids.

We can confirm by measuring the pH of an aqueous solution of a weak base of known concentration that only a fraction of the base reacts with water (Figure 14.4.5). The remaining weak base is present as the unreacted form. The equilibrium constant for the ionization of a weak base, K_b, is called the **ionization constant** of the weak base, and is equal to the reaction quotient when the reaction is at equilibrium. For trimethylamine, at equilibrium:

$$K_b = \frac{[(CH3)3NH+][OH-]}{[(CH3)3N]}$$



Figure 9.3.5: pH paper indicates that a 0.1-M solution of NH_3 (left) is weakly basic. The solution has a pOH of 3 ($[OH^-]$ = 0.001 M) because the weak base NH_3 only partially reacts with water. A 0.1-M solution of NaOH (right) has a pOH of 1 because NaOH is a strong base (credit: modification of work by Sahar Atwa).

The ionization constants of several weak bases are given in Table 9.3.2 and Table E2.

Table 9.3.2: Ionization Constants of Some Weak Bases

Ionization Reaction	K_b at 25 °C
$(CH_3)_2NH + H_2O \rightleftharpoons (CH_3)_2NH_2^+ + OH^-$	5.9×10^{-4}
$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$	4.4×10^{-4}
$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$	6.3×10^{-5}
$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.8×10^{-5}
$C_6H_5NH_2 + H_2O \rightleftharpoons C_6N_5NH_3^+ + OH^-$	4.3×10^{-10}

Example 9.3.3: Determination of K_a from Equilibrium Concentrations

Acetic acid is the principal ingredient in vinegar; that's why it tastes sour. At equilibrium, a solution contains $[CH_3CO_2H]$ = 0.0787 *M* and $[H_3O^+] = [CH_3CO_2^-] = 0.00118\ M$. What is the value of K_a for acetic acid?



Vinegar is a solution of acetic acid, a weak acid. (credit: modification of work by “HomeSpot HQ”/Flickr)

Solution

We are asked to calculate an equilibrium constant from equilibrium concentrations. At equilibrium, the value of the equilibrium constant is equal to the reaction quotient for the reaction:

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$

$$K_a = \frac{[H3O+][CH3CO2-]}{[CH3CO2H]}$$

$$= \frac{(0.00118)(0.00118)}{0.0787}$$

$$= 1.77 \times 10^{-5}$$

Exercise 9.3.3

What is the equilibrium constant for the ionization of the HSO_4^- ion, the weak acid used in some household cleansers:

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$$

In one mixture of $NaHSO_4$ and Na_2SO_4 at equilibrium, $[H_3O^+]$ = 0.027 *M*; $[HSO_4^-] = 0.29\ M$; and $[SO_4^{2-}] = 0.13\ M$.

Answer

K_a for $HSO_4^- = 1.2 \times \times 10^{-2}$

Example 9.3.4: Determination of K_b from Equilibrium Concentrations

Caffeine, $C_8H_{10}N_4O_2$ is a weak base. What is the value of K_b for caffeine if a solution at equilibrium has $[C_8H_{10}N_4O_2]$ = 0.050 *M*, $[C_8H_{10}N_4O_2H^+]$ = 5.0 × 10^{-3} *M*, and $[OH^-]$ = 2.5 × 10^{-3} *M*?

Solution

At equilibrium, the value of the equilibrium constant is equal to the reaction quotient for the reaction:

$$C_8H_{10}N_4O_2(aq) + H_2O(l) \rightleftharpoons C_8H_{10}N_4O_2H^+(aq) + OH^-(aq)$$

so

$$K_b = \frac{[C8H10N4O2H+][OH-]}{[C8H10N4O2]} = \frac{(5.0 \times 10^{-3})(2.5 \times 10^{-3})}{0.050} = 2.5 \times 10^{-4}$$

Exercise 9.3.4

What is the equilibrium constant for the ionization of the HPO_4^{2-} ion, a weak base:

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + OH^-(aq)$$

In a solution containing a mixture of NaH_2PO_4 and Na_2HPO_4 at equilibrium with:

- $[OH^-] = 1.3 \times 10^{-6} M$
- $[H_2PO_4^-]$=0.042 M and
- $[HPO_4^{2-}]$=0.341 M.

Answer

K_b for $HPO_4^{2-} = 1.6 \times 10^{-7}$

Example 9.3.5: Determination of K_a or K_b from pH

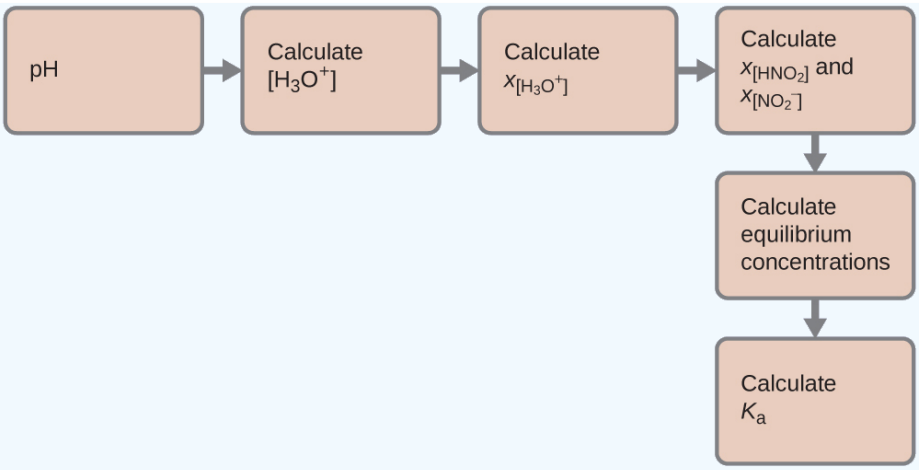
The pH of a 0.0516-*M* solution of nitrous acid, HNO_2, is 2.34. What is its K_a?

$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$$

Solution

We determine an equilibrium constant starting with the initial concentrations of HNO_2, H_3O^+, and NO_2^- as well as one of the final concentrations, the concentration of hydronium ion at equilibrium. (Remember that pH is simply another way to express the concentration of hydronium ion.)

We can solve this problem with the following steps in which *x* is a change in concentration of a species in the reaction:



We can summarize the various concentrations and changes as shown here. Because water is the solvent, it has a fixed activity equal to 1. Any small amount of water produced or used up during the reaction will not change water's role as the solvent, so the value of its activity remains equal to 1 throughout the reaction.

	HNO_2 + H_2O ⇌ H_3O^+ + NO_2^-			
Initial concentration (*M*)	0.0516		~0	0
Change (*M*)	$-x$	+	x	x
Equilibrium concentration (*M*)	$[HNO_2]_i + (-x) = 0.0516 + (-x)$		$[H_3O]^+ + x[NO_2]^- + x \sim 0 + x$	0.0046

To get the various values in the ICE (Initial, Change, Equilibrium) table, we first calculate $[H_3O^+]$, the equilibrium concentration of H_3O^+, from the pH:

$$[H_3O^+] = 10^{-2.34} = 0.0046\ M$$

The change in concentration of H_3O^+, $x_{[H_3O^+]}$, is the difference between the equilibrium concentration of H_3O^+, which we determined from the pH, and the initial concentration, $[H_3O^+]_i$. The initial concentration of H_3O^+ is its concentration in pure water, which is so much less than the final concentration that we approximate it as zero (~0).

The change in concentration of NO_2^- is equal to the change in concentration of $[H_3O^+]$. For each 1 mol of H_3O^+ that forms, 1 mol of NO_2^- forms. The equilibrium concentration of HNO_2 is equal to its initial concentration plus the change in its concentration.

Now we can fill in the ICE table with the concentrations at equilibrium, as shown here:

	HNO_2 + H_2O ⇌ H_3O^+ + NO_2^-			
Initial concentration (*M*)	0.0516		~0	0
Change (*M*)	$-x$	+	$x = 0.0046$	$x = 0.0046$
Equilibrium concentration (*M*)	0.0470		0.0046	0.0046

Finally, we calculate the value of the equilibrium constant using the data in the table:

$$K_a = \frac{[H3O+][NO2-]}{[HNO2]} = \frac{(0.0046)(0.0046)}{(0.0470)} = 4.5 \times 10^{-4}$$

Exercise 9.3.5

The pH of a solution of household ammonia, a 0.950-*M* solution of NH_3, is 11.612. What is K_b for NH_3.

Answer

$K_b = 1.8 \times 10^{-5}$

Example 9.3.6: Equilibrium Concentrations in a Solution of a Weak Acid

Formic acid, HCO_2H, is the irritant that causes the body's reaction to ant stings.



The pain of an ant's sting is caused by formic acid. (credit: John Tann)

What is the concentration of hydronium ion and the pH in a 0.534-*M* solution of formic acid?

$$\mathrm{HCO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HCO_2^-}(aq) \quad K_a = 1.8 \times 10^{-4}$$

Solution

1. Determine x and equilibrium concentrations. The equilibrium expression is:

$$\mathrm{HCO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HCO_2^-}(aq)$$

Because water is the solvent, it has a fixed activity equal to 1. Any small amount of water produced or used up during the reaction will not change water's role as the solvent, so the value of its activity remains equal to 1 throughout the reaction so we do not need to consider it when setting up the ICE table.

The table shows initial concentrations (concentrations before the acid ionizes), changes in concentration, and equilibrium concentrations follows (the data given in the problem appear in color):

	HCO_2H +	H_2O ⇌	H_3O^+
Initial concentration (*M*)	0.534	~0	0
Change (*M*)	−*x*	*x*	*x*
Equilibrium concentration (*M*)	0.534 + (−*x*)	0 + *x* = *x*	0 + *x* = *x*

2. Solve for x and the equilibrium concentrations. At equilibrium:

$$K_a = 1.8 \times 10^{-4} = \frac{[H3O+][HCO2-]}{[HCO2H]}$$

$$= \frac{(x)(x)}{0.534 - x} = 1.8 \times 10^{-4}$$

Now solve for x. Because the initial concentration of acid is reasonably large and K_a is very small, we assume that $x << 0.534$, which *permits* us to simplify the denominator term as $(0.534 - x) = 0.534$. This gives:

$$K_a = 1.8 \times 10^{-4} = \frac{x^2}{0.534}$$

Solve for x as follows:

$$x^2 = 0.534 \times (1.8 \times 10^{-4})$$
$$= 9.6 \times 10^{-5}$$
$$x = \sqrt{9.6 \times 10^{-5}}$$
$$= 9.8 \times 10^{-3}$$

To check the assumption that x is small compared to 0.534, we calculate:

$$\frac{x}{0.534} = \frac{9.8 \times 10^{-3}}{0.534}$$
$$= 1.8 \times 10^{-2}\,(1.8$$

x is less than 5% of the initial concentration; the assumption is valid.

We find the equilibrium concentration of hydronium ion in this formic acid solution from its initial concentration and the change in that concentration as indicated in the last line of the table:

$$[H_3O^+] = \ 0 + x = 0 + 9.8 \times 10^{-3}\ M.$$
$$= 9.8 \times 10^{-3}\ M$$

The pH of the solution can be found by taking the negative log of the $[H_3O^+]$, so:

$$pH = -\log(9.8 \times 10^{-3}) = 2.01$$

? Exercise 9.3.6: acetic acid

Only a small fraction of a weak acid ionizes in aqueous solution. What is the percent ionization of acetic acid in a 0.100-*M* solution of acetic acid, CH_3CO_2H?

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2{}^-(aq) \quad K_a = 1.8 \times 10^{-5}$$

Hint

Determine $[CH_3CO_2{}^-]$ at equilibrium.) Recall that the percent ionization is the fraction of acetic acid that is ionized × 100, or $\frac{[CH3CO2-]}{[CH3CO2H]_{initial}} \times 100$.

Answer

percent ionization = 1.3%

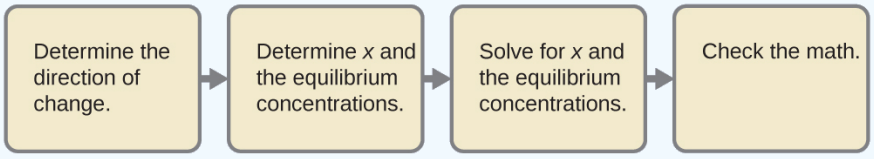
The following example shows that the concentration of products produced by the ionization of a weak base can be determined by the same series of steps used with a weak acid.

✓ Example 9.3.7: Equilibrium Concentrations in a Solution of a Weak Base

Find the concentration of hydroxide ion in a 0.25-*M* solution of trimethylamine, a weak base:

$$(CH_3)_3N(aq) + H_2O(l) \rightleftharpoons (CH_3)_3NH^+(aq) + OH^-(aq) \quad K_b = 6.3 \times 10^{-5}$$

Solution This problem requires that we calculate an equilibrium concentration by determining concentration changes as the ionization of a base goes to equilibrium. The solution is approached in the same way as that for the ionization of formic acid in Example 9.3.6. The reactants and products will be different and the numbers will be different, but the logic will be the same:



1. Determine x and equilibrium concentrations. The table shows the changes and concentrations:

	$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$			
Initial concentration (*M*)	0.25		0	~0
Change (*M*)	$-x$		x	x
Equilibrium concentration (*M*)	$0.25 + (-x)$		$0 + x$	$\sim 0 + x$

2. Solve for x and the equilibrium concentrations. At equilibrium:

$$K_b = \frac{[(CH3)3NH+][OH-]}{[(CH3)3N]} = \frac{(x)(x)}{0.25 - x =} 6.3 \times 10^{-5}$$

If we assume that x is small relative to 0.25, then we can replace $(0.25 - x)$ in the preceding equation with 0.25. Solving the simplified equation gives:

$$x = 4.0 \times 10^{-3}$$

This change is less than 5% of the initial concentration (0.25), so the assumption is justified.

Recall that, for this computation, x is equal to the equilibrium concentration of *hydroxide ion* in the solution (see earlier tabulation):

$$([OH^-] = 0 + x = x = 4.0 \times 10^{-3}\ M$$
$$= 4.0 \times 10^{-3}\ M$$

Then calculate pOH as follows:

$$\text{pOH} = -\log(4.3 \times 10^{-3}) = 2.40$$

Using the relation introduced in the previous section of this chapter:

$$\text{pH} + \text{pOH} = \text{p}K_w = 14.00$$

permits the computation of pH:

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 2.37 = 11.60$$

Check the work. A check of our arithmetic shows that $K_b = 6.3 \times 10^{-5}$.

? Exercise 9.3.7

a. Show that the calculation in Step 2 of this example gives an x of 4.3×10^{-3} and the calculation in Step 3 shows $K_b = 6.3 \times 10^{-5}$.

b. Find the concentration of hydroxide ion in a 0.0325-*M* solution of ammonia, a weak base with a K_b of 1.76×10^{-5}.

Calculate the percent ionization of ammonia, the fraction ionized × 100, or $\frac{[NH4+]}{[NH3]} \times 100\%$

Answer a

$7.56 \times 10^{-4}\ M$, 2.33%

Answer b

2.33%

Some weak acids and weak bases ionize to such an extent that the simplifying assumption that x is small relative to the initial concentration of the acid or base is inappropriate. As we solve for the equilibrium concentrations in such cases, we will see that we cannot neglect the change in the initial concentration of the acid or base, and we must solve the equilibrium equations by using the quadratic equation.

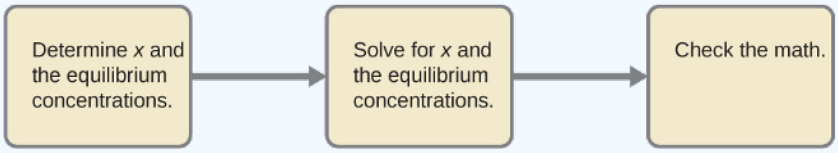
Example 9.3.8: Equilibrium Concentrations in a Solution of a Weak Acid

Sodium bisulfate, $NaHSO_4$, is used in some household cleansers because it contains the HSO_4^- ion, a weak acid. What is the pH of a 0.50-*M* solution of HSO_4^-?

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq) \quad K_a = 1.2 \times 10^{-2}$$

Solution

We need to determine the equilibrium concentration of the hydronium ion that results from the ionization of HSO_4^- so that we can use $[H_3O^+]$ to determine the pH. As in the previous examples, we can approach the solution by the following steps:



1. Determine x and equilibrium concentrations. This table shows the changes and concentrations:

	HSO_4^- + H_2O ⇌	H_3O^+ +	SO_4^{2-}
Initial concentration (*M*)	0.50	~0	0
Change (*M*)	$-x$	x	x
Equilibrium concentration (*M*)	$0.50 + (-x) = 0.50 - x$	$0 + x = x$	$0 + x = x$

2. Solve for x and the concentrations.

As we begin solving for x, we will find this is more complicated than in previous examples. As we discuss these complications we should not lose track of the fact that it is still the purpose of this step to determine the value of x.

At equilibrium:

$$K_a = 1.2 \times 10^{-2} = \frac{[H3O+][SO4^{2-}]}{[HSO4-]} = \frac{(x)(x)}{0.50 - x}$$

If we assume that x is small and approximate $(0.50 - x)$ as 0.50, we find:

$$x = 7.7 \times 10^{-2}$$

When we check the assumption, we confirm:

$$\frac{x}{[HSO_4^-]_i} \overset{?}{\leq} 0.05$$

which for this system is

$$\frac{x}{0.50} = \frac{7.7 \times 10^{-2}}{0.50} = 0.15(15\%)$$

The value of x is not less than 5% of 0.50, so the assumption is not valid. We need the quadratic formula to find x.

The equation:

$$K_a = 1.2 \times 10^{-2} = \frac{(x)(x)}{0.50 - x}$$

gives

$$6.0 \times 10^{-3} - 1.2 \times 10^{-2}x = x^{2+}$$

or

$$x^{2+} + 1.2 \times 10^{-2}x - 6.0 \times 10^{-3} = 0$$

This equation can be solved using the quadratic formula. For an equation of the form

$$ax^{2+} + bx + c = 0,$$

x is given by the quadratic equation:

$$x = \frac{-b \pm \sqrt{b^{2+} - 4ac}}{2a}$$

In this problem, $a = 1$, $b = 1.2 \times 10^{-3}$, and $c = -6.0 \times 10^{-3}$.

Solving for x gives a negative root (which cannot be correct since concentration cannot be negative) and a positive root:

$$x = 7.2 \times 10^{-2}$$

Now determine the hydronium ion concentration and the pH:

$$\begin{aligned}[\mathrm{H_3O^+}] = \ & 0 + x = 0 + 7.2 \times 10^{-2}\ M \\ & = 7.2 \times 10^{-2}\ M\end{aligned}$$

The pH of this solution is:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = -\log 7.2 \times 10^{-2} = 1.14$$

? Exercise 9.3.8

a. Show that the quadratic formula gives $x = 7.2 \times 10^{-2}$.

b. Calculate the pH in a 0.010-*M* solution of caffeine, a weak base:

$$\mathrm{C_8H_{10}N_4O_2}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{C_8H_{10}N_4O_2H^+}(aq) + \mathrm{OH^-}(aq) \quad K_\mathrm{b} = 2.5 \times 10^{-4}$$

Hint

It will be necessary to convert [OH^-] to [H_3O^+] or pOH to pH toward the end of the calculation.

Answer

pH 11.16

The Relative Strengths of Strong Acids and Bases

Strong acids, such as **HCl**, **HBr**, and **HI**, all exhibit the same strength in water. The water molecule is such a strong base compared to the conjugate bases Cl^-, Br^-, and I^- that ionization of these strong acids is essentially complete in aqueous solutions. In solvents less basic than water, we find **HCl**, **HBr**, and **HI** differ markedly in their tendency to give up a proton to the solvent. For example, when dissolved in ethanol (a weaker base than water), the extent of ionization increases in the order **HCl < HBr < HI**, and so **HI** is demonstrated to be the strongest of these acids. The inability to discern differences in strength among strong acids dissolved in water is known as the leveling effect of water.

Water also exerts a leveling effect on the strengths of strong bases. For example, the oxide ion, O^{2-}, and the amide ion, $\mathbf{NH_2^-}$, are such strong bases that they react completely with water:

$$\mathrm{O^{2-}}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{OH^-}(aq) + \mathrm{OH^-}(aq)$$

$$\mathrm{NH_2^-}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{NH_3}(aq) + \mathrm{OH^-}(aq)$$

Thus, O^{2-} and $\mathbf{NH_2^-}$ appear to have the same base strength in water; they both give a 100% yield of hydroxide ion.

In the absence of any leveling effect, the acid strength of binary compounds of hydrogen with nonmetals (A) increases as the H-A bond strength decreases down a group in the periodic table. For group 17, the order of increasing acidity is **HF < HCl < HBr < HI**.

Likewise, for group 16, the order of increasing acid strength is $H_2O < H_2S < H_2Se < H_2Te$. Across a row in the periodic table, the acid strength of binary hydrogen compounds increases with increasing electronegativity of the nonmetal atom because the polarity of the H-A bond increases. Thus, the order of increasing acidity (for removal of one proton) across the second row is $\mathbf{CH_4 < NH_3 < H_2O < HF}$; across the third row, it is $\mathbf{SiH_4 < PH_3 < H_2S < HCl}$ (see Figure **9.3.6**).

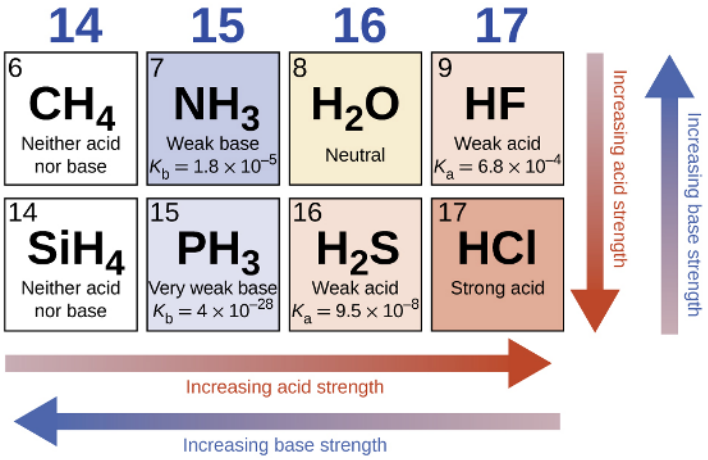
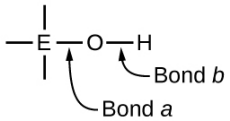


Figure **9.3.6**: As you move from left to right and down the periodic table, the acid strength increases. As you move from right to left and up, the base strength increases.

This diagram has two rows and four columns. Red arrows point left across the bottom of the figure and down at the right side and are labeled “Increasing acid strength.” Blue arrows point left across the bottom and up at the right side of the figure and are labeled “Increasing base strength.” The first column is labeled 14 at the top and two white squares are beneath it. The first has the number 6 in the upper left corner and the formula C H subscript 4 in the center along with designation Neither acid nor base. The second square contains the number 14 in the upper left corner, the formula C H subscript 4 at the center and the designation Neither acid nor base. The second column is labeled 15 at the top and two blue squares are beneath it. The first has the number 7 in the upper left corner and the formula N H subscript 3 in the center along with the designation Weak base and K subscript b equals 1.8 times 10 superscript negative 5. The second square contains the number 15 in the upper left corner, the formula P H subscript 3 at the center and the designation Very weak base and K subscript b equals 4 times 10 superscript negative 28. The third column is labeled 16 at the top and two squares are beneath it. The first is shaded tan and has the number 8 in the upper left corner and the formula H subscript 2 O in the center along with the designation neutral. The second square is shaded pink, contains the number 16 in the upper left corner, the formula H subscript 2 S at the center and the designation Weak acid and K subscript a equals 9.5 times 10 superscript negative 8. The fourth column is labeled 17 at the top and two squares are beneath it. The first is shaded pink, has the number 9 in the upper left corner and the formula H F in the center along with the designation Weak acid and K subscript a equals 6.8 times 10 superscript negative 4. The second square is shaded a deeper pink, contains the number 17 in the upper left corner, the formula H C l at the center, and the designation Strong acid.

Compounds containing oxygen and one or more hydroxyl (OH) groups can be acidic, basic, or amphoteric, depending on the position in the periodic table of the central atom E, the atom bonded to the hydroxyl group. Such compounds have the general formula $O_nE(OH)_m$, and include sulfuric acid, $\mathbf{O_2S(OH)_2}$, sulfurous acid, $\mathbf{OS(OH)_2}$, nitric acid, $\mathbf{O_2NOH}$, perchloric acid, $\mathbf{O_3ClOH}$, aluminum hydroxide, $\mathbf{Al(OH)_3}$, calcium hydroxide, $\mathbf{Ca(OH)_2}$, and potassium hydroxide, $\mathbf{KOH}$:



A diagram is shown that includes a central atom designated with the letter E. Single bonds extend above, below, left, and right of the E. An O atom is bonded to the right of the E, and an arrow points to the bond labeling it, “Bond a.” An H atom is single bonded to the right of the O atom. An arrow pointing to this bond connects it to the label, “Bond b.”

If the central atom, E, has a low electronegativity, its attraction for electrons is low. Little tendency exists for the central atom to form a strong covalent bond with the oxygen atom, and bond *a* between the element and oxygen is more readily broken than bond *b* between oxygen and hydrogen. Hence bond *a* is ionic, hydroxide ions are released to the solution, and the material behaves as a base—this is the case with $Ca(OH)_2$ and KOH. Lower electronegativity is characteristic of the more metallic elements; hence, the metallic elements form ionic hydroxides that are by definition basic compounds.

If, on the other hand, the atom E has a relatively high electronegativity, it strongly attracts the electrons it shares with the oxygen atom, making bond *a* relatively strongly covalent. The oxygen-hydrogen bond, bond *b*, is thereby weakened because electrons are displaced toward E. Bond *b* is polar and readily releases hydrogen ions to the solution, so the material behaves as an acid. High electronegativities are characteristic of the more nonmetallic elements. Thus, nonmetallic elements form covalent compounds containing acidic −OH groups that are called oxyacids.

Increasing the oxidation number of the central atom E also increases the acidity of an oxyacid because this increases the attraction of E for the electrons it shares with oxygen and thereby weakens the O-H bond. Sulfuric acid, H_2SO_4, or $O_2S(OH)_2$ (with a sulfur oxidation number of +6), is more acidic than sulfurous acid, H_2SO_3, or $OS(OH)_2$ (with a sulfur oxidation number of +4). Likewise nitric acid, HNO_3, or O_2NOH (N oxidation number = +5), is more acidic than nitrous acid, HNO_2, or ONOH (N oxidation number = +3). In each of these pairs, the oxidation number of the central atom is larger for the stronger acid (Figure **9.3.7**).

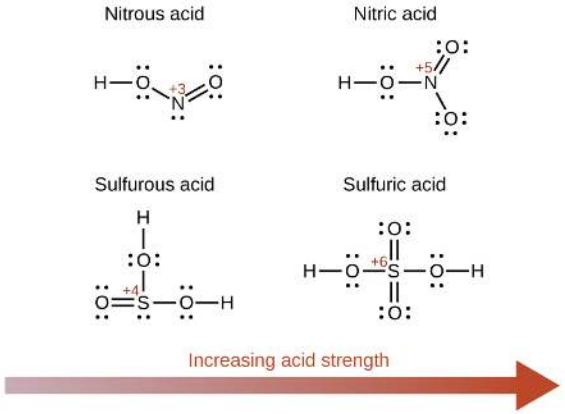


Figure **9.3.7**: As the oxidation number of the central atom E increases, the acidity also increases.

A diagram is shown that includes four structural formulas for acids. A red, right pointing arrow is placed beneath the structures which is labeled “Increasing acid strength.” At the top left, the structure of Nitrous acid is provided. It includes an H atom to which an O atom with two unshared electron pairs is connected with a single bond to the right. A single bond extends to the right and slightly below to a N atom with one unshared electron pair. A double bond extends up and to the right from this N atom to an O atom which has two unshared electron pairs. To the upper right is a structure for Nitric acid. This structure differs from the previous structure in that the N atom is directly to the right of the first O atom and a second O atom with three unshared electron pairs is connected with a single bond below and to the right of the N atom which has no unshared electron pairs. At the lower left, an O atom with two unshared electron pairs is double bonded to its right to an S atom with a single unshared electron pair. An O atom with two unshared electron pairs is bonded above and an H atom is single bonded to this O atom. To the right of the S atom is a single bond to another O atom with two unshared electron pairs to which an H atom is single bonded. This structure is labeled “Sulfurous acid.” A similar structure which is labeled “Sulfuric acid” is placed in the lower right region of the figure. This structure differs in that an H atom is single bonded to the left of the first O atom, leaving it with two unshared electron pairs and a fourth O atom with two unshared electron pairs is double bonded beneath the S atom, leaving it with no unshared electron pairs.

Hydroxy compounds of elements with intermediate electronegativities and relatively high oxidation numbers (for example, elements near the diagonal line separating the metals from the nonmetals in the periodic table) are usually amphoteric. This means that the hydroxy compounds act as acids when they react with strong bases and as bases when they react with strong acids. The amphoterism of aluminum hydroxide, which commonly exists as the hydrate $\mathbf{Al(H_2O)_3(OH)_3}$, is reflected in its solubility in both strong acids and strong bases. In strong bases, the relatively insoluble hydrated aluminum hydroxide, $\mathbf{Al(H_2O)_3(OH)_3}$, is converted into the soluble ion, $\mathbf{[Al(H_2O)_2(OH)_4]^-}$, by reaction with hydroxide ion:

$$\mathbf{[Al(H_2O)_3(OH)_3](\mathit{aq}) + OH^-(\mathit{aq}) \rightleftharpoons H_2O(\mathit{l}) + [Al(H_2O)_2(OH)_4]^-(\mathit{aq})}$$

In this reaction, a proton is transferred from one of the aluminum-bound H_2O molecules to a hydroxide ion in solution. The $\mathbf{Al(H_2O)_3(OH)_3}$ compound thus acts as an acid under these conditions. On the other hand, when dissolved in strong acids, it is converted to the soluble ion $\mathbf{[Al(H_2O)_6]^{3+}}$ by reaction with hydronium ion:

$$\mathbf{3\,H_3O^+(\mathit{aq}) + Al(H_2O)_3(OH)_3(\mathit{aq}) \rightleftharpoons Al(H_2O)_6^{3+}(\mathit{aq}) + 3\,H_2O(\mathit{l})}$$

In this case, protons are transferred from hydronium ions in solution to $\mathbf{Al(H_2O)_3(OH)_3}$, and the compound functions as a base.

Summary

The strengths of Brønsted-Lowry acids and bases in aqueous solutions can be determined by their acid or base ionization constants. Stronger acids form weaker conjugate bases, and weaker acids form stronger conjugate bases. Thus strong acids are completely ionized in aqueous solution because their conjugate bases are weaker bases than water. Weak acids are only partially ionized because their conjugate bases are strong enough to compete successfully with water for possession of protons. Strong bases react with water to quantitatively form hydroxide ions. Weak bases give only small amounts of hydroxide ion. The strengths of the binary acids increase from left to right across a period of the periodic table ($CH_4 < NH_3 < H_2O < HF$), and they increase down a group ($HF < HCl < HBr < HI$). The strengths of oxyacids that contain the same central element increase as the oxidation number of the element increases ($H_2SO_3 < H_2SO_4$). The strengths of oxyacids also increase as the electronegativity of the central element increases [$H_2SeO_4 < H_2SO_4$].

Key Equations

- $K_a = \frac{[H3O+][A-]}{[HA]}$
- $K_b = \frac{[HB+][OH-]}{[B]}$
- $K_a \times K_b = 1.0 \times 10^{-14} = K_w \text{ (at room temperature)}$
- $\text{Percent ionization} = \frac{[H3O+]_{eq}}{[HA]_0} \times 100$

Glossary

acid ionization constant (K_a)
equilibrium constant for the ionization of a weak acid

base ionization constant (K_b)
equilibrium constant for the ionization of a weak base

leveling effect of water
any acid stronger than H_3O^+, or any base stronger than OH^- will react with water to form H_3O^+, or OH^-, respectively; water acts as a base to make all strong acids appear equally strong, and it acts as an acid to make all strong bases appear equally strong

oxyacid
compound containing a nonmetal and one or more hydroxyl groups

percent ionization
ratio of the concentration of the ionized acid to the initial acid concentration, times 100

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9.4: Polyprotic Acids

Learning Objectives

- Extend previously introduced equilibrium concepts to acids and bases that may donate or accept more than one proton

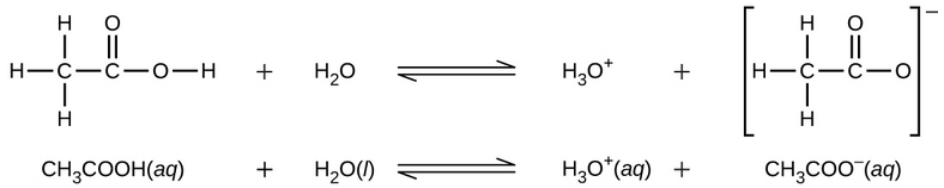
We can classify acids by the number of protons per molecule that they can give up in a reaction. Acids such as $\mathbf{HCl}$, $\mathbf{HNO_3}$, and $\mathbf{HCN}$ that contain one ionizable hydrogen atom in each molecule are called monoprotic acids. Their reactions with water are:

$$\mathbf{HCl}(aq) + \mathbf{H_2O}(l) \longrightarrow \mathbf{H_3O^+}(aq) + \mathbf{Cl^-}(aq)$$

$$\mathbf{HNO_3}(aq) + \mathbf{H_2O}(l) \longrightarrow \mathbf{H_3O^+}(aq) + \mathbf{NO_3^-}(aq)$$

$$\mathbf{HCN}(aq) + \mathbf{H_2O}(l) \longrightarrow \mathbf{H_3O^+}(aq) + \mathbf{CN^-}(aq)$$

Even though it contains four hydrogen atoms, acetic acid, $\mathbf{CH_3CO_2H}$, is also monoprotic because only the hydrogen atom from the carboxyl group ($\mathbf{-COOH}$) reacts with bases:



This image contains two equilibrium reactions. The first shows a C atom bonded to three H atoms and another C atom. The second C atom is double bonded to an O atom and also forms a single bond to another O atom. The second O atom is bonded to an H atom. There is a plus sign and then the molecular formula H subscript 2 O. An equilibrium arrow follows the H subscript 2 O. To the right of the arrow is H subscript 3 O superscript positive sign. There is a plus sign. The final structure shows a C atom bonded the three H atoms and another C atom. This second C atom is double bonded to an O atom and single bonded to another O atom. The entire structure is in brackets and a superscript negative sign appears outside the brackets. The second reaction shows C H subscript 3 C O O H (a q) plus H subscript 2 O (l) equilibrium arrow H subscript 3 O (a q) plus C H subscript 3 C O O superscript negative sign (a q).

Similarly, monoprotic bases are bases that will accept a single proton.

Diprotic Acids

Diprotic acids contain two ionizable hydrogen atoms per molecule; ionization of such acids occurs in two steps. The first ionization always takes place to a greater extent than the second ionization. For example, sulfuric acid, a strong acid, ionizes as follows:

- **The first ionization is**

$$\mathbf{H_2SO_4}(aq) + \mathbf{H_2O}(l) \rightleftharpoons \mathbf{H_3O^+}(aq) + \mathbf{HSO_4^-}(aq)$$

with $K_{a1} > 10^2$; *complete dissociation*.

- **The second ionization is**

$$\mathbf{HSO_4^-}(aq) + \mathbf{H_2O}(l) \rightleftharpoons \mathbf{H_3O^+}(aq) + \mathbf{SO_4^{2-}}(aq)$$

with $K_{a2} = 1.2 \times 10^{-2}$.

This stepwise ionization process occurs for all polyprotic acids. When we make a solution of a weak diprotic acid, we get a solution that contains a mixture of acids. Carbonic acid, $\mathbf{H_2CO_3}$, is an example of a weak diprotic acid. The first ionization of carbonic acid yields hydronium ions and bicarbonate ions in small amounts.

- **First Ionization**

$$\mathbf{H_2CO_3}(aq) + \mathbf{H_2O}(l) \rightleftharpoons \mathbf{H_3O^+}(aq) + \mathbf{HCO_3^-}(aq)$$

with

$$K_{H_2CO_3} = \frac{[H3O+][HCO3-]}{[H2CO3]} = 4.3 \times 10^{-7}$$

The bicarbonate ion can also act as an acid. It ionizes and forms hydronium ions and carbonate ions in even smaller quantities.

- **Second Ionization**

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$$

with

$$K_{HCO_3^-} = \frac{[H3O+][CO3^2-]}{[HCO3-]} = 4.7 \times 10^{-11}$$

$K_{H_2CO_3}$ is larger than $K_{HCO_3^-}$ by a factor of 10^4, so H_2CO_3 is the dominant producer of hydronium ion in the solution. This means that little of the HCO_3^- formed by the ionization of H_2CO_3 ionizes to give hydronium ions (and carbonate ions), and the concentrations of H_3O^+ and HCO_3^- are practically equal in a pure aqueous solution of H_2CO_3.

If the first ionization constant of a weak diprotic acid is larger than the second by a factor of at least 20, it is appropriate to treat the first ionization separately and calculate concentrations resulting from it before calculating concentrations of species resulting from subsequent ionization. This can simplify our work considerably because we can determine the concentration of H_3O^+ and the conjugate base from the first ionization, then determine the concentration of the conjugate base of the second ionization in a solution with concentrations determined by the first ionization.

Example 9.4.1: Ionization of a Diprotic Acid

When we buy soda water (carbonated water), we are buying a solution of carbon dioxide in water. The solution is acidic because CO_2 reacts with water to form carbonic acid, H_2CO_3. What are $[H_3O^+]$, $[HCO_3^-]$, and $[CO_3^{2-}]$ in a saturated solution of CO_2 with an initial $[H_2CO_3] = 0.033\ M$?

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq) \quad K_{a1} = 4.3 \times 10^{-7} \qquad \text{(equilibrium step 1)}$$

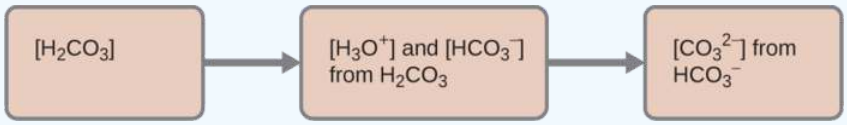
$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq) \quad K_{a2} = 4.7 \times 10^{-11} \qquad \text{(equilibrium step 2)}$$

Solution

As indicated by the ionization constants, H_2CO_3 is a much stronger acid than HCO_3^-, so H_2CO_3 is the dominant producer of hydronium ion in solution. Thus there are two parts in the solution of this problem:

1. Using the customary four steps, we determine the concentration of H_3O^+ and HCO_3^- produced by ionization of H_2CO_3.
2. Then we determine the concentration of CO_3^{2-} in a solution with the concentration of H_3O^+ and HCO_3^- determined in (1).

To summarize:



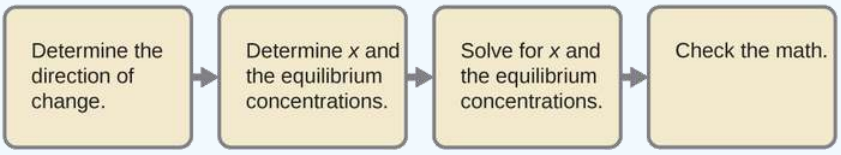
Four tan rectangles are shown that are connected with right pointing arrows. The first is labeled “left bracket H subscript 2 C O subscript 3 right bracket.” The second is labeled “left bracket H subscript 3 O superscript plus right bracket and left bracket H C O subscript 3 superscript negative right bracket from H subscript 2 C O subscript 3.” The third is labeled “left bracket C O subscript 3 superscript 2 negative right bracket from H C O subscript 3 superscript negative.”

1. First Ionization: Determine the concentrations of H_3O^+ *and* HCO_3^-.

Since equilibrium step 1 is has a much bigger $K_{a1} = 4.3 \times 10^{-7}$ than $K_{a2} = 4.7 \times 10^{-11}$ for equilibrium step 2, we can safely ignore the second ionization step and focus only on the first step (but address it in next part of problem).

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq) \quad K_{a1} = 4.3 \times 10^{-7}$$

As for the ionization of any other weak acid:



Four tan rectangles are shown that are connected with right pointing arrows. The first is labeled “Determine the direction of change.” The second is labeled “Determine x and the equilibrium concentrations.” The third is labeled “Solve for x and the equilibrium concentrations.” The fourth is labeled “Check the math.”

An abbreviated table of changes and concentrations shows:

Abbreviated table of changes and concentrations

ICE Table	$H_2CO_3(aq)$	$H_2O(l)$	$H_3O^+(aq)$	$HCO_3^-(aq)$
Initial (M)	$0.033\ M$	-	0	0
Change (M)	$-x$	-	$+x$	$+x$
Equilibrium (M)	$0.033\ M - x$	-	x	x

Substituting the equilibrium concentrations into the equilibrium constant gives us:

$$K_{H_2CO_3} = \frac{[H3O+][HCO3-]}{[H2CO3]} = \frac{(x)(x)}{0.033 - x} = 4.3 \times 10^{-7}$$

Solving the preceding equation making our standard assumptions gives:

$$x = 1.2 \times 10^{-4}$$

Thus:

$$[H_2CO_3] = 0.033\ M$$

$$[H_3O^+] = [HCO_3^-] = 1.2 \times 10^{-4}\ M$$

2. Second Ionization: Determine the concentration of CO_3^{2-} in a solution at equilibrium.

Since the equilibrium step 1 is has a much bigger K_a than equilibrium step 2, we can the equilibrium conditions calculated from first part of example as the initial conditions for an ICER Table for the equilibrium step 2:

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$$

ICER Table for the equilibrium step 2:

ICE Table	$HCO_3^-(aq)$	$H_2O(l)$	$H_3O^+(aq)$	$CO_3^{2-}(aq)$
Initial (M)	$1.2 \times 10^{-4}\ M$	-	$1.2 \times 10^{-4}\ M$	0
Change (M)	$-y$	-	$+y$	$+y$
Equilibrium (M)	$1.2 \times 10^{-4}\ M - y$	-	$1.2 \times 10^{-4}\ M + y$	y

$$K_{HCO_3^-} = \frac{[H3O+][CO3^2-]}{[HCO3-]} = \frac{(1.2 \times 10^{-4}\ M + y)(y)}{(1.2 \times 10^{-4}\ M - y)}$$

To avoid solving a quadratic equation, we can assume $y \ll 1.2 \times 10^{-4}\ M$ so

$$K_{HCO_3^-} = 4.7 \times 10^{-11} \approx \frac{(1.2 \times 10^{-4}\ M)(y)}{(1.2 \times 10^{-4}\ M)}$$

Rearranging to solve for y

$$y \approx \frac{(4.7 \times 10^{-11})(1.2 \times 10^{-4}\ M)}{1.2 \times 10^{-4}\ M}$$

$$[CO_3^{2-}] = y \approx 4.7 \times 10^{-11}$$

To summarize:

In part 1 of this example, we found that the H_2CO_3 in a 0.033-M solution ionizes slightly and at equilibrium $[H_2CO_3] = 0.033\ M$, $[H_3O^+] = 1.2 \times 10^{-4}$, and $[HCO_3^-] = 1.2 \times 10^{-4}\ M$. In part 2, we determined that $[CO_3^{2-}] = 5.6 \times 10^{-11}\ M$.

? Exercise 9.4.2: Hydrogen Sulfide

The concentration of H_2S in a saturated aqueous solution at room temperature is approximately 0.1 M. Calculate $[H_3O^+]$, $[HS^-]$, and $[S^{2-}]$ in the solution:

$$H_2S(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HS^-(aq) \quad K_{a1} = 8.9 \times 10^{-8}$$

$$HS^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + S^{2-}(aq) \quad K_{a2} = 1.0 \times 10^{-19}$$

Answer

$[H_2S] = 0.1M$, $[H_3O^+] = [HS^-] = 0.0001\ M$, $[S^{2-}] = 1 \times 10^{-19}\ M$

We note that the concentration of the sulfide ion is the same as K_{a2}. This is due to the fact that each subsequent dissociation occurs to a lesser degree (as acid gets weaker).

Triprotic Acids

A triprotic acid is an acid that has three dissociable protons that undergo stepwise ionization: Phosphoric acid is a typical example:

- **The first ionization is**

$$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_4^-(aq)$$

with $K_{a1} = 7.5 \times 10^{-3}$.

- **The second ionization is**

$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq)$$

with $K_{a2} = 6.2 \times 10^{-8}$.

- **The third ionization is**

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq)$$

with $K_{a3} = 4.2 \times 10^{-13}$.

As with the diprotic acids, the differences in the ionization constants of these reactions tell us that in each successive step the degree of ionization is significantly weaker. This is a general characteristic of polyprotic acids and successive ionization constants often differ by a factor of about 10^5 to 10^6. This set of three dissociation reactions may appear to make calculations of equilibrium concentrations in a solution of H_3PO_4 complicated. However, because the successive ionization constants differ by a factor of 10^5 to 10^6, the calculations can be broken down into a series of parts similar to those for diprotic acids.

Polyprotic bases can accept more than one hydrogen ion in solution. The carbonate ion is an example of a diprotic base, since it can accept up to two protons. Solutions of alkali metal carbonates are quite alkaline, due to the reactions:

$$H_2O(l) + CO_3^{2-}(aq) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$$

and

$$\mathrm{H_2O}(l) + \mathrm{HCO_3^-}(aq) \rightleftharpoons \mathrm{H_2CO_3}(aq) + \mathrm{OH^-}(aq)$$

Summary

An acid that contains more than one ionizable proton is a polyprotic acid. The protons of these acids ionize in steps. The differences in the acid ionization constants for the successive ionizations of the protons in a polyprotic acid usually vary by roughly five orders of magnitude. As long as the difference between the successive values of K_a of the acid is greater than about a factor of 20, it is appropriate to break down the calculations of the concentrations of the ions in solution into a series of steps.

Glossary

diprotic acid

acid containing two ionizable hydrogen atoms per molecule. A diprotic acid ionizes in two steps

diprotic base

base capable of accepting two protons. The protons are accepted in two steps

monoprotic acid

acid containing one ionizable hydrogen atom per molecule

stepwise ionization

process in which an acid is ionized by losing protons sequentially

triprotic acid

acid that contains three ionizable hydrogen atoms per molecule; ionization of triprotic acids occurs in three steps

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9.5: Buffers

Learning Objectives

- Describe the composition and function of acid–base buffers
- Calculate the pH of a buffer before and after the addition of added acid or base

A mixture of a weak acid and its conjugate base (or a mixture of a weak base and its conjugate acid) is called a buffer solution, or a buffer. Buffer solutions resist a change in pH when small amounts of a strong acid or a strong base are added (Figure 9.5.1). A solution of acetic acid (CH_3COOH and sodium acetate CH_3COONa) is an example of a buffer that consists of a weak acid and its salt. An example of a buffer that consists of a weak base and its salt is a solution of ammonia ($NH_3(aq)$) and ammonium chloride ($NH_4Cl(aq)$).



Figure 9.5.1: (a) The unbuffered solution on the left and the buffered solution on the right have the same pH (pH 8); they are basic, showing the yellow color of the indicator methyl orange at this pH. (b) After the addition of 1 mL of a 0.01-M HCl solution, the buffered solution has not detectably changed its pH but the unbuffered solution has become acidic, as indicated by the change in color of the methyl orange, which turns red at a pH of about 4. (credit: modification of work by Mark Ott)

How Buffers Work

A mixture of acetic acid and sodium acetate is acidic because the K_a of acetic acid is greater than the K_b of its conjugate base acetate. It is a buffer because it contains both the weak acid and its salt. Hence, it acts to keep the hydronium ion concentration (and the pH) almost constant by the addition of either a small amount of a strong acid or a strong base. If we add a base such as sodium hydroxide, the hydroxide ions react with the few hydronium ions present. Then more of the acetic acid reacts with water, restoring the hydronium ion concentration almost to its original value:

$$CH_3CO_2H(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + CH_3CO_2^-(aq)$$

The pH changes very little. If we add an acid such as hydrochloric acid, most of the hydronium ions from the hydrochloric acid combine with acetate ions, forming acetic acid molecules:

$$H_3O^+(aq) + CH_3CO_2^-(aq) \longrightarrow CH_3CO_2H(aq) + H_2O(l)$$

Thus, there is very little increase in the concentration of the hydronium ion, and the pH remains practically unchanged (Figure 9.5.2).

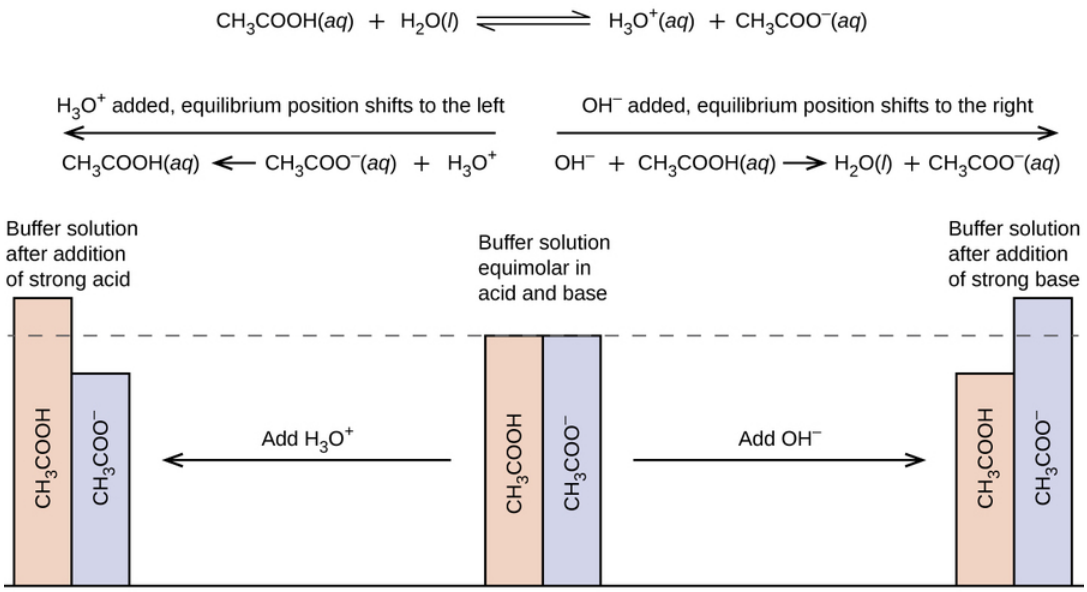


Figure **9.5.2**: This diagram shows the buffer action of these reactions.

A mixture of ammonia and ammonium chloride is basic because the K_b for ammonia is greater than the K_a for the ammonium ion. It is a buffer because it also contains the salt of the weak base. If we add a base (hydroxide ions), ammonium ions in the buffer react with the hydroxide ions to form ammonia and water and reduce the hydroxide ion concentration almost to its original value:

$$\mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq) \longrightarrow \mathrm{NH_3}(aq) + \mathrm{H_2O}(l)$$

If we add an acid (hydronium ions), ammonia molecules in the buffer mixture react with the hydronium ions to form ammonium ions and reduce the hydronium ion concentration almost to its original value:

$$\mathrm{H_3O^+}(aq) + \mathrm{NH_3}(aq) \longrightarrow \mathrm{NH_4^+}(aq) + \mathrm{H_2O}(l)$$

The three parts of the following example illustrate the change in pH that accompanies the addition of base to a buffered solution of a weak acid and to an unbuffered solution of a strong acid.

Example 9.5.1: pH Changes in Buffered and Unbuffered Solutions

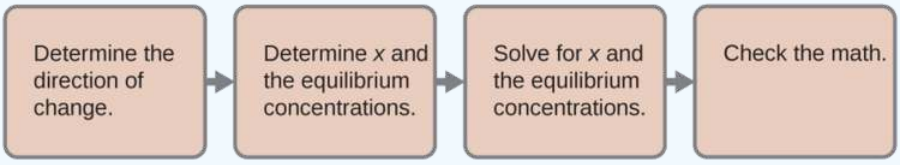
Acetate buffers are used in biochemical studies of enzymes and other chemical components of cells to prevent pH changes that might change the biochemical activity of these compounds.

a. Calculate the pH of an acetate buffer that is a mixture with 0.10 *M* acetic acid and 0.10 *M* sodium acetate.
b. Calculate the pH after 1.0 mL of 0.10 *M* NaOH is added to 100 mL of this buffer, giving a solution with a volume of 101 mL.

Solution

a. Calculate the pH of an acetate buffer that is a mixture with 0.10 *M* acetic acid and 0.10 *M* sodium acetate.

To determine the pH of the buffer solution we use a typical equilibrium calculation (as illustrated in earlier Examples):



1. *Determine the direction of change.* The equilibrium in a mixture of H_3O^+, $\mathrm{CH_3CO_2^-}$, and CH_3CO_2H is:

$$\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CH_3CO_2^-}(aq)$$

The equilibrium constant for CH_3CO_2H is not given, so we look it up in Table E1: $K_a = 1.8 \times 10^{-5}$. With $[CH_3CO_2H] = [CH_3CO_2^-] = 0.10\ M$ and $[H_3O^+] = \sim 0\ M$, the reaction shifts to the right to form H_3O^+.

2. *Determine* x *and equilibrium concentrations*. A table of changes and concentrations follows:

	$[CH_3CO_2H] + [H_2O] \rightleftharpoons H_3O^+ + [CH_3CO_2^-]$		
Initial concentration (*M*)	0.10	~0	0.10
Change (*M*)	$-x$	x	x
Equilibrium constant (*M*)	$0.10 - x$	x	$0.10 + x$

- *Solve for x and the equilibrium concentrations.* We find:

$$x = 1.8 \times 10^{-5}\ M$$

- and

$$[H_3O^+] = 0 + x = 1.8 \times 10^{-5}\ M$$

Thus:

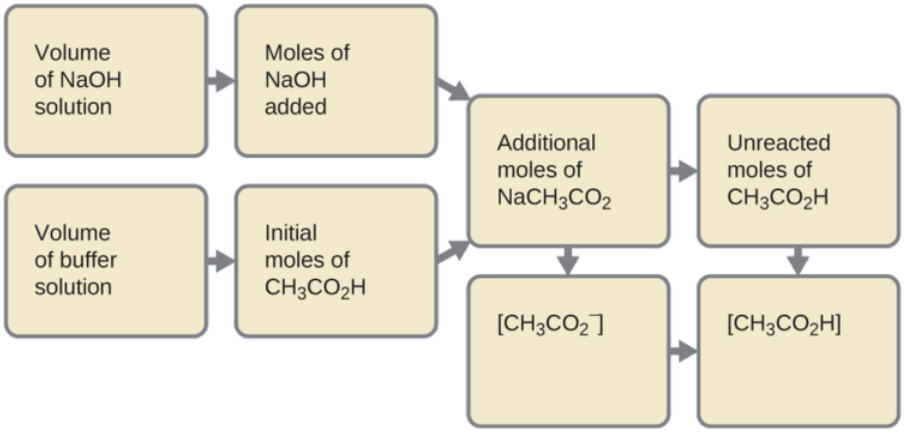
$$pH = -\log[H_3O^+] = -\log(1.8 \times 10^{-5})$$

$$= 4.74$$

4. *Check the work*. If we calculate all calculated equilibrium concentrations, we find that the equilibrium value of the reaction coefficient, $Q = K_a$.

(b) Calculate the pH after 1.0 mL of 0.10 *M* NaOH is added to 100 mL of this buffer, giving a solution with a volume of 101 mL.

First, we calculate the concentrations of an intermediate mixture resulting from the complete reaction between the acid in the buffer and the added base. Then we determine the concentrations of the mixture at the new equilibrium:



1. *Determine the moles of NaOH*. One milliliter (0.0010 L) of 0.10 *M* NaOH contains:

$$0.0010\,\cancel{L} \times \left(\frac{0.10\ \text{mol NaOH}}{1\,\cancel{L}}\right) = 1.0 \times 10^{-4}\ \text{mol NaOH}$$

2. *Determine the moles of CH_2CO_2H*. Before reaction, 0.100 L of the buffer solution contains:

$$0.100\,\cancel{L} \times \left(\frac{0.100\ \text{mol } CH_3CO_2H}{1\,\cancel{L}}\right) = 1.00 \times 10^{-2}\ \text{mol } CH_3CO_2H$$

3. *Solve for the amount of $NaCH_3CO_2$ produced.* The 1.0×10^{-4} mol of NaOH neutralizes 1.0×10^{-4} mol of CH_3CO_2H, leaving:

$$(1.0 \times 10^{-2}) - (0.01 \times 10^{-2}) = 0.99 \times 10^{-2} \text{ mol } CH_3CO_2H$$

and producing 1.0×10^{-4} mol of $NaCH_3CO_2$. This makes a total of:

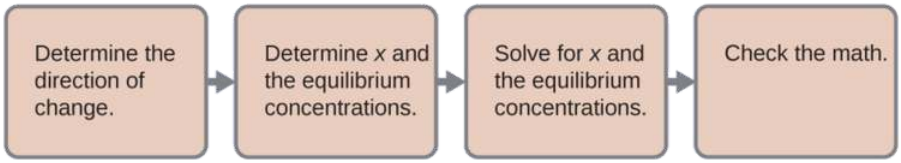
[\mathrm{(1.0×10^{−2})+(0.01×10^{−2})=1.01×10^{−2}\:mol\:NaCH_3CO_2} \nonumber \]

4. *Find the molarity of the products.* After reaction, CH_3CO_2H and $NaCH_3CO_2$ are contained in 101 mL of the intermediate solution, so:

$$[CH_3CO_2H] = \frac{9.9 \times 10^{-3} \text{ mol}}{0.101 \text{ L}} = 0.098\ M$$

$$[NaCH_3CO_2] = \frac{1.01 \times 10^{-2} \text{ mol}}{0.101 \text{ L}} = 0.100\ M$$

Now we calculate the pH after the intermediate solution, which is 0.098 *M* in CH_3CO_2H and 0.100 *M* in $NaCH_3CO_2$, comes to equilibrium. The calculation is very similar to that in part (a) of this example:



This series of calculations gives a pH = 4.75. Thus the addition of the base barely changes the pH of the solution.

(c) For comparison, calculate the pH after 1.0 mL of 0.10 *M* NaOH is added to 100 mL of a solution of an unbuffered solution with a pH of 4.74 (a 1.8×10^{-5}-*M* solution of HCl). The volume of the final solution is 101 mL.

Solution

This 1.8×10^{-5}-*M* solution of HCl has the same hydronium ion concentration as the 0.10-*M* solution of acetic acid-sodium acetate buffer described in part (a) of this example. The solution contains:

$$0.100 \text{ L} \times \left(\frac{1.8 \times 10^{-5} \text{ mol HCl}}{1 \text{ L}} \right) = 1.8 \times 10^{-6} \text{ mol HCl}$$

As shown in part (b), 1 mL of 0.10 *M* NaOH contains 1.0×10^{-4} mol of NaOH. When the NaOH and HCl solutions are mixed, the HCl is the limiting reagent in the reaction. All of the HCl reacts, and the amount of NaOH that remains is:

$$(1.0 \times 10^{-4}) - (1.8 \times 10^{-6}) = 9.8 \times 10^{-5}\ M$$

The concentration of NaOH is:

$$\frac{9.8 \times 10^{-5}\ M \text{ NaOH}}{0.101 \text{ L}} = 9.7 \times 10^{-4}\ M$$

The pOH of this solution is:

$$\text{pOH} = -\log[OH^-] = -\log(9.7 \times 10^{-4}) = 3.01$$

The pH is:

$$\text{pH} = 14.00 - \text{pOH} = 10.99$$

The pH changes from 4.74 to 10.99 in this unbuffered solution. This compares to the change of 4.74 to 4.75 that occurred when the same amount of NaOH was added to the buffered solution described in part (b).

? Exercise 9.5.1

Show that adding 1.0 mL of 0.10 *M* HCl changes the pH of 100 mL of a 1.8×10^{-5} *M* HCl solution from 4.74 to 3.00.

Answer

Initial pH of 1.8×10^{-5} *M* HCl; pH = $-\log[H_3O^+] = -\log[1.8 \times 10^{-5}] = 4.74$

Moles of H_3O^+ added by addition of 1.0 mL of 0.10 *M* HCl: 0.10 moles/L × 0.0010 L = 1.0×10^{-4} moles; final pH after addition of 1.0 mL of 0.10 *M* HCl:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log\left(\frac{\text{total moles H}_3\text{O}^+}{\text{total volume}}\right) = -\log\left(\frac{1.0 \times 10^{-4}\ \text{mol} + 1.8 \times 10^{-6}\ \text{mol}}{101\ \text{mL}\left(\frac{1\ \text{L}}{1000\ \text{mL}}\right)}\right) = 3.00$$

Buffer Capacity

Buffer solutions do not have an unlimited capacity to keep the pH relatively constant (Figure **9.5.3**). If we add so much base to a buffer that the weak acid is exhausted, no more buffering action toward the base is possible. On the other hand, if we add an excess of acid, the weak base would be exhausted, and no more buffering action toward any additional acid would be possible. In fact, we do not even need to exhaust all of the acid or base in a buffer to overwhelm it; its buffering action will diminish rapidly as a given component nears depletion.



Figure **9.5.3**: The indicator color (methyl orange) shows that a small amount of acid added to a buffered solution of pH 8 (beaker on the left) has little affect on the buffered system (middle beaker). However, a large amount of acid exhausts the buffering capacity of the solution and the pH changes dramatically (beaker on the right). (credit: modification of work by Mark Ott)

The buffer capacity is the amount of acid or base that can be added to a given volume of a buffer solution before the pH changes significantly, usually by one unit. Buffer capacity depends on the amounts of the weak acid and its conjugate base that are in a buffer mixture. For example, 1 L of a solution that is 1.0 *M* in acetic acid and 1.0 *M* in sodium acetate has a greater buffer capacity than 1 L of a solution that is 0.10 *M* in acetic acid and 0.10 *M* in sodium acetate even though both solutions have the same pH. The first solution has more buffer capacity because it contains more acetic acid and acetate ion.

Selection of Suitable Buffer Mixtures

There are two useful rules of thumb for selecting buffer mixtures:

1. A good buffer mixture should have about equal concentrations of both of its components. A buffer solution has generally lost its usefulness when one component of the buffer pair is less than about 10% of the other. Figure **9.5.4** shows an acetic acid-acetate ion buffer as base is added. The initial pH is 4.74. A change of 1 pH unit occurs when the acetic acid concentration is reduced to 11% of the acetate ion concentration.

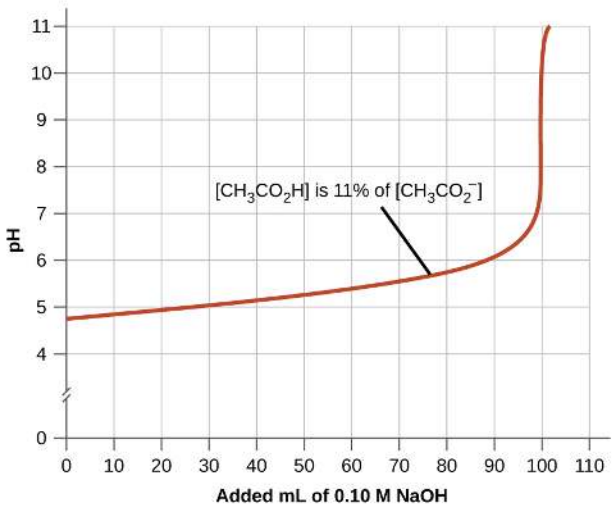


Figure **9.5.4**: The graph, an illustration of buffering action, shows change of pH as an increasing amount of a 0.10-M NaOH solution is added to 100 mL of a buffer solution in which, initially, $[CH_3CO_2H] = 0.10\ M$ and $[CH_3CO_2^-] = 0.10\ M$.

2. Weak acids and their salts are better as buffers for pHs less than 7; weak bases and their salts are better as buffers for pHs greater than 7.

Blood is an important example of a buffered solution, with the principal acid and ion responsible for the buffering action being carbonic acid, H_2CO_3, and the bicarbonate ion, HCO_3^-. When an excess of hydrogen ion enters the blood stream, it is removed primarily by the reaction:

$$H_3O^+(aq) + HCO_3^-(aq) \longrightarrow H_2CO_3(aq) + H_2O(l)$$

When an excess of the hydroxide ion is present, it is removed by the reaction:

$$OH^-(aq) + H_2CO_3(aq) \longrightarrow HCO_3^-(aq) + H_2O(l)$$

The pH of human blood thus remains very near 7.35, that is, slightly basic. Variations are usually less than 0.1 of a pH unit. A change of 0.4 of a pH unit is likely to be fatal.

The Henderson-Hasselbalch Approximation

The ionization-constant expression for a solution of a weak acid can be written as:

$$K_a = \frac{[H3O+][A-]}{[HA]}$$

Rearranging to solve for $[H_3O^+]$, we get:

$$[H_3O^+] = K_a \times \frac{[HA]}{[A-]}$$

Taking the negative logarithm of both sides of this equation, we arrive at:

$$-\log[H_3O^+] = -\log K_a - \log\frac{[HA]}{[A^-]}$$

which can be written as

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

where pK_a is the negative of the common logarithm of the ionization constant of the weak acid ($pK_a = -\log K_a$). This equation relates the pH, the ionization constant of a weak acid, and the concentrations of the weak acid and its salt in a buffered solution. Scientists often use this expression, called the Henderson-Hasselbalch approximation, to calculate the pH of buffer solutions. It is important to note that the "x is small" assumption must be valid to use this equation.

Lawrence Joseph Henderson and Karl Albert Hasselbalch

Lawrence Joseph Henderson (1878–1942) was an American physician, biochemist and physiologist, to name only a few of his many pursuits. He obtained a medical degree from Harvard and then spent 2 years studying in Strasbourg, then a part of Germany, before returning to take a lecturer position at Harvard. He eventually became a professor at Harvard and worked there his entire life. He discovered that the acid-base balance in human blood is regulated by a buffer system formed by the dissolved carbon dioxide in blood. He wrote an equation in 1908 to describe the carbonic acid-carbonate buffer system in blood. Henderson was broadly knowledgeable; in addition to his important research on the physiology of blood, he also wrote on the adaptations of organisms and their fit with their environments, on sociology and on university education. He also founded the Fatigue Laboratory, at the Harvard Business School, which examined human physiology with specific focus on work in industry, exercise, and nutrition.

In 1916, Karl Albert Hasselbalch (1874–1962), a Danish physician and chemist, shared authorship in a paper with Christian Bohr in 1904 that described the Bohr effect, which showed that the ability of hemoglobin in the blood to bind with oxygen was inversely related to the acidity of the blood and the concentration of carbon dioxide. The pH scale was introduced in 1909 by another Dane, Sørensen, and in 1912, Hasselbalch published measurements of the pH of blood. In 1916, Hasselbalch expressed Henderson's equation in logarithmic terms, consistent with the logarithmic scale of pH, and thus the Henderson-Hasselbalch equation was born.

Medicine: The Buffer System in Blood

The normal pH of human blood is about 7.4. The carbonate buffer system in the blood uses the following equilibrium reaction:

$$\mathrm{CO_2}(g) + 2\,\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2CO_3}(aq) \rightleftharpoons \mathrm{HCO_3^-}(aq) + \mathrm{H_3O^+}(aq)$$

The concentration of carbonic acid, H_2CO_3 is approximately 0.0012 *M*, and the concentration of the hydrogen carbonate ion, $\mathbf{HCO_3^-}$, is around 0.024 *M*. Using the Henderson-Hasselbalch equation and the pK_a of carbonic acid at body temperature, we can calculate the pH of blood:

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\text{base}]}{[\text{acid}]} = 6.1 + \log\frac{0.024}{0.0012} = 7.4$$

The fact that the H_2CO_3 concentration is significantly lower than that of the $\mathbf{HCO_3^-}$ ion may seem unusual, but this imbalance is due to the fact that most of the by-products of our metabolism that enter our bloodstream are acidic. Therefore, there must be a larger proportion of base than acid, so that the capacity of the buffer will not be exceeded.

Lactic acid is produced in our muscles when we exercise. As the lactic acid enters the bloodstream, it is neutralized by the $\mathbf{HCO_3^-}$ ion, producing H_2CO_3. An enzyme then accelerates the breakdown of the excess carbonic acid to carbon dioxide and water, which can be eliminated by breathing. In fact, in addition to the regulating effects of the carbonate buffering system on the pH of blood, the body uses breathing to regulate blood pH. If the pH of the blood decreases too far, an increase in breathing removes CO_2 from the blood through the lungs driving the equilibrium reaction such that $[H_3O^+]$ is lowered. If the blood is too alkaline, a lower breath rate increases CO_2 concentration in the blood, driving the equilibrium reaction the other way, increasing $[H^+]$ and restoring an appropriate pH.

Summary

A solution containing a mixture of an acid and its conjugate base, or of a base and its conjugate acid, is called a buffer solution. Unlike in the case of an acid, base, or salt solution, the hydronium ion concentration of a buffer solution does not change greatly when a small amount of acid or base is added to the buffer solution. The base (or acid) in the buffer reacts with the added acid (or base).

Key Equations

- $pK_a = -\log K_a$
- $pK_b = -\log K_b$
- $\mathrm{pH} = pK_a + \log \frac{[A^-]}{[HA]}$

Glossary

buffer capacity

amount of an acid or base that can be added to a volume of a buffer solution before its pH changes significantly (usually by one pH unit)

buffer

mixture of a weak acid or a weak base and the salt of its conjugate; the pH of a buffer resists change when small amounts of acid or base are added

Henderson-Hasselbalch equation

equation used to calculate the pH of buffer solutions

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9.6: Acid-Base Titrations

Learning Objectives

- Interpret titration curves for strong and weak acid-base systems
- Compute sample pH at important stages of a titration
- Explain the function of acid-base indicators

As seen in the chapter on the stoichiometry of chemical reactions, titrations can be used to quantitatively analyze solutions for their acid or base concentrations. In this section, we will explore the changes in the concentrations of the acidic and basic species present in a solution during the process of a titration.

Titration Curves

Previously, when we studied acid-base reactions in solution, we focused only on the point at which the acid and base were stoichiometrically equivalent. No consideration was given to the pH of the solution before, during, or after the neutralization.

Example 9.6.1: Calculating pH for Titration Solutions: Strong Acid/Strong Base

A titration is carried out for 25.00 mL of 0.100 *M* HCl (strong acid) with 0.100 *M* of a strong base NaOH the titration curve is shown in Figure **9.6.1**. Calculate the pH at these volumes of added base solution:

a. 0.00 mL
b. 12.50 mL
c. 25.00 mL
d. 37.50 mL

Solution

Since HCl is a strong acid, we can assume that all of it dissociates. The initial concentration of H_3O^+ is $[\mathbf{H_3O^+}]_0 = 0.100\ M$. When the base solution is added, it also dissociates completely, providing OH^- ions. The H_3O^+ and OH^- ions neutralize each other, so only those of the two that were in excess remain, and their concentration determines the pH. Thus, the solution is initially acidic (pH < 7), but eventually all the hydronium ions present from the original acid are neutralized, and the solution becomes neutral. As more base is added, the solution turns basic.

The total initial amount of the hydronium ions is:

$$\mathbf{n(H^+)_0 = [H_3O^+]_0 \times 0.02500\ L = 0.002500\ mol}$$

Once X mL of the 0.100-*M* base solution is added, the number of moles of the OH^- ions introduced is:

$$\mathbf{n(OH^-)_0} = 0.100\ M \times \mathbf{X\ mL} \times \left(\frac{\mathbf{1\ L}}{\mathbf{1000\ mL}}\right)$$

The total volume becomes:

$$V = (\mathbf{25.00\ mL + X\ mL})\left(\frac{\mathbf{1\ L}}{\mathbf{1000\ mL}}\right)$$

The number of moles of H_3O^+ becomes:

$$\mathbf{n(H^+) = n(H^+)_0 - n(OH^-)_0 = 0.002500\ mol} - 0.100\ M \times \mathbf{X\ mL} \times \left(\frac{\mathbf{1\ L}}{\mathbf{1000\ mL}}\right)$$

The concentration of H_3O^+ is:

$$[\mathbf{H_3O^+}] = \frac{\mathbf{n(H^+)}}{\mathbf{V}} = \frac{\mathbf{0.002500\ mol} - 0.100\ M \times \mathbf{X\ mL} \times \left(\frac{\mathbf{1\ L}}{\mathbf{1000\ mL}}\right)}{(\mathbf{25.00\ mL + X\ mL})\left(\frac{\mathbf{1\ L}}{\mathbf{1000\ mL}}\right)}$$

$$= \frac{0.002500\ \text{mol} \times \left(\frac{1000\ \text{mL}}{1\ \text{L}}\right) - 0.100\ M \times \text{X mL}}{25.00\ \text{mL} + \text{X mL}}$$

with the definition of $\mathbf{pH}$:

$$\text{pH} = -\log([\text{H}_3\text{O}^+]) \tag{9.6.1}$$

The preceding calculations work if $\text{n}(\text{H}^+)_0 - \text{n}(\text{OH}^-)_0 > 0$ and so n(H^+) > 0. When $\text{n}(\text{H}^+)_0 = \text{n}(\text{OH}^-)_0$, the H_3O^+ ions from the acid and the OH^- ions from the base mutually neutralize. At this point, the only hydronium ions left are those from the autoionization of water, and there are no OH^- particles to neutralize them. Therefore, in this case:

$$[\text{H}_3\text{O}^+] = [\text{OH}^-\ ],\ [\text{H}_3\text{O}^+] = K_\text{w} = 1.0 \times 10^{-14};\ [\text{H}_3\text{O}^+] = 1.0 \times 10^{-7}$$

$$\text{pH} = -\log(1.0 \times 10^{-7}) = 7.00$$

Finally, when $\text{n}(\text{OH}^-)_0 > \text{n}(\text{H}^+)_0$, there are not enough H_3O^+ ions to neutralize all the OH^- ions, and instead of $\text{n}(\text{H}^+) = \text{n}(\text{H}^+)_0 - \text{n}(\text{OH}^-)_0$, we calculate: $\text{n}(\text{OH}^-) = \text{n}(\text{OH}^-)_0 - \text{n}(\text{H}^+)_0$

In this case:

$$[\text{OH}^-] = \frac{\text{n}(\text{OH}^-)}{V} = \frac{0.100\ M \times \text{X mL} \times \left(\frac{1\ \text{L}}{1000\ \text{mL}}\right) - 0.002500\ \text{mol}}{(25.00\ \text{mL} + \text{X mL})\left(\frac{1\ \text{L}}{1000\ \text{mL}}\right)}$$

$$= \frac{0.100\ M \times \text{X mL} - 0.002500\ \text{mol} \times \left(\frac{1000\ \text{mL}}{1\ \text{L}}\right)}{25.00\ \text{mL} + \text{X mL}}$$

then using the definition of pOH and its relationship to pH in room temperature aqueous solutios (Equation 9.6.1):

$$\begin{aligned} pH &= 14 - pOH \\ &= 14 + \log([OH^-]) \end{aligned}$$

Let us now consider the four specific cases presented in this problem:

(a) X = 0 mL

$$[\text{H}_3\text{O}^+] = \frac{\text{n}(\text{H}^+)}{V} = \frac{0.002500\ \text{mol} \times \left(\frac{1000\ \text{mL}}{1\ \text{L}}\right)}{25.00\ \text{mL}} = 0.1\ M$$

then using the definition of pH (Equation 9.6.1):

$$\begin{aligned} pH &= -\log(0.100) \\ &= 1.000 \end{aligned}$$

(b) X = 12.50 mL

$$[\text{H}_3\text{O}^+] = \frac{\text{n}(\text{H}^+)}{V} = \frac{0.002500\ \text{mol} \times \left(\frac{1000\ \text{mL}}{1\ \text{L}}\right) - 0.100\ M \times 12.50\ \text{mL}}{25.00\ \text{mL} + 12.50\ \text{mL}} = 0.0333\ M$$

then using the definition of pH (Equation 9.6.1):

$$\begin{aligned} pH &= -\log(0.0333) \\ &= 1.477 \end{aligned}$$

(c) X = 25.00 mL

Since the volumes and concentrations of the acid and base solutions are the same:

$$\text{n}(\text{H}^+)_0 = \text{n}(\text{OH}^-)_0$$

and

$$pH = 7.000$$

as described earlier.

(d) X = 37.50 mL

In this case:

$$\mathrm{n(OH^-)_0 > n(H^+)_0}$$

$$[\mathrm{OH^-}] = \frac{\mathrm{n(OH^-)}}{V} = \frac{0.100\ M \times 35.70\ \mathrm{mL} - 0.002500\ \mathrm{mol} \times \left(\frac{1000\ \mathrm{mL}}{1\ \mathrm{L}}\right)}{25.00\ \mathrm{mL} + 37.50\ \mathrm{mL}} = 0.0200\ M$$

then using the definition of pH (Equation 9.6.1):

$$\begin{aligned} [pH &= 14 - pOH \\ &= 14 + \log([OH^-]) \\ &= 14 + \log(0.0200) \\ &= 12.30 \end{aligned}$$

Exercise 9.6.1

Calculate the pH for the strong acid/strong base titration between 50.0 mL of 0.100 *M* $HNO_3(aq)$ and 0.200 *M* NaOH (titrant) at the listed volumes of added base:

a. 0.00 mL,
b. 15.0 mL,
c. 25.0 mL, and
d. 40.0 mL.

Answer a

0.00: 1.000

Answer b

15.0: 1.5111

Answer c

25.0: 7e. Do not delete this text first.

Answer d

40.0: 12.523

In Example **9.6.1**, we calculated pH at four points during a titration. Table **9.6.1** shows a detailed sequence of changes in the pH of a strong acid and a weak acid in a titration with NaOH.

Table **9.6.1**: pH Values in the Titrations of a Strong Acid with a Strong Base and of a Weak Acid with a Strong Base

Volume of 0.100 M NaOH Added (mL)	Moles of NaOH Added	pH Values 0.100 M HCl[1]	pH Values 0.100 M CH_3CO_2H[2]
0.0	0.0	1.00	2.87
5.0	0.00050	1.18	4.14
10.0	0.00100	1.37	4.57
15.0	0.00150	1.60	4.92
20.0	0.00200	1.95	5.35
22.0	0.00220	2.20	5.61
24.0	0.00240	2.69	6.13
24.5	0.00245	3.00	6.44
24.9	0.00249	3.70	7.14
25.0	0.00250	7.00	8.72
25.1	0.00251	10.30	10.30
25.5	0.00255	11.00	11.00
26.0	0.00260	11.29	11.29
28.0	0.00280	11.75	11.75
30.0	0.00300	11.96	11.96
35.0	0.00350	12.22	12.22
40.0	0.00400	12.36	12.36
45.0	0.00450	12.46	12.46
50.0	0.00500	12.52	12.52

1. Titration of 25.00 mL of 0.100 *M* HCl (0.00250 mol of HCI) with 0.100 *M* NaOH.
2. Titration of 25.00 mL of 0.100 *M* CH_3CO_2H (0.00250 mol of CH_3CO_2H) with 0.100 *M* NaOH.

The simplest acid-base reactions are those of a strong acid with a strong base. Table **9.6.1** shows data for the titration of a 25.0-mL sample of 0.100 *M* hydrochloric acid with 0.100 *M* sodium hydroxide. The values of the pH measured after successive additions of small amounts of NaOH are listed in the first column of this table, and are graphed in Figure **9.6.1**, in a form that is called a titration curve. The pH increases slowly at first, increases rapidly in the middle portion of the curve, and then increases slowly again. The point of inflection (located at the midpoint of the vertical part of the curve) is the equivalence point for the titration. It indicates when equivalent quantities of acid and base are present. For the titration of a strong acid with a strong base, the equivalence point occurs at a pH of 7.00 and the points on the titration curve can be calculated using solution stoichiometry (Table **9.6.1** and Figure **9.6.1**).

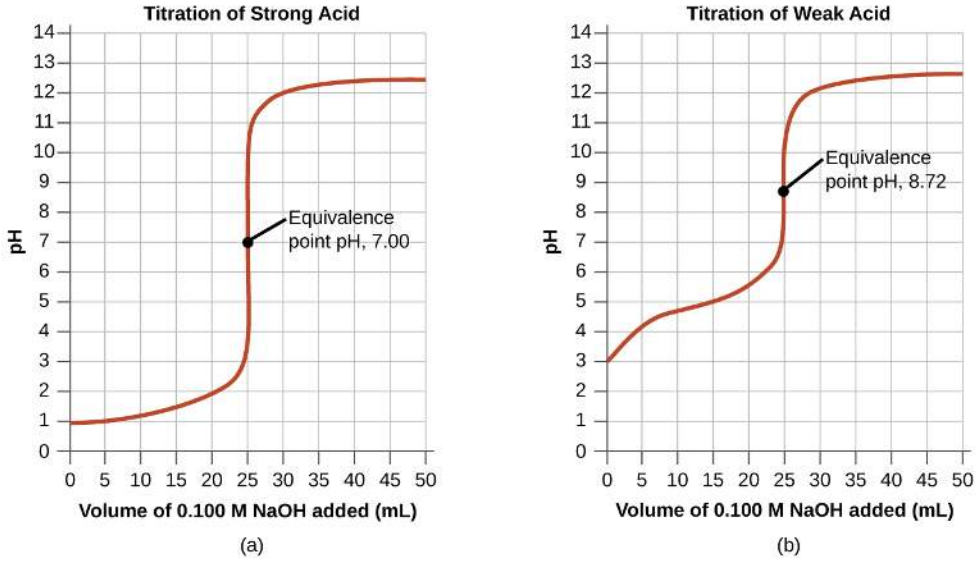


Figure **9.6.1**: (a) The titration curve for the titration of 25.00 mL of 0.100 M HCl (strong acid) with 0.100 M NaOH (strong base) has an equivalence point of 7.00 pH. (b) The titration curve for the titration of 25.00 mL of 0.100 M CH_3CO_2H (weak acid) with 0.100 M NaOH (strong base) has an equivalence point of 8.72 pH.

Two graphs are shown. The first graph on the left is titled “Titration of Weak Acid.” The horizontal axis is labeled “Volume of 0.100 M N a O H added (m L).” Markings and vertical gridlines are provided every 5 units from 0 to 50. The vertical axis is labeled “p H” and is marked every 1 unis beginning at 0 extending to 14. A red curve is drawn on the graph which increases steadily from the point (0, 3) up to about (20, 5.5) after which the graph has a vertical section from (25, 7) up to (25, 11). The graph then levels off to a value of about 12.5 from about 40 m L up to 50 m L. The midpoint of the vertical segment of the curve is labeled “Equivalence point p H, 8.72.” The second graph on the right is titled “Titration of Strong Acid.” The horizontal axis is labeled “Volume of 0.100 M N a O H added (m L).” Markings and vertical gridlines are provided every 5 units from 0 to 50. The vertical axis is labeled “p H” and is marked every 1 units beginning at 0 extending to 14. A red curve is drawn on the graph which increases gradually from the point (0, 1) up to about (22.5, 2.2) after which the graph has a vertical section from (25, 4) up to nearly (25, 11). The graph then levels off to a value of about 12.4 from about 40 m L up to 50 m L. The midpoint of the vertical segment of the curve is labeled “Equivalence point p H, 7.00.”

The titration of a weak acid with a strong base (or of a weak base with a strong acid) is somewhat more complicated than that just discussed, but it follows the same general principles. Let us consider the titration of 25.0 mL of 0.100 *M* acetic acid (a weak acid) with 0.100 *M* sodium hydroxide and compare the titration curve with that of the strong acid. Table **9.6.1** gives the pH values during the titration, Figure **9.6.1***b* shows the titration curve.

Although the initial volume and molarity of the acids are the same, there are important differences between the two titration curves. The titration curve for the weak acid begins at a higher value (less acidic) and maintains higher pH values up to the equivalence point. This is because acetic acid is a weak acid, which is only partially ionized. The pH at the equivalence point is also higher (8.72 rather than 7.00) due to the hydrolysis of acetate, a weak base that raises the pH:

$$\mathrm{CH_3CO_2^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{CH_3CO_2H}(l) + \mathrm{OH^-}(aq)$$

After the equivalence point, the two curves are identical because the pH is dependent on the excess of hydroxide ion in both cases.

✔ Example **9.6.2**: Titration of a Weak Acid with a Strong Base

The titration curve shown in Figure **9.6.1***b* is for the titration of 25.00 mL of 0.100 *M* CH_3CO_2H with 0.100 *M* NaOH. The reaction can be represented as:

$$\mathrm{CH_3CO_2H + OH^- \longrightarrow CH_3CO_2^- + H_2O}$$

a. What is the initial pH before any amount of the NaOH solution has been added? $K_a = 1.8 \times 10^{-5}$ for CH_3CO_2H.
b. Find the pH after 25.00 mL of the NaOH solution have been added.
c. Find the pH after 12.50 mL of the NaOH solution has been added.
d. Find the pH after 37.50 mL of the NaOH solution has been added.

Solution

(a) Assuming that the dissociated amount is small compared to 0.100 *M*, we find that:

$$K_a = \frac{[H3O+][CH3CO2-]}{[CH3CO2H]} \approx \frac{[H3O+]^2}{[CH3CO2H]_0}$$

and

$$[H_3O^+] = \sqrt{K_a \times [CH_3CO_2H]} = \sqrt{1.8 \times 10^{-5} \times 0.100} = 1.3 \times 10^{-3}$$

$$pH = -\log(1.3 \times 10^{-3}) = 2.87$$

(b) After 25.00 mL of NaOH are added, the number of moles of NaOH and CH_3CO_2H are equal because the amounts of the solutions and their concentrations are the same. All of the CH_3CO_2H has been converted to $CH_3CO_2^-$. The concentration of the $CH_3CO_2^-$ ion is:

$$\frac{0.00250\ \text{mol}}{0.0500\ \text{L}} = 0.0500\ \text{M} CH_3CO_2^-$$

The equilibrium that must be focused on now is the basicity equilibrium for $CH_3CO_2^-$:

$$CH_3CO_2^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq)$$

so we must determine K_b for the base by using the ion product constant for water:

$$K_b = \frac{[CH3CO2H][OH-]}{[CH3CO2-]}$$

$$K_a = \frac{[CH3CO2-][H+]}{[CH3CO2H]}, \text{ so } \frac{[CH3CO2H]}{[CH3CO2-]} = \frac{[H^+]}{K_a}.$$

Since $K_w = [H^+][OH^-]$:

$$K_b = \frac{[H^+][OH^-]}{K_a} \tag{9.6.2}$$

$$= \frac{K_w}{K_a} \tag{9.6.3}$$

$$= \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} \tag{9.6.4}$$

$$= 5.6 \times 10^{-10} \tag{9.6.5}$$

Let us denote the concentration of each of the products of this reaction, CH_3CO_2H and OH^-, as *x*. Using the assumption that *x* is small compared to 0.0500 *M*, $K_b = \frac{x^2}{0.0500\ M}$, and then:

$$x = [OH^-] = 5.3 \times 10^{-6}$$

$$pOH = -\log(5.3 \times 10^{-6}) = 5.28$$

$$pH = 14.00 - 5.28 = 8.72$$

Note that the pH at the equivalence point of this titration is significantly greater than 7.

(c) In (a), 25.00 mL of the NaOH solution was added, and so practically all the CH_3CO_2H was converted into $CH_3CO_2^-$. In this case, only 12.50 mL of the base solution has been introduced, and so only half of all the CH_3CO_2H is converted into $CH_3CO_2^-$. The total initial number of moles of CH_3CO_2H is 0.02500L × 0.100 $\underline{M}$ = 0.00250 mol, and so after adding the NaOH, the numbers of moles of CH_3CO_2H and $CH_3CO_2^-$ are both approximately equal to $\frac{0.00250\ \text{mol}}{2} = 0.00125\ \text{mol}$, and their concentrations are the same.

Since the amount of the added base is smaller than the original amount of the acid, the equivalence point has not been reached, the solution remains a buffer, and we can use the Henderson-Hasselbalch equation:

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[Base]}{[Acid]} = -\log(K_a) + \log\frac{[CH3CO2-]}{[CH3CO2H]} = -\log(1.8\times10^{-5}) + \log(1)$$

(as the concentrations of $\mathbf{CH_3CO_2^-}$ and CH_3CO_2H are the same)

Thus:

$$\mathrm{pH} = -\log(1.8\times10^{-5}) = 4.74$$

(the pH = the pK_a at the halfway point in a titration of a weak acid)

(d) After 37.50 mL of NaOH is added, the amount of NaOH is 0.03750 L × 0.100 *M* = 0.003750 mol NaOH. Since this is past the equivalence point, the excess hydroxide ions will make the solution basic, and we can again use stoichiometric calculations to determine the pH:

$$[\mathrm{OH^-}] = \frac{(0.003750\ \mathrm{mol} - 0.00250\ \mathrm{mol})}{0.06250\ \mathrm{L}} = 2.00\times10^{-2}\ M$$

So:

$$\mathrm{pOH} = -\log(2.00\times10^{-2}) = 1.70,\ \text{and}\ \mathrm{pH} = 14.00 - 1.70 = 12.30$$

Note that this result is the same as for the strong acid-strong base titration example provided, since the amount of the strong base added moves the solution past the equivalence point.

? Exercise 9.6.2

Calculate the pH for the weak acid/strong base titration between 50.0 mL of 0.100 *M* HCOOH(*aq*) (formic acid) and 0.200 *M* NaOH (titrant) at the listed volumes of added base:

a. 0.00 mL,
b. 15.0 mL,
c. 25.0 mL, and
d. 30.0 mL.

Answer a

0.00 mL: 2.37

Answer b

15.0 mL: 3.92

Answer c

25.00 mL: 8.29

Answer d

30.0 mL: 12.097

Acid-Base Indicators

Certain organic substances change color in dilute solution when the hydronium ion concentration reaches a particular value. For example, phenolphthalein is a colorless substance in any aqueous solution with a hydronium ion concentration greater than 5.0×10^{-9} *M* (pH < 8.3). In more basic solutions where the hydronium ion concentration is less than 5.0×10^{-9} *M* (pH > 8.3), it is red or pink. Substances such as phenolphthalein, which can be used to determine the pH of a solution, are called acid-base indicators. Acid-base indicators are either weak organic acids or weak organic bases.

The equilibrium in a solution of the acid-base indicator methyl orange, a weak acid, can be represented by an equation in which we use **HIn** as a simple representation for the complex methyl orange molecule:

$$\underbrace{\mathrm{HIn\,(aq)}}_{\text{red}} + \mathrm{H_2O\,(l)} \rightleftharpoons \mathrm{H_3O^+\,(aq)} + \underbrace{\mathrm{In^-\,(aq)}}_{\text{yellow}}$$

$$K_a = \frac{[H3O+][In-]}{[HIn]} = 4.0 \times 10^{-4}$$

The anion of methyl orange, $\mathbf{In^-}$, is yellow, and the nonionized form, **HIn**, is red. When we add acid to a solution of methyl orange, the increased hydronium ion concentration shifts the equilibrium toward the nonionized red form, in accordance with Le Chatelier's principle. If we add base, we shift the equilibrium towards the yellow form. This behavior is completely analogous to the action of buffers.

An indicator's color is the visible result of the ratio of the concentrations of the two species In^- and **HIn**. If most of the indicator (typically about 60−90% or more) is present as $\mathbf{In^-}$, then we see the color of the $\mathbf{In^-}$ ion, which would be yellow for methyl orange. If most is present as **HIn**, then we see the color of the **HIn** molecule: red for methyl orange. For methyl orange, we can rearrange the equation for K_a and write:

$$\frac{[\mathrm{In^-}]}{[\mathrm{HIn}]} = \frac{[\text{substance with yellow color}]}{[\text{substance with red color}]} = \frac{K_a}{[\mathrm{H_3O^+}]} \tag{9.6.6}$$

Equation 9.6.6 shows us how the ratio of $\frac{[In-]}{[HIn]}$ varies with the concentration of hydronium ion. The above expression describing the indicator equilibrium can be rearranged:

$$\frac{[H_3O^+]}{K_a} = \frac{[HIn]}{[In^-]} \tag{9.6.7}$$

$$\log\left(\frac{[H_3O^+]}{K_a}\right) = \log\left(\frac{[HIn]}{[In^-]}\right) \tag{9.6.8}$$

$$\log([H_3O^+]) - \log(K_a) = -\log\left(\frac{[In^-]}{[HIn]}\right) \tag{9.6.9}$$

$$-pH + pK_a = -\log\left(\frac{[In^-]}{[HIn]}\right) \tag{9.6.10}$$

$$pH = pK_a + \log\left(\frac{[In^-]}{[HIn]}\right) \tag{9.6.11}$$

or in general terms

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right) \tag{9.6.12}$$

Equation 9.6.12 is the same as the *Henderson-Hasselbalch equation*, which can be used to describe the equilibrium of indicators.

When $[H_3O^+]$ has the same numerical value as K_a, the ratio of $[In^-]$ to [HIn] is equal to 1, meaning that 50% of the indicator is present in the red form (HIn) and 50% is in the yellow ionic form (In^-), and the solution appears orange in color. When the hydronium ion concentration increases to 8×10^{-4} *M* (a pH of 3.1), the solution turns red. No change in color is visible for any further increase in the hydronium ion concentration (decrease in pH). At a hydronium ion concentration of 4×10^{-5} *M* (a pH of 4.4), most of the indicator is in the yellow ionic form, and a further decrease in the hydronium ion concentration (increase in pH) does not produce a visible color change. The pH range between 3.1 (red) and 4.4 (yellow) is the color-change interval of methyl orange; the pronounced color change takes place between these pH values.

There are many different acid-base indicators that cover a wide range of pH values and can be used to determine the approximate pH of an unknown solution by a process of elimination. Universal indicators and pH paper contain a mixture of indicators and exhibit different colors at different pHs. Figure **9.6.2** presents several indicators, their colors, and their color-change intervals.

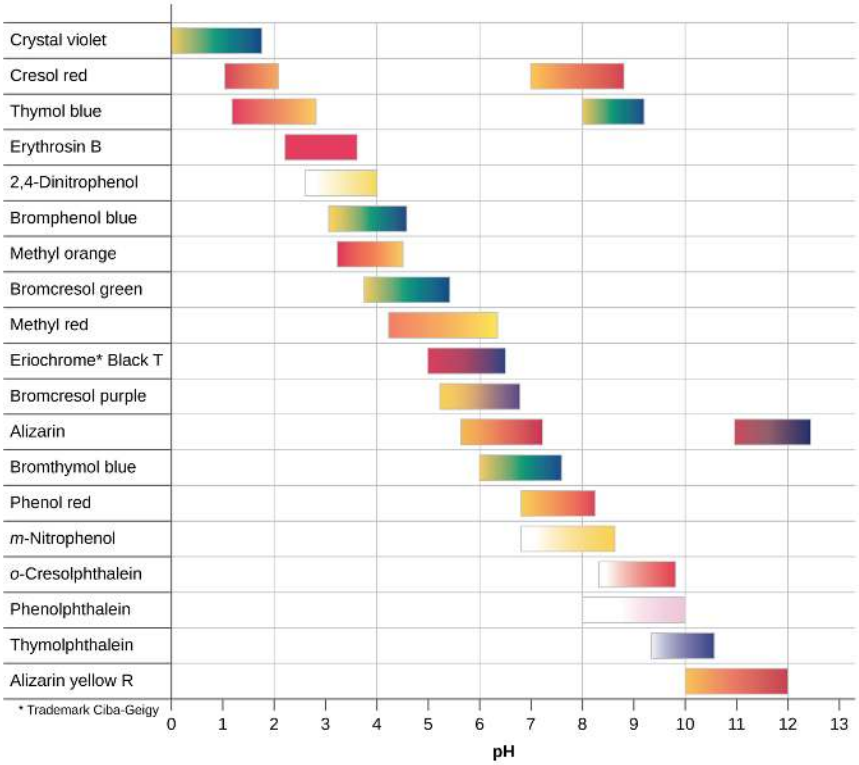


Figure **9.6.2**: This chart illustrates the ranges of color change for several acid-base indicators.

Titration curves help us pick an indicator that will provide a sharp color change at the equivalence point. The best selection would be an indicator that has a color change interval that brackets the pH at the equivalence point of the titration.

The color change intervals of three indicators are shown in Figure **9.6.3**. The equivalence points of both the titration of the strong acid and of the weak acid are located in the color-change interval of phenolphthalein. We can use it for titrations of either strong acid with strong base or weak acid with strong base.

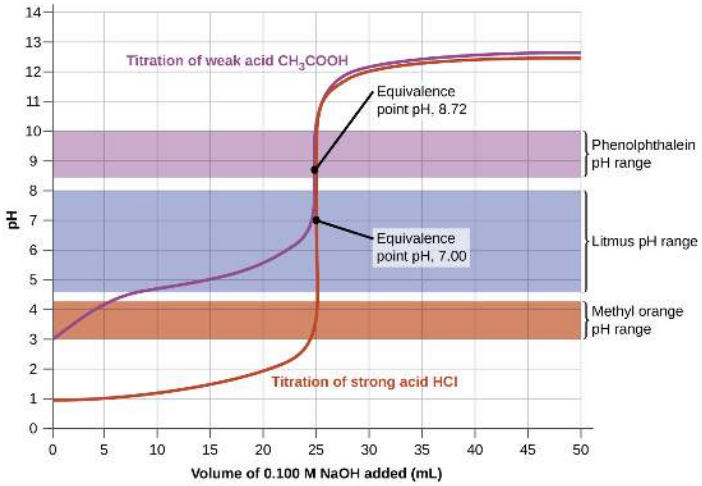


Figure **9.6.3**: The graph shows a titration curve for the titration of 25.00 mL of 0.100 M CH_3CO_2H (weak acid) with 0.100 M NaOH (strong base) and the titration curve for the titration of HCl (strong acid) with NaOH (strong base). The pH ranges for the color change of phenolphthalein, litmus, and methyl orange are indicated by the shaded areas.

A graph is shown which is titled “Titration of Weak Acid.” The horizontal axis is labeled “Volume of 0.100 M N a O H added (m L)” and begins at 0 with markings every 5 units up to 50. The vertical axis is labeled “p H” and begins at 0 and increases by single units up to 14. A red curve is drawn on the graph. The curve begins at (0, 3) and passes through the points (5, 4.1), (10, 4.7), (15, 5), (20, 5.5), and (22.5, 6), after which it rapidly increases, forming a vertical section centered at the point (25, 8.7). The rapid increase of the curve then levels off and the curve passes through the points (30, 12), (35, 12.4), (40, 12.5), (45, 12.6), and (50, 12.6). A brown rectangle extends horizontally across the graph covering the p H of 3 to 4.2 range. To the right, this rectangle is labeled “Methyl orange p H range.” A blue rectangle extends horizontally across the graph covering the p H of 4.6 to 8 range. To the right, this rectangle is labeled “Litmus p H range.” A purple rectangle extends horizontally across the graph covering the p H of 8.4 to 10 range. To the right, this rectangle is labeled “Phenolphthalein p H range.” The midpoint of the vertical segment of the curve is labeled “Equivalence point p H, 8.72.”

Litmus is a suitable indicator for the HCl titration because its color change brackets the equivalence point. However, we should not use litmus for the CH_3CO_2H titration because the pH is within the color-change interval of litmus when only about 12 mL of NaOH has been added, and it does not leave the range until 25 mL has been added. The color change would be very gradual, taking place during the addition of 13 mL of NaOH, making litmus useless as an indicator of the equivalence point.

We could use methyl orange for the HCl titration, but it would not give very accurate results: (1) It completes its color change slightly before the equivalence point is reached (but very close to it, so this is not too serious); (2) it changes color, as Figure **9.6.2** demonstrates, during the addition of nearly 0.5 mL of NaOH, which is not so sharp a color change as that of litmus or phenolphthalein; and (3) it goes from yellow to orange to red, making detection of a precise endpoint much more challenging than the colorless to pink change of phenolphthalein. Figure **9.6.2** shows us that methyl orange would be completely useless as an indicator for the CH_3CO_2H titration. Its color change begins after about 1 mL of NaOH has been added and ends when about 8 mL has been added. The color change is completed long before the equivalence point (which occurs when 25.0 mL of NaOH has been added) is reached and hence provides no indication of the equivalence point.

We base our choice of indicator on a calculated pH, the pH at the equivalence point. At the equivalence point, equimolar amounts of acid and base have been mixed, and the calculation becomes that of the pH of a solution of the salt resulting from the titration.

Summary

A titration curve is a graph that relates the change in pH of an acidic or basic solution to the volume of added titrant. The characteristics of the titration curve are dependent on the specific solutions being titrated. The pH of the solution at the equivalence point may be greater than, equal to, or less than 7.00. The choice of an indicator for a given titration depends on the expected pH at the equivalence point of the titration, and the range of the color change of the indicator.

Glossary

acid-base indicator

organic acid or base whose color changes depending on the pH of the solution it is in

color-change interval

range in pH over which the color change of an indicator takes place

titration curve

plot of the pH of a solution of acid or base versus the volume of base or acid added during a titration

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9.E: Acid-Base Equilibria (Exercises)

14.1: Brønsted-Lowry Acids and Bases

Q14.1.1

Write equations that show NH_3 as both a conjugate acid and a conjugate base.

S14.1.1

One example for NH_3 as a conjugate acid: $\mathbf{NH_2^- + H^+ \longrightarrow NH_3}$; as a conjugate base: $\mathbf{NH_4^+(aq) + OH^-(aq) \longrightarrow NH_3(aq) + H_2O(l)}$

Q14.1.2

Write equations that show $\mathbf{H_2PO_4^-}$ acting both as an acid and as a base.

Q14.1.3

Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:

a. $\mathbf{H_3O^+}$
b. HCl
c. NH_3
d. CH_3CO_2H
e. $\mathbf{NH_4^+}$
f. $\mathbf{HSO_4^-}$

S14.1.3

a. $\mathbf{H_3O^+(aq) \longrightarrow H^+(aq) + H_2O_{(l)}}$;
b. $\mathbf{HCl(l) \longrightarrow H^+(aq) + Cl^-(aq)}$;
c. $\mathbf{NH_3(aq) \longrightarrow H^+(aq) + NH_2^-(aq)}$;
d. $\mathbf{CH_3CO_2H(aq) \longrightarrow H^+(aq) + CH_3CO_2^-(aq)}$;
e. $\mathbf{NH_4^+(aq) \longrightarrow H^+(aq) + NH_3(aq)}$;
f. $\mathbf{HSO_4^-(aq) \longrightarrow H^+(aq) + SO_4^{2-}(aq)}$

Q14.1.4

Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:

a. HNO_3
b. $\mathbf{PH_4^+}$
c. H_2S
d. CH_3CH_2COOH
e. $\mathbf{H_2PO_4^-}$
f. HS^-

Q14.1.5

Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry base:

a. H_2O
b. $\mathbf{OH^-}$
c. NH_3
d. CN^-
e. S^{2-}
f. $\mathbf{H_2PO_4^-}$

S14.1.5

a. $\mathbf{H_2O_{(l)} + H^+(aq) \longrightarrow H_3O^+(aq)}$
b. $\mathbf{OH^-(aq) + H^+(aq) \longrightarrow H_2O_{(l)}}$
c. $\mathbf{NH_3(aq) + H^+(aq) \longrightarrow NH_4^+(aq)}$;
d. $\mathbf{CN^-(aq) + H^+(aq) \longrightarrow HCN(aq)}$
e. $\mathbf{S^{2-}(aq) + H^+(aq) \longrightarrow HS^-(aq)}$
f. $\mathbf{H_2PO_4^-(aq) + H^+(aq) \longrightarrow H_3PO_4(aq)}$

Q14.1.6

Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry base:

a. HS^-
b. $\mathbf{PO_4^{3-}}$
c. $\mathbf{NH_2^-}$
d. C_2H_5OH
e. O^{2-}
f. $\mathbf{H_2PO_4^-}$

Q14.1.7

What is the conjugate acid of each of the following? What is the conjugate base of each?

a. $\mathbf{OH^-}$
b. H_2O
c. $\mathbf{HCO_3^-}$
d. NH_3
e. $\mathbf{HSO_4^-}$
f. H_2O_2
g. HS^-
h. $\mathbf{H_5N_2^+}$

S14.1.7

H_2O, O^{2-}; H_3O^+, $\mathbf{OH^-}$; H_2CO_3, $\mathbf{CO_3^{2-}}$; $\mathbf{NH_4^+}$, $\mathbf{NH_2^-}$; H_2SO_4, $\mathbf{SO_4^{2-}}$; $\mathbf{H_3O_2^+}$, $\mathbf{HO_2^-}$; H_2S; S^{2-}; $\mathbf{H_6N_2^{2+}}$, H_4N_2

Q14.1.8

What is the conjugate acid of each of the following? What is the conjugate base of each?

a. H_2S
b. $\mathbf{H_2PO_4^-}$
c. PH_3
d. HS^-
e. $\mathbf{HSO_3^-}$
f. $\mathbf{H_3O_2^+}$
g. H_4N_2
h. CH_3OH

Q14.1.9

Identify and label the Brønsted-Lowry acid, its conjugate base, the Brønsted-Lowry base, and its conjugate acid in each of the following equations:

a. $\mathbf{HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-}$
b. $\mathbf{CN^- + H_2O \longrightarrow HCN + OH^-}$
c. $\mathbf{H_2SO_4 + Cl^- \longrightarrow HCl + HSO_4^-}$
d. $\mathbf{HSO_4^- + OH^- \longrightarrow SO_4^{2-} + H_2O}$

e. $O^{2-} + H_2O \longrightarrow 2\,OH^-$
f. $[Cu(H_2O)_3(OH)]^+ + [Al(H_2O)_6]^{3+} \longrightarrow [Cu(H_2O)_4]^{2+} + [Al(H_2O)_5(OH)]^{2+}$
g. $H_2S + NH_2^- \longrightarrow HS^- + NH_3$

S14.1.9

The labels are Brønsted-Lowry acid = BA; its conjugate base = CB; Brønsted-Lowry base = BB; its conjugate acid = CA. HNO_3(BA), H_2O(BB), H_3O^+(CA), **NO_3^- (CB)**; CN^-(BB), H_2O(BA), HCN(CA), **OH^-** (CB); H_2SO_4(BA), Cl^-(BB), HCl(CA), **HSO_4^- (CB)**; **HSO_4^- (BA)**, OH^-(BB), **SO_4^{2-} (CB)**, H_2O(CA); O^{2-}(BB), H2O(BA) **OH^-** (CB and CA); $[Cu(H_2O)_3(OH)]^+$(BB), $[Al(H_2O)_6]^{3+}$(BA), $[Cu(H_2O)_4]^{2+}$(CA), $[Al(H_2O)_5(OH)]^{2+}$(CB); H_2S(BA), **NH_2^- (BB)**, HS^-(CB), NH_3(CA)

Q14.1.10

Identify and label the Brønsted-Lowry acid, its conjugate base, the Brønsted-Lowry base, and its conjugate acid in each of the following equations:

a. $NO_2^- + H_2O \longrightarrow HNO_2 + OH^-$
b. $HBr + H_2O \longrightarrow H_3O^+ + Br^-$
c. $HS^- + H_2O \longrightarrow H_2S + OH^-$
d. $H_2PO_4^- + OH^- \longrightarrow HPO_4^{2-} + H_2O$
e. $H_2PO_4^- + HCl \longrightarrow H_3PO_4 + Cl^-$
f. $[Fe(H_2O)_5(OH)]^{2+} + [Al(H_2O)_6]^{3+} \longrightarrow [Fe(H_2O)_6]^{3+} + [Al(H_2O)_5(OH)]^{2+}$
g. $CH_3OH + H^- \longrightarrow CH_3O^- + H_2$

Q14.1.11

What are amphiprotic species? Illustrate with suitable equations.

S14.1.11

Amphiprotic species may either gain or lose a proton in a chemical reaction, thus acting as a base or an acid. An example is H_2O.

- As an acid: $H_2O(aq) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$.
- As a base: $H_2O(aq) + HCl(aq) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$

Q14.1.12

State which of the following species are amphiprotic and write chemical equations illustrating the amphiprotic character of these species:

a. H_2O
b. $H_2PO_4^-$
c. S^{2-}
d. CO_3^{2-}
e. HSO_4^-

Q14.1.13

State which of the following species are amphiprotic and write chemical equations illustrating the amphiprotic character of these species.

a. NH_3
b. HPO_4^-
c. Br^-
d. NH_4^+
e. ASO_4^{3-}

S14.113

amphiprotic: $NH_3 + H_3O^+ \longrightarrow NH_4OH + H_2O$, $NH_3 + OCH_3^- \longrightarrow NH_2^- + CH_3OH$; $HPO_4^{2-} + OH^- \longrightarrow PO_4^{3-} + H_2O$, $HPO_4^{2-} + HClO_4 \longrightarrow H_2PO_4^- + ClO_4^-$; not amphiprotic: Br^-; NH_4^+; AsO_4^{3-}

Q14.1.14

Is the self ionization of water endothermic or exothermic? The ionization constant for water (K_w) is $\mathbf{2.9 \times 10^{-14}}$ at 40 °C and $\mathbf{9.6 \times 10^{-14}}$ at 60 °C.

14.2: pH and pOH

Q14.2.1

Explain why a sample of pure water at 40 °C is neutral even though $[H_3O^+] = 1.7 \times 10^{-7}$ *M*. K_w is 2.9×10^{-14} at 40 °C.

S14.2.1

In a neutral solution $[H_3O^+] = [OH^-]$. At 40 °C,

$[H_3O^+] = [OH^-] = (2.910^{-14})^{1/2} = 1.7 \times 10^{-7}$.

Q14.2.2

The ionization constant for water (K_w) is 2.9×10^{-14} at 40 °C. Calculate $[H_3O^+]$, $[OH^-]$, pH, and pOH for pure water at 40 °C.

Q14.2.3

The ionization constant for water (K_w) is 9.614×10^{-14} at 60 °C. Calculate $[H_3O^+]$, $[OH^-]$, pH, and pOH for pure water at 60 °C.

S14.2.3

x = 3.101×10^{-7} M = $[H_3O^+] = [OH^-]$

pH = -log 3.101×10^{-7} = −(−6.5085) = 6.5085

pOH = pH = 6.5085

Q14.2.4

Calculate the pH and the pOH of each of the following solutions at 25 °C for which the substances ionize completely:

a. 0.200 *M* HCl
b. 0.0143 *M* NaOH
c. 3.0 *M* HNO_3
d. 0.0031 *M* $Ca(OH)_2$

Q14.2.5

Calculate the pH and the pOH of each of the following solutions at 25 °C for which the substances ionize completely:

a. 0.000259 *M* $HClO_4$
b. 0.21 *M* NaOH
c. 0.000071 *M* $Ba(OH)_2$
d. 2.5 *M* KOH

S14.2.5

pH = 3.587; pOH = 10.413; pH = 0.68; pOH = 13.32; pOH = 3.85; pH = 10.15; pH = −0.40; pOH = 14.4

Q14.2.6

What are the pH and pOH of a solution of 2.0 M HCl, which ionizes completely?

Q14.2.6

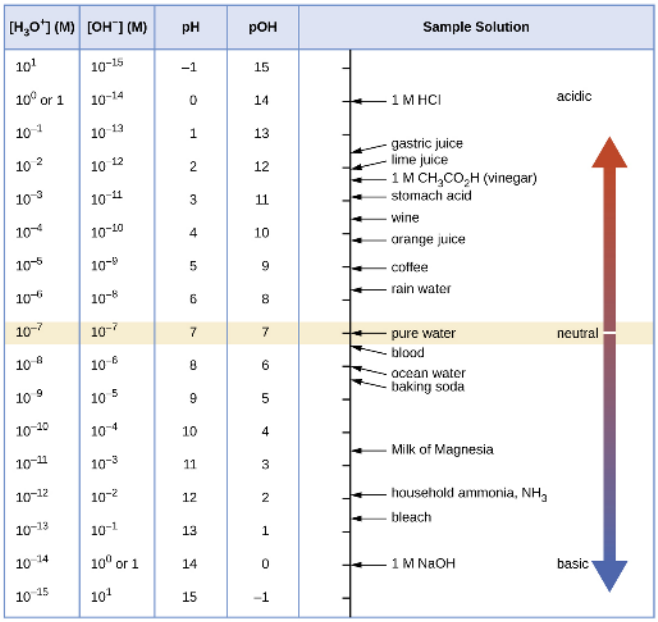
What are the hydronium and hydroxide ion concentrations in a solution whose pH is 6.52?

S14.2.6

$[H_3O^+] = 3.0 \times 10^{-7}$ *M*; $[OH^-] = 3.3 \times 10^{-8}$ *M*

Q14.2.7

Calculate the hydrogen ion concentration and the hydroxide ion concentration in wine from its pH. See below Figure for useful information.



Q14.2.8

Calculate the hydronium ion concentration and the hydroxide ion concentration in lime juice from its pH. See Figure for useful information.

S14.2.9

$[H_3O^+] = 1 \times 10^{-2}\ M$; $[OH^-] = 1 \times 10^{-12}\ M$

Q14.2.9

The hydronium ion concentration in a sample of rainwater is found to be $1.7 \times 10^{-6}\ M$ at 25 °C. What is the concentration of hydroxide ions in the rainwater?

Q14.2.10

The hydroxide ion concentration in household ammonia is $3.2 \times 10^{-3}\ M$ at 25 °C. What is the concentration of hydronium ions in the solution?

S14.2.10

$[OH^-] = 3.1 \times 10^{-12}\ M$

14.3: Relative Strengths of Acids and Bases

Q14.3.1

Explain why the neutralization reaction of a strong acid and a weak base gives a weakly acidic solution.

Q14.3.2

Explain why the neutralization reaction of a weak acid and a strong base gives a weakly basic solution.

The salt ionizes in solution, but the anion slightly reacts with water to form the weak acid. This reaction also forms OH^-, which causes the solution to be basic.

Q14.3.3

Use this list of important industrial compounds (and Figure) to answer the following questions regarding: CaO, $Ca(OH)_2$, CH_3CO_2H, CO_2, HCl, H_2CO_3, HF, HNO_2, HNO_3, H_3PO_4, H_2SO_4, NH_3, NaOH, Na_2CO_3.

a. Identify the strong Brønsted-Lowry acids and strong Brønsted-Lowry bases.
b. List those compounds in that can behave as Brønsted-Lowry acids with strengths lying between those of H_3O^+ and H_2O.
c. List those compounds in that can behave as Brønsted-Lowry bases with strengths lying between those of H_2O and OH^-.

Q14.3.4

The odor of vinegar is due to the presence of acetic acid, CH_3CO_2H, a weak acid. List, in order of descending concentration, all of the ionic and molecular species present in a 1-*M* aqueous solution of this acid.

S14.3.4

$[H_2O] > [CH_3CO_2H] > [\mathbf{H_3O^+}] \approx [\mathbf{CH_3CO_2^-}] > [OH^-]$

Q14.3.5

Household ammonia is a solution of the weak base NH_3 in water. List, in order of descending concentration, all of the ionic and molecular species present in a 1-*M* aqueous solution of this base.

Q14.3.4

Explain why the ionization constant, K_a, for H_2SO_4 is larger than the ionization constant for H_2SO_3.

S14.3.4

The oxidation state of the sulfur in H_2SO_4 is greater than the oxidation state of the sulfur in H_2SO_3.

Q14.3.7

Explain why the ionization constant, K_a, for HI is larger than the ionization constant for HF.

Q14.3.8

Gastric juice, the digestive fluid produced in the stomach, contains hydrochloric acid, HCl. Milk of Magnesia, a suspension of solid $Mg(OH)_2$ in an aqueous medium, is sometimes used to neutralize excess stomach acid. Write a complete balanced equation for the neutralization reaction, and identify the conjugate acid-base pairs.

S14.3.8

$$\underset{\text{BB}}{\mathbf{Mg(OH)_2}}(s) + \underset{\text{BA}}{\mathbf{HCl}}(aq) \longrightarrow \underset{\text{CB}}{\mathbf{Mg^{2+}}}(aq) + 2\,\underset{\text{CA}}{\mathbf{Cl^-}}(aq) + 2\,\mathbf{H_2O}(l)$$

Q14.3.9

Nitric acid reacts with insoluble copper(II) oxide to form soluble copper(II) nitrate, $Cu(NO_3)_2$, a compound that has been used to prevent the growth of algae in swimming pools. Write the balanced chemical equation for the reaction of an aqueous solution of HNO_3 with CuO.

Q14.3.10

What is the ionization constant at 25 °C for the weak acid $\mathbf{CH_3NH_3^+}$, the conjugate acid of the weak base CH_3NH_2, $K_b = 4.4 \times 10^{-4}$.

S14.3.10

$\boldsymbol{K_a = 2.3 \times 10^{-11}}$

Q14.3.11

What is the ionization constant at 25 °C for the weak acid $\mathbf{(CH_3)_2NH_2^+}$, the conjugate acid of the weak base $(CH_3)_2NH$, $K_b = 7.4 \times 10^{-4}$?

Q14.3.12

Which base, CH_3NH_2 or $(CH_3)_2NH$, is the strongest base? Which conjugate acid, $\mathbf{(CH_3)_2NH_2^+}$ or $(CH_3)_2NH$, is the strongest acid?

S14.3.12

The strongest base or strongest acid is the one with the larger K_b or K_a, respectively. In these two examples, they are $(CH_3)_2NH$ and $\mathbf{CH_3NH_3^+}$.

Q14.3.3

Which is the stronger acid, $\mathbf{NH_4^+}$ or HBrO?

Q14.3.14

Which is the stronger base, $(CH_3)_3N$ or $\mathbf{H_2BO_3^-}$?

S14.3.14

triethylamine.

Q14.3.15

Predict which acid in each of the following pairs is the stronger and explain your reasoning for each.

a. H_2O or HF
b. $B(OH)_3$ or $Al(OH)_3$
c. $\mathbf{HSO_3^-}$ or $\mathbf{HSO_4^-}$
d. NH_3 or H_2S
e. H_2O or H_2Te

Q14.3.16

Predict which compound in each of the following pairs of compounds is more acidic and explain your reasoning for each.

a. $\mathbf{HSO_4^-}$ or $\mathbf{HSeO_4^-}$
b. NH_3 or H_2O
c. PH_3 or HI
d. NH_3 or PH_3
e. H_2S or HBr

S14.3.16

a. $\mathbf{HSO_4^-}$; higher electronegativity of the central ion. H_2O;
b. NH_3 is a base and water is neutral, or decide on the basis of K_a values. HI;
c. PH_3 is weaker than HCl; HCl is weaker than HI. Thus, PH_3 is weaker than HI.
d. PH_3; in binary compounds of hydrogen with nonmetals, the acidity increases for the element lower in a group.
e. HBr; in a period, the acidity increases from left to right; in a group, it increases from top to bottom. Br is to the left and below S, so HBr is the stronger acid.

Q14.3.17

Rank the compounds in each of the following groups in order of increasing acidity or basicity, as indicated, and explain the order you assign.

a. acidity: HCl, HBr, HI
b. basicity: H_2O, OH^-, H^-, Cl^-
c. basicity: $Mg(OH)_2$, $Si(OH)_4$, $ClO_3(OH)$ (Hint: Formula could also be written as $HClO_4$).
d. acidity: HF, H_2O, NH_3, CH_4

Q14.3.18

Rank the compounds in each of the following groups in order of increasing acidity or basicity, as indicated, and explain the order you assign.

a. acidity: $NaHSO_3$, $NaHSeO_3$, $NaHSO_4$
b. basicity: $\mathbf{BrO_2^-}$, $\mathbf{ClO_2^-}$, $\mathbf{IO_2^-}$
c. acidity: HOCl, HOBr, HOI
d. acidity: HOCl, HOClO, $HOClO_2$, $HOClO_3$
e. basicity: $\mathbf{NH_2^-}$, HS^-, HTe^-, $\mathbf{PH_2^-}$
f. basicity: BrO^-, $\mathbf{BrO_2^-}$, $\mathbf{BrO_3^-}$, $\mathbf{BrO_4^-}$

S14.3.18

a. $NaHSeO_3 < NaHSO_3 < NaHSO_4$; in polyoxy acids, the more electronegative central element—S, in this case—forms the stronger acid. The larger number of oxygen atoms on the central atom (giving it a higher oxidation state) also creates a greater release of hydrogen atoms, resulting in a stronger acid. As a salt, the acidity increases in the same manner.
b. $\mathbf{ClO_2^- < BrO_2^- < IO_2^-}$; the basicity of the anions in a series of acids will be the opposite of the acidity in their oxyacids. The acidity increases as the electronegativity of the central atom increases. Cl is more electronegative than Br, and I is the least electronegative of the three.
c. HOI < HOBr < HOCl; in a series of the same form of oxyacids, the acidity increases as the electronegativity of the central atom increases. Cl is more electronegative than Br, and I is the least electronegative of the three.
d. HOCl < HOClO < $HOClO_2$ < $HOClO_3$; in a series of oxyacids of the same central element, the acidity increases as the number of oxygen atoms increases (or as the oxidation state of the central atom increases).
e. $\mathbf{HTe^- < HS^- \ll PH_2^- < NH_2^-}$; $\mathbf{PH_2^-}$ and $\mathbf{NH_2^-}$ are anions of weak bases, so they act as strong bases toward H^+. $\mathbf{HTe^-}$ and HS^- are anions of weak acids, so they have less basic character. In a periodic group, the more electronegative element has the more basic anion.
f. $\mathbf{BrO_4^- < BrO_3^- < BrO_2^- < BrO^-}$; with a larger number of oxygen atoms (that is, as the oxidation state of the central ion increases), the corresponding acid becomes more acidic and the anion consequently less basic.

Q14.3.19

Both HF and HCN ionize in water to a limited extent. Which of the conjugate bases, F^- or CN^-, is the stronger base? See Table.

Q14.3.20

The active ingredient formed by aspirin in the body is salicylic acid, $C_6H_4OH(CO_2H)$. The carboxyl group ($-CO_2H$) acts as a weak acid. The phenol group (an OH group bonded to an aromatic ring) also acts as an acid but a much weaker acid. List, in order of descending concentration, all of the ionic and molecular species present in a 0.001-*M* aqueous solution of $C_6H_4OH(CO_2H)$.

$$\mathbf{[H_2O] > [C_6H_4OH(CO_2H)] > [H^+]_0 > [C_6H_4OH(CO_2)^-] \gg [C_6H_4O(CO_2H)^-] > [OH^-]}$$

What do we represent when we write:

$$\mathbf{CH_3CO_2H}(aq) + \mathbf{H_2O}(l) \rightleftharpoons \mathbf{H_3O^+}(aq) + \mathbf{CH_3CO_2^-}(aq)? \tag{9.E.1}$$

Q14.3.21

Explain why equilibrium calculations are not necessary to determine ionic concentrations in solutions of certain strong electrolytes such as NaOH and HCl. Under what conditions are equilibrium calculations necessary as part of the determination of the concentrations of all ions of some other strong electrolytes in solution?

S14.3.21

Strong electrolytes are 100% ionized, and, as long as the component ions are neither weak acids nor weak bases, the ionic species present result from the dissociation of the strong electrolyte. Equilibrium calculations are necessary when one (or more) of the ions is a weak acid or a weak base.

Q14.3.22

Are the concentrations of hydronium ion and hydroxide ion in a solution of an acid or a base in water directly proportional or inversely proportional? Explain your answer.

Q14.3.23

What two common assumptions can simplify calculation of equilibrium concentrations in a solution of a weak acid?

S14.3.23

1. Assume that the change in initial concentration of the acid as the equilibrium is established can be neglected, so this concentration can be assumed constant and equal to the initial value of the total acid concentration.
2. Assume we can neglect the contribution of water to the equilibrium concentration of H_3O^+.

Q14.3.24

What two common assumptions can simplify calculation of equilibrium concentrations in a solution of a weak base?

Q14.3.25

Which of the following will increase the percent of NH_3 that is converted to the ammonium ion in water (Hint: Use LeChâtelier's principle.)?

a. addition of NaOH
b. addition of HCl
c. addition of NH_4Cl

S14.3.25

The addition of HCl

Q14.3.26

Which of the following will increase the percent of HF that is converted to the fluoride ion in water?

a. addition of NaOH
b. addition of HCl
c. addition of NaF

Q14.3.27

What is the effect on the concentrations of $\mathbf{NO_2^-}$, HNO_2, and OH^- when the following are added to a solution of KNO_2 in water:

a. HCl
b. HNO_2
c. NaOH
d. NaCl
e. KNO

The equation for the equilibrium is:

$$\mathbf{NO_2^-}(aq) + \mathbf{H_2O}(l) \rightleftharpoons \mathbf{HNO_2}(aq) + \mathbf{OH^-}(aq) \tag{9.E.2}$$

S14.3.27

a. Adding HCl will add H_3O^+ ions, which will then react with the OH^- ions, lowering their concentration. The equilibrium will shift to the right, increasing the concentration of HNO_2, and decreasing the concentration of $\mathbf{NO_2^-}$ ions.
b. Adding HNO_2 increases the concentration of HNO_2 and shifts the equilibrium to the left, increasing the concentration of $\mathbf{NO_2^-}$ ions and decreasing the concentration of OH^- ions.
c. Adding NaOH adds OH^- ions, which shifts the equilibrium to the left, increasing the concentration of $\mathbf{NO_2^-}$ ions and decreasing the concentrations of HNO_2.
d. Adding NaCl has no effect on the concentrations of the ions.

e. Adding KNO_2 adds NO_2^- ions and shifts the equilibrium to the right, increasing the HNO_2 and OH^- ion concentrations.

Q14.3.28

What is the effect on the concentration of hydrofluoric acid, hydronium ion, and fluoride ion when the following are added to separate solutions of hydrofluoric acid?

a. HCl
b. KF
c. NaCl
d. KOH
e. HF

The equation for the equilibrium is:

$$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq) \tag{9.E.3}$$

Q14.3.29

Why is the hydronium ion concentration in a solution that is 0.10 *M* in HCl and 0.10 *M* in HCOOH determined by the concentration of HCl?

S14.3.29

This is a case in which the solution contains a mixture of acids of different ionization strengths. In solution, the HCO_2H exists primarily as HCO_2H molecules because the ionization of the weak acid is suppressed by the strong acid. Therefore, the HCO_2H contributes a negligible amount of hydronium ions to the solution. The stronger acid, HCl, is the dominant producer of hydronium ions because it is completely ionized. In such a solution, the stronger acid determines the concentration of hydronium ions, and the ionization of the weaker acid is fixed by the $[H_3O^+]$ produced by the stronger acid.

Q14.3.30

From the equilibrium concentrations given, calculate K_a for each of the weak acids and K_b for each of the weak bases.

CH_3CO_2H: $[H_3O^+] = 1.34 \times 10^{-3}$ *M*;

$[CH_3CO_2^-] = 1.34 \times 10^{-3}$ *M*;

$[CH_3CO_2H] = 9.866 \times 10^{-2}$ *M*;

ClO^-: $[OH^-] = 4.0 \times 10^{-4}$ *M*;

$[HClO] = 2.38 \times 10^{-5}$ *M*;

$[ClO^-] = 0.273$ *M*;

HCO_2H: $[HCO_2H] = 0.524$ *M*;

$[H_3O^+] = 9.8 \times 10^{-3}$ *M*; $[HCO_2^-] = 9.8 \times 10^{-3}$ *M*;

$C_6H_5NH_3^+$: $[C_6H_5NH_3^+] = 0.233$ *M*;

$[C_6H_5NH_2] = 2.3 \times 10^{-3}$ *M*;

$[H_3O^+] = 2.3 \times 10^{-3}$ *M*

From the equilibrium concentrations given, calculate K_a for each of the weak acids and K_b for each of the weak bases.

NH_3: $[OH^-] = 3.1 \times 10^{-3}$ *M*;

$[NH_4^+] = 3.1 \times 10^{-3}$ *M*;

$[NH_3] = 0.533$ *M*;

HNO_2: $[H_3O^+] = 0.011$ *M*;

$[NO_2^-] = 0.0438$ *M*;

$[HNO_2] = 1.07$ *M*;

$(CH_3)_3N$: $[(CH_3)_3N] = 0.25\ M$;

$[(CH_3)_3NH^+] = 4.3 \times 10^{-3}\ M$;

$[OH^-] = 4.3 \times 10^{-3}\ M$;

$\mathbf{NH_4^+}$: $[\mathbf{NH_4^+}] = 0.100\ M$;

$[NH_3] = 7.5 \times 10^{-6}\ M$;

$[H_3O^+] = 7.5 \times 10^{-6}\ M$

a. $\mathbf{K_b = 1.8 \times 10^{-5}}$;
b. $\mathbf{K_a = 4.5 \times 10^{-4}}$;
c. $\mathbf{K_b = 7.4 \times 10^{-5}}$;
d. $\mathbf{K_a = 5.6 \times 10^{-10}}$

Q14.3.31

Determine K_b for the nitrite ion, $\mathbf{NO_2^-}$. In a 0.10-*M* solution this base is 0.0015% ionized.

Q14.3.32

Determine K_a for hydrogen sulfate ion, $\mathbf{HSO_4^-}$. In a 0.10-*M* solution the acid is 29% ionized.

S14.3.32

$\mathbf{K_a = 1.2 \times 10^{-2}}$

Q14.3.33

Calculate the ionization constant for each of the following acids or bases from the ionization constant of its conjugate base or conjugate acid:

a. F^-
b. $\mathbf{NH_4^+}$
c. $\mathbf{AsO_4^{3-}}$
d. $\mathbf{(CH_3)_2NH_2^+}$
e. $\mathbf{NO_2^-}$
f. $\mathbf{HC_2O_4^-}$ (as a base)

Q14.3.52

Calculate the ionization constant for each of the following acids or bases from the ionization constant of its conjugate base or conjugate acid:

1. HTe^- (as a base)
2. $\mathbf{(CH_3)_3NH^+}$
3. $\mathbf{HAsO_4^{3-}}$ (as a base)
4. $\mathbf{HO_2^-}$ (as a base)
5. $\mathbf{C_6H_5NH_3^+}$
6. $\mathbf{HSO_3^-}$ (as a base)

S14.3.52

a. $\mathbf{K_b = 4.3 \times 10^{-12}}$;
b. $\mathbf{K_a = 1.4 \times 10^{-10}}$;
c. $\mathbf{K_b = 1 \times 10^{-7}}$;
d. $\mathbf{K_b = 4.2 \times 10^{-3}}$;
e. $\mathbf{K_b = 4.2 \times 10^{-3}}$;
f. $\mathbf{K_b = 8.3 \times 10^{-13}}$

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Q14.3.53

For which of the following solutions must we consider the ionization of water when calculating the pH or pOH?

a. 3×10^{-8} *M* HNO_3
b. 0.10 g HCl in 1.0 L of solution
c. 0.00080 g NaOH in 0.50 L of solution
d. 1×10^{-7} *M* $Ca(OH)_2$
e. 0.0245 *M* KNO_3

Q14.3.54

Even though both NH_3 and $C_6H_5NH_2$ are weak bases, NH_3 is a much stronger acid than $C_6H_5NH_2$. Which of the following is correct at equilibrium for a solution that is initially 0.10 *M* in NH_3 and 0.10 *M* in $C_6H_5NH_2$?

a. $[OH^-] = [NH_4^+]$
b. $[NH_4^+] = [C_6H_5NH_3^+]$
c. $[OH^-] = [C_6H_5NH_3^+]$
d. $[NH_3] = [C_6H_5NH_2]$
e. both a and b are correct

is the correct statement.

Q14.3.55

Calculate the equilibrium concentration of the nonionized acids and all ions in a solution that is 0.25 *M* in HCO_2H and 0.10 *M* in HClO.

Q14.3.56

Calculate the equilibrium concentration of the nonionized acids and all ions in a solution that is 0.134 *M* in HNO_2 and 0.120 *M* in HBrO.

S14.3.56

$[H_3O^+] = 7.5 \times 10^{-3}$ *M*

$[HNO_2] = 0.126$ $[OH^-] = 1.3 \times 10^{-12}$ *M* $[BrO^-] = 3.2 \times 10^{-8}$ *M* $[HBrO] = 0.120$ *M*

Q14.3.57

Calculate the equilibrium concentration of the nonionized bases and all ions in a solution that is 0.25 *M* in CH_3NH_2 and 0.10 *M* in C_5H_5N ($K_b = 1.7 \times 10^{-9}$).

Q14.3.58

Calculate the equilibrium concentration of the nonionized bases and all ions in a solution that is 0.115 *M* in NH_3 and 0.100 *M* in $C_6H_5NH_2$.

S14.3.58

$[OH^-] = [NO_4^+] = 0.0014$ *M*

$[NH_3] = 0.144$ *M* $[H_3O^+] = 6.9 \times 10^{-12}$ *M* $[C_6H_5NH_3^+] = 3.9 \times 10^{-8}$ *M* $[C_6H_5NH_2] = 0.100$ *M*

Q14.3.59

Using the K_a values in Appendix H, place $Al(H_2O)_6^{3+}$ in the correct location in Figure.

Q14.3.60

Calculate the concentration of all solute species in each of the following solutions of acids or bases. Assume that the ionization of water can be neglected, and show that the change in the initial concentrations can be neglected. Ionization constants can be found in Appendix H and Appendix I.

a. 0.0092 *M* HClO, a weak acid
b. 0.0784 *M* $C_6H_5NH_2$, a weak base
c. 0.0810 *M* HCN, a weak acid
d. 0.11 *M* $(CH_3)_3N$, a weak base
e. 0.120 *M* $\mathbf{Fe(H_2O)_6^{2+}}$ a weak acid, $K_a = 1.6 \times 10^{-7}$

S14.3.60

$$\frac{[H3O+][ClO-]}{[HClO]} = \frac{(x)(x)}{(0.0092 - x)} \approx \frac{(x)(x)}{0.0092} = 3.5 \times 10^{-8}$$

Solving for *x* gives 1.79×10^{-5} *M*. This value is less than 5% of 0.0092, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$[H_3O^+] = [ClO] = 1.8 \times 10^{-5}$ *M*[HClO] = 0.00092 *M* $[OH^-] = 5.6 \times 10^{-10}$ *M*;

$$\frac{[C6H5NH3+][OH-]}{[C6H5NH2]} = \frac{(x)(x)}{(0.0784 - x)} \approx \frac{(x)(x)}{0.0784} = 4.6 \times 10^{-10}$$

Solving for *x* gives 6.01×10^{-6} *M*.

This value is less than 5% of 0.0784, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are: $\mathbf{[CH_3CO_2^-]}$ = $[OH^-] = 6.0 \times 10^{-6}$ *M* $[C_6H_5NH_2] = 0.00784$ $[H_3O^+] = 1.7\times 10^{-9}$ *M*; $\frac{[H3O+][CN-]}{[HCN]} = \frac{(x)(x)}{(0.0810 - x)} \approx \frac{(x)(x)}{0.0810} = 4 \times 10^{-10}$ Solving for *x* gives 5.69×10^{-6} *M*. This value is less than 5% of 0.0810, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are: $[H_3O^+] = [CN^-] = 5.7 \times 10^{-6}$ *M* [HCN] = 0.0810 *M* $[OH^-] = 1.8 \times 10^{-9}$ *M*; $\frac{[(CH3)3NH+][OH-]}{[(CH3)3N]} = \frac{(x)(x)}{(0.11 - x)} \approx \frac{(x)(x)}{0.11} = 7.4 \times 10^{-5}$ Solving for *x* gives 2.85×10^{-3} *M*. This value is less than 5% of 0.11, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are: $[(CH_3)_3NH^+] = [OH^-] = 2.9 \times 10^{-3}$ *M* $[(CH_3)_3N] = 0.11$ *M* $[H_3O^+] = 3.5 \times 10^{-12}$ *M*; $\frac{[Fe(H2O)5(OH)+][H3O+]}{[Fe(H2O)6^2+]} = \frac{(x)(x)}{(0.120 - x)} \approx \frac{(x)(x)}{0.120} = 1.6 \times 10^{-7}$ Solving for *x* gives 1.39×10^{-4} *M*. This value is less than 5% of 0.120, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are: $[Fe(H_2O)_5(OH)^+] = [H_3O^+] = 1.4 \times 10^{-4}$ *M* $\mathbf{[Fe(H_2O)_6^{2+}]} = 0.120$ *M* $[OH^-] = 7.2 \times 10^{-11}$ *M*

Q14.3.61

Propionic acid, $C_2H_5CO_2H$ ($K_a = 1.34 \times 10^{-5}$), is used in the manufacture of calcium propionate, a food preservative. What is the hydronium ion concentration in a 0.698-*M* solution of $C_2H_5CO_2H$?

Q14.3.62

White vinegar is a 5.0% by mass solution of acetic acid in water. If the density of white vinegar is 1.007 g/cm^3, what is the pH?

S14.3.62

pH = 2.41

Q14.3.63

The ionization constant of lactic acid, $CH_3CH(OH)CO_2H$, an acid found in the blood after strenuous exercise, is 1.36×10^{-4}. If 20.0 g of lactic acid is used to make a solution with a volume of 1.00 L, what is the concentration of hydronium ion in the solution?

Q14.3.64

Nicotine, $C_{10}H_{14}N_2$, is a base that will accept two protons ($K_1 = 7 \times 10^{-7}$, $K_2 = 1.4 \times 10^{-11}$). What is the concentration of each species present in a 0.050-*M* solution of nicotine?

S14.3.64

$[C_{10}H_{14}N_2] = 0.049$ *M*

$[C_{10}H_{14}N_2H^+] = 1.9 \times 10^{-4}$ *M* $\mathbf{[C_{10}H_{14}N_2H_2^{2+}]} = 1.4 \times 10^{-11}$ *M* $[OH^-] = 1.9 \times 10^{-4}$ *M* $[H_3O^+] = 5.3 \times 10^{-11}$ *M*

Q14.3.65

The pH of a 0.20-*M* solution of HF is 1.92. Determine K_a for HF from these data.

Q14.3.66

The pH of a 0.15-*M* solution of $\mathbf{HSO_4^-}$ is 1.43. Determine K_a for $\mathbf{HSO_4^-}$ from these data.

S14.3.66

$\boldsymbol{K_a = 1.2 \times 10^{-2}}$

Q14.3.67

The pH of a 0.10-*M* solution of caffeine is 11.16. Determine K_b for caffeine from these data:

$$\mathbf{C_8H_{10}N_4O_2}(aq) + \mathbf{H_2O}(l) \rightleftharpoons \mathbf{C_8H_{10}N_4O_2H^+}(aq) + \mathbf{OH^-}(aq)$$

Q14.3.68

The pH of a solution of household ammonia, a 0.950 M solution of NH_3, is 11.612. Determine K_b for NH_3 from these data.

S14.3.68

$\boldsymbol{K_b = 1.77 \times 10^{-5}}$

14.4: Hydrolysis of Salt Solutions

Q14.4.1

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

a. $Al(NO_3)_3$
b. RbI
c. $KHCO_2$
d. CH_3NH_3Br

Q14.4.2

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

a. $FeCl_3$
b. K_2CO_3
c. NH_4Br
d. $KClO_4$

S14.4.2

acidic; basic; acidic; neutral

Q14.4.3

Novocaine, $C_{13}H_{21}O_2N_2Cl$, is the salt of the base procaine and hydrochloric acid. The ionization constant for procaine is 7×10^{-6}. Is a solution of novocaine acidic or basic? What are $[H_3O^+]$, $[OH^-]$, and pH of a 2.0% solution by mass of novocaine, assuming that the density of the solution is 1.0 g/mL.

14.5: Polyprotic Acids

Q15.5.1

Which of the following concentrations would be practically equal in a calculation of the equilibrium concentrations in a 0.134-*M* solution of H_2CO_3, a diprotic acid:

- $\mathbf{[H_3O^+]}$,
- $[\boldsymbol{OH^-}]$
- $[\boldsymbol{H_2CO_3}]$

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- $[HCO_3^-]$
- $[CO_3^{2-}]$

No calculations are needed to answer this question.

S15.5.1

$[H_3O^+]$ and $[HCO_3^-]$ are equal, H_3O^+ and HCO_3^- are practically equal

Q15.5.2

Calculate the concentration of each species present in a 0.050-*M* solution of H_2S.

Q15.5.3

Calculate the concentration of each species present in a 0.010-*M* solution of phthalic acid, $C_6H_4(CO_2H)_2$.

S15.5.3

$$C_6H_4(CO_2H)_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_4(CO_2H)(CO_2)^-(aq) \quad K_a = 1.1 \times 10^{-3}$$

$$C_6H_4(CO_2H)(CO_2)(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_4(CO_2)_2^{2-}(aq) \quad K_a = 3.9 \times 10^{-6}$$

$[C_6H_4(CO_2H)_2]$ 7.2×10^{-3} *M*, $[C_6H_4(CO_2H)(CO_2)^-] = [H_3O^+]$ 2.8×10^{-3} *M*, $[C_6H_4(CO_2)_2^{2-}]$ 3.9×10^{-6} *M*, $[OH^-]$ 3.6×10^{-12} *M*

Q15.5.4

Salicylic acid, $HOC_6H_4CO_2H$, and its derivatives have been used as pain relievers for a long time. Salicylic acid occurs in small amounts in the leaves, bark, and roots of some vegetation (most notably historically in the bark of the willow tree). Extracts of these plants have been used as medications for centuries. The acid was first isolated in the laboratory in 1838.

1. Both functional groups of salicylic acid ionize in water, with $K_a = 1.0 \times 10^{-3}$ for the—CO_2H group and 4.2×10^{-13} for the −OH group. What is the pH of a saturated solution of the acid (solubility = 1.8 g/L).
2. Aspirin was discovered as a result of efforts to produce a derivative of salicylic acid that would not be irritating to the stomach lining. Aspirin is acetylsalicylic acid, $CH_3CO_2C_6H_4CO_2H$. The $-CO_2H$ functional group is still present, but its acidity is reduced, $K_a = 3.0 \times 10^{-4}$. What is the pH of a solution of aspirin with the same concentration as a saturated solution of salicylic acid (See Part a).
3. Under some conditions, aspirin reacts with water and forms a solution of salicylic acid and acetic acid:

$$CH_3CO_2C_6H_4CO_2H(aq) + H_2O(l) \longrightarrow HOC_6H_4CO_2H(aq) + CH_3CO_2H(aq) \tag{9.E.4}$$

   i. Which of the acids salicylic acid or acetic acid produces more hydronium ions in solution such a solution?
   ii. What are the concentrations of molecules and ions in a solution produced by the hydrolysis of 0.50 g of aspirin dissolved in enough water to give 75 mL of solution?

Q15.5.5

The ion HTe^- is an amphiprotic species; it can act as either an acid or a base.

a. What is K_a for the acid reaction of HTe^- with H_2O?
b. What is K_b for the reaction in which HTe^- functions as a base in water?
c. Demonstrate whether or not the second ionization of H_2Te can be neglected in the calculation of $[HTe^-]$ in a 0.10 M solution of H_2Te.

S15.5.5

a. $K_{a2} = 1 \times 10^{-5}$;
b. $K_b = 4.3 \times 10^{-12}$;
c. $\frac{[Te^{2-}][H3O+]}{[HTe-]} = \frac{(x)(0.0141 + x)}{(0.0141 - x)} \approx \frac{(x)(0.0141)}{0.0141} = 1 \times 10^{-5}$. Solving for *x* gives 1×10^{-5} *M*. Therefore, compared with 0.014 *M*, this value is negligible (0.071%).

14.6: Buffers

Q14.6.1

Explain why a buffer can be prepared from a mixture of NH_4Cl and NaOH but not from NH_3 and NaOH.

Q14.6.2

Explain why the pH does not change significantly when a small amount of an acid or a base is added to a solution that contains equal amounts of the acid H_3PO_4 and a salt of its conjugate base NaH_2PO_4.

S14.6.2

Excess H_3O^+ is removed primarily by the reaction:

$\mathbf{H_3O^+(aq) + H_2PO_4^-(aq) \longrightarrow H_3PO_4(aq) + H_2O(l)}$ Excess base is removed by the reaction: $\mathbf{OH^-(aq) + H_3PO_4(aq) \longrightarrow H_2PO_4^-(aq) + H_2O(l)}$

Q14.6.3

Explain why the pH does not change significantly when a small amount of an acid or a base is added to a solution that contains equal amounts of the base NH_3 and a salt of its conjugate acid NH_4Cl.

Q14.6.4

What is $[H_3O^+]$ in a solution of 0.25 *M* CH_3CO_2H and 0.030 *M* $NaCH_3CO_2$?

$\mathbf{CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq) \quad K_a = 1.8 \times 10^{-5}}$

S14.6.4

$[H_3O^+] = 1.5 \times 10^{-4}\ M$

Q14.6.5

What is $[H_3O^+]$ in a solution of 0.075 *M* HNO_2 and 0.030 *M* $NaNO_2$?

S14.6.6

$\mathbf{HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq) \quad K_a = 4.5 \times 10^{-5}}$

Q14.6.6

What is $[OH^-]$ in a solution of 0.125 *M* CH_3NH_2 and 0.130 *M* CH_3NH_3Cl?

S14.6.6

$\mathbf{CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq) \quad K_b = 4.4 \times 10^{-4}}$

$[OH^-] = 4.2 \times 10^{-4}\ M$

Q14.6.7

What is $[OH^-]$ in a solution of 1.25 *M* NH_3 and 0.78 *M* NH_4NO_3?

S14.6.7

$\mathbf{NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \quad K_b = 1.8 \times 10^{-5}}$

Q14.6.8

What concentration of NH_4NO_3 is required to make $[OH^-] = 1.0 \times 10^{-5}$ in a 0.200-*M* solution of NH_3?

S14.6.8

$[NH_4NO_3] = 0.36\ M$

Q14.6.9A

What concentration of NaF is required to make $[H_3O^+] = 2.3 \times 10^{-4}$ in a 0.300-*M* solution of HF?

Q14.6.9B

What is the effect on the concentration of acetic acid, hydronium ion, and acetate ion when the following are added to an acidic buffer solution of equal concentrations of acetic acid and sodium acetate:

a. HCl
b. KCH_3CO_2
c. NaCl
d. KOH
e. CH_3CO_2H

S14.6.10

a. The added HCl will increase the concentration of H_3O^+ slightly, which will react with $\mathbf{CH_3CO_2^-}$ and produce CH_3CO_2H in the process. Thus, $[\mathbf{CH_3CO_2^-}]$ decreases and $[CH_3CO_2H]$ increases.
b. The added KCH_3CO_2 will increase the concentration of $[\mathbf{CH_3CO_2^-}]$ which will react with H_3O^+ and produce CH_3CO_2 H in the process. Thus, $[H_3O^+]$ decreases slightly and $[CH_3CO_2H]$ increases.
c. The added NaCl will have no effect on the concentration of the ions.
d. The added KOH will produce OH^- ions, which will react with the H_3O^+, thus reducing $[H_3O^+]$. Some additional CH_3CO_2H will dissociate, producing $[\mathbf{CH_3CO_2^-}]$ ions in the process. Thus, $[CH_3CO_2H]$ decreases slightly and $[\mathbf{CH_3CO_2^-}]$ increases.
e. The added CH_3CO_2H will increase its concentration, causing more of it to dissociate and producing more $[\mathbf{CH_3CO_2^-}]$ and H_3O^+ in the process. Thus, $[H_3O^+]$ increases slightly and $[\mathbf{CH_3CO_2^-}]$ increases.

Q14.6.11

What is the effect on the concentration of ammonia, hydroxide ion, and ammonium ion when the following are added to a basic buffer solution of equal concentrations of ammonia and ammonium nitrate:

a. KI
b. NH_3
c. HI
d. NaOH
e. NH_4Cl

What will be the pH of a buffer solution prepared from 0.20 mol NH_3, 0.40 mol NH_4NO_3, and just enough water to give 1.00 L of solution?

pH = 8.95

Calculate the pH of a buffer solution prepared from 0.155 mol of phosphoric acid, 0.250 mole of KH_2PO_4, and enough water to make 0.500 L of solution.

How much solid $NaCH_3CO_2 \cdot 3H_2O$ must be added to 0.300 L of a 0.50-*M* acetic acid solution to give a buffer with a pH of 5.00? (Hint: Assume a negligible change in volume as the solid is added.)

37 g (0.27 mol)

What mass of NH_4Cl must be added to 0.750 L of a 0.100-*M* solution of NH_3 to give a buffer solution with a pH of 9.26? (Hint: Assume a negligible change in volume as the solid is added.)

Q14.6.1

A buffer solution is prepared from equal volumes of 0.200 *M* acetic acid and 0.600 *M* sodium acetate. Use 1.80×10^{-5} as K_a for acetic acid.

1. What is the pH of the solution?
2. Is the solution acidic or basic?

Q14.6.1

What is the pH of a solution that results when 3.00 mL of 0.034 *M* HCl is added to 0.200 L of the original buffer?

a. pH = 5.222;
b. The solution is acidic. (c) pH = 5.221

Q14.6.1

A 5.36–g sample of NH_4Cl was added to 25.0 mL of 1.00 *M* NaOH and the resulting solution diluted to 0.100 L.

a. What is the pH of this buffer solution?
b. Is the solution acidic or basic?
c. What is the pH of a solution that results when 3.00 mL of 0.034 *M* HCl is added to the solution?

Which acid in [link] is most appropriate for preparation of a buffer solution with a pH of 3.1? Explain your choice.

To prepare the best buffer for a weak acid HA and its salt, the ratio $\frac{[H_3O^+]}{K_a}$ should be as close to 1 as possible for effective buffer action. The $[H_3O^+]$ concentration in a buffer of pH 3.1 is $[H_3O^+] = 10^{-3.1} = 7.94 \times 10^{-4}$ *M*

We can now solve for K_a of the best acid as follows:

$$\frac{[H_3O^+]}{K_a} = 1$$

$$K_a = \frac{[H_3O^+]}{1} = 7.94 \times 10^{-4}$$

In [link], the acid with the closest K_a to 7.94×10^{-4} is HF, with a K_a of 7.2×10^{-4}.

Which acid in [link] is most appropriate for preparation of a buffer solution with a pH of 3.7? Explain your choice.

Which base in [link] is most appropriate for preparation of a buffer solution with a pH of 10.65? Explain your choice.

For buffers with pHs > 7, you should use a weak base and its salt. The most effective buffer will have a ratio $\frac{[OH^-]}{K_b}$ that is as close to 1 as possible. The pOH of the buffer is 14.00 − 10.65 = 3.35. Therefore, $[OH^-]$ is $[OH^-] = 10^{-pOH} = 10^{-3.35} = 4.467 \times 10^{-4}$ *M*.

We can now solve for K_b of the best base as follows: $\frac{[OH^-]}{K_b} = 1$ $K_b = [OH^-] = 4.47 \times 10^{-4}$ In [link], the base with the closest K_b to 4.47×10^{-4} is CH_3NH_2, with a $K_b = 4.4 \times 10^{-4}$.

Which base in [link] is most appropriate for preparation of a buffer solution with a pH of 9.20? Explain your choice.

Q14.6.4

Saccharin, $C_7H_4NSO_3H$, is a weak acid ($K_a = 2.1 \times 10^{-2}$). If 0.250 L of diet cola with a buffered pH of 5.48 was prepared from 2.00×10^{-3} g of sodium saccharide, $Na(C_7H_4NSO_3)$, what are the final concentrations of saccharine and sodium saccharide in the solution?

S14.6.4

The molar mass of sodium saccharide is 205.169 g/mol. Using the abbreviations HA for saccharin and NaA for sodium saccharide the number of moles of NaA in the solution is:

9.75×10^{-6} mol. This ionizes initially to form saccharin ions, A^-, with: $[A^-] = 3.9 \times 10^{-5}$ *M*

Q14.6.5

What is the pH of 1.000 L of a solution of 100.0 g of glutamic acid ($C_5H_9NO_4$, a diprotic acid; $K_1 = 8.5 \times 10^{-5}$, $K_2 = 3.39 \times 10^{-10}$) to which has been added 20.0 g of NaOH during the preparation of monosodium glutamate, the flavoring agent? What is the pH when exactly 1 mol of NaOH per mole of acid has been added?

14.7: Acid-Base Titrations

Q14.7.1

Explain how to choose the appropriate acid-base indicator for the titration of a weak base with a strong acid.

S14.7.1

At the equivalence point in the titration of a weak base with a strong acid, the resulting solution is slightly acidic due to the presence of the conjugate acid. Thus, pick an indicator that changes color in the acidic range and brackets the pH at the equivalence point. Methyl orange is a good example.

Q14.7.2

Explain why an acid-base indicator changes color over a range of pH values rather than at a specific pH.

Q14.7.3

Why can we ignore the contribution of water to the concentrations of H_3O^+ in the solutions of following acids:

- 0.0092 *M* HClO, a weak acid
- 0.0810 *M* HCN, a weak acid
- 0.120 *M* $\mathbf{Fe(H_2O)_6^{2+}}$ a weak acid, $K_a = 1.6 \times 10^{-7}$

but not the contribution of water to the concentration of OH^-?

S14.7.3

In an acid solution, the only source of OH^- ions is water. We use K_w to calculate the concentration. If the contribution from water was neglected, the concentration of OH^- would be zero.

Q14.7.4

We can ignore the contribution of water to the concentration of OH^- in a solution of the following bases:

0.0784 *M* $C_6H_5NH_2$, a weak base

0.11 *M* $(CH_3)_3N$, a weak base

but not the contribution of water to the concentration of H_3O^+?

Q14.7.5

Draw a curve for a series of solutions of HF. Plot $[H_3O^+]_{total}$ on the vertical axis and the total concentration of HF (the sum of the concentrations of both the ionized and nonionized HF molecules) on the horizontal axis. Let the total concentration of HF vary from 1×10^{-10} *M* to 1×10^{-2} *M*.


A graph is shown that is titled “Plot of [H subscript 3 O superscript +] Against [H F].” The horizontal axis is labeled “[H F], M.” The axis begins at 10 superscript negative 10 and includes markings every 10 superscript 2 units up to 1.0. The vertical axis is labeled “[H subscript 3 O superscript plus], M” and begins at 10 superscript negative 10 and increases by 10 superscript 2 up to 1.0. A black curve starts at the left side of the graph at (10 superscript negative 10, 10 superscript negative 7). The line extends horizontally to a horizontal axis value of 10 superscript negative 8. After this, the line gradually increases at a steady rate to a value just over 10 superscript negative 3 at a horizontal axis value of 10 superscript negative 2.

Q14.7.6

Draw a curve similar to that shown in Figure for a series of solutions of NH_3. Plot $[OH^-]$ on the vertical axis and the total concentration of NH_3 (both ionized and nonionized NH_3 molecules) on the horizontal axis. Let the total concentration of NH_3 vary from 1×10^{-10} *M* to 1×10^{-2} *M*.

Q14.7.7

Calculate the pH at the following points in a titration of 40 mL (0.040 L) of 0.100 *M* barbituric acid ($K_a = 9.8 \times 10^{-5}$) with 0.100 *M* KOH.

1. no KOH added
2. 20 mL of KOH solution added
3. 39 mL of KOH solution added
4. 40 mL of KOH solution added
5. 41 mL of KOH solution added

S14.7.7

1. pH = 2.50;
2. pH = 4.01;
3. pH = 5.60;
4. pH = 8.35;
5. pH = 11.08

Q14.7.8

The indicator dinitrophenol is an acid with a K_a of 1.1×10^{-4}. In a 1.0×10^{-4}-M solution, it is colorless in acid and yellow in base. Calculate the pH range over which it goes from 10% ionized (colorless) to 90% ionized (yellow).

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CHAPTER OVERVIEW

10: Thermodynamics

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General Chemistry

Among the many capabilities of chemistry is its ability to predict if a process will occur under specified conditions. Thermodynamics, the study of relationships between the energy and work associated with chemical and physical processes, provides this predictive ability. Previous chapters in this text have described various applications of thermochemistry, an important aspect of thermodynamics concerned with the heat flow accompanying chemical reactions and phase transitions. This chapter will introduce additional thermodynamic concepts, including those that enable the prediction of any chemical or physical changes under a given set of conditions.

10.1: Spontaneity

10.2: Entropy

10.3: The Second and Third Laws of Thermodynamics

10.4: Gibbs Energy

10.E: Thermodynamics (Exercises)

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10.1: Spontaneity

Learning Objectives

- Distinguish between spontaneous and nonspontaneous processes
- Describe the dispersal of matter and energy that accompanies certain spontaneous processes

In this section, consider the differences between two types of changes in a system: Those that occur spontaneously and those that occur only with the continuous input of energy. In doing so, we'll gain an understanding as to why some systems are naturally inclined to change in one direction under certain conditions. We'll also gain insight into how the spontaneity of a process affects the distribution of energy and matter within the system.

Spontaneous and Nonspontaneous Processes

Processes have a natural tendency to occur in one direction under a given set of conditions. Water will naturally flow downhill, but uphill flow requires outside intervention such as the use of a pump. A spontaneous process is one that occurs naturally under certain conditions. A nonspontaneous process, on the other hand, will not take place unless it is "driven" by the continual input of energy from an external source. A process that is spontaneous in one direction under a particular set of conditions is nonspontaneous in the reverse direction. At room temperature and typical atmospheric pressure, for example, ice will spontaneously melt, but water will not spontaneously freeze.

The spontaneity of a process is *not* correlated to the speed of the process. A spontaneous change may be so rapid that it is essentially instantaneous or so slow that it cannot be observed over any practical period of time. To illustrate this concept, consider the decay of radioactive isotopes, a topic more thoroughly treated in the chapter on nuclear chemistry. Radioactive decay is by definition a spontaneous process in which the nuclei of unstable isotopes emit radiation as they are converted to more stable nuclei. All the decay processes occur spontaneously, but the rates at which different isotopes decay vary widely. Technetium-99m is a popular radioisotope for medical imaging studies that undergoes relatively rapid decay and exhibits a half-life of about six hours. Uranium-238 is the most abundant isotope of uranium, and its decay occurs much more slowly, exhibiting a half-life of more than four billion years (Figure **10.1.1**).

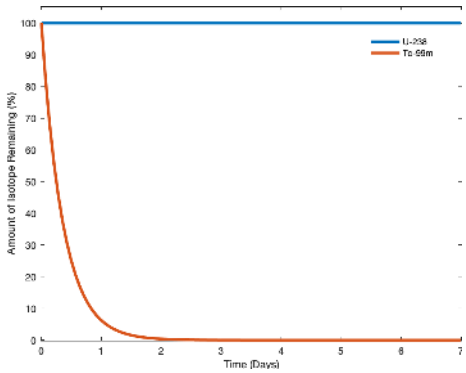


Figure **10.1.1**: Both U-238 and Tc-99m undergo spontaneous radioactive decay, but at drastically different rates. Over the course of one week, essentially all of a Tc-99m sample and none of a U-238 sample will have decayed. (CC by 4.0; Morgan Johnson via LibreTexts)

Two curves are shown to represent U-238 and Tc-99m respectively. The vertical axes represents the percentage of isotope remaining and the horizontal axes is the time that has elapsed in days.

As another example, consider the conversion of diamond into graphite (Figure **10.1.2**).

$$\mathbf{C(s, diamond) \longrightarrow C(s, graphite)} \tag{10.1.1}$$

The phase diagram for carbon indicates that graphite is the stable form of this element under ambient atmospheric pressure, while diamond is the stable allotrope at very high pressures, such as those present during its geologic formation. Thermodynamic calculations of the sort described in the last section of this chapter indicate that the conversion of diamond to graphite at ambient pressure occurs spontaneously, yet diamonds are observed to exist, and persist, under these conditions. Though the process is spontaneous under typical ambient conditions, its rate is extremely slow, and so for all practical purposes diamonds are indeed "forever." Situations such as these emphasize the important distinction between the thermodynamic and the kinetic aspects of a process. In this particular case, diamonds are said to be *thermodynamically unstable* but *kinetically stable* under ambient conditions.

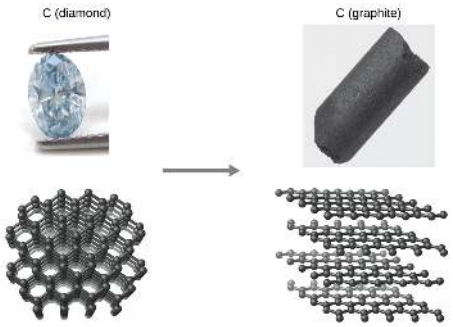


Figure **10.1.2**: The conversion of carbon from the diamond allotrope to the graphite allotrope is spontaneous at ambient pressure, but its rate is immeasurably slow at low to moderate temperatures. This process is known as graphitization, and its rate can be increased to easily measurable values at temperatures in the 1000–2000 K range. (credit "diamond" photo: modification of work by "Fancy Diamonds"/Flickr; credit "graphite" photo: modification of work by images-of-elements.com/carbon.php)

Comparison of diamond and graphite shown in its physical form as well as its molecular arrangement respectively.

Dispersal of Matter and Energy

As we extend our discussion of thermodynamic concepts toward the objective of predicting spontaneity, consider now an isolated system consisting of two flasks connected with a closed valve. Initially there is an ideal gas on the left and a vacuum on the right (Figure **10.1.3**). When the valve is opened, the gas spontaneously expands to fill both flasks. Recalling the definition of pressure-volume work from the chapter on thermochemistry, note that no work has been done because the pressure in a vacuum is zero.

$$w = -P\Delta V \tag{10.1.2}$$

$$= 0 \ \ (\mathbf{P = 0 \ in \ a \ vaccum}) \tag{10.1.3}$$

Note as well that since the system is isolated, no heat has been exchanged with the surroundings (q = 0). The first law of thermodynamics confirms that there has been no change in the system's internal energy as a result of this process.

$$\Delta U = q + w \qquad \text{(First Law of Thermodynamics)}$$
$$= 0 + 0 = 0 \qquad (10.1.4)$$

The spontaneity of this process is therefore not a consequence of any change in energy that accompanies the process. Instead, the movement of the gas appears to be related to the greater, more *uniform dispersal of matter* that results when the gas is allowed to expand. Initially, the system was comprised of one flask containing matter and another flask containing nothing. After the spontaneous process took place, the matter was distributed both more widely (occupying twice its original volume) and more uniformly (present in equal amounts in each flask).

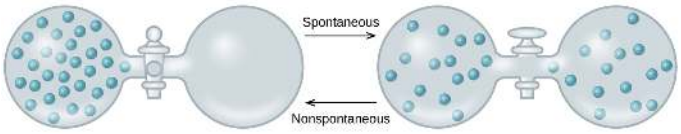


Figure **10.1.3**: An isolated system consists of an ideal gas in one flask that is connected by a closed valve to a second flask containing a vacuum. Once the valve is opened, the gas spontaneously becomes evenly distributed between the flasks.
When the valve is closed, all of the gas molecules accumulating only in one side of the flask. The diagram with the open valve shows gas being equally distributed among the two flasks. The dispersion of the gas is labeled as spontaneous while the reverse is labeled as non spontaneous.

Now consider two objects at different temperatures: object X at temperature T_X and object Y at temperature T_Y, with $T_X > T_Y$ (Figure **10.1.4**). When these objects come into contact, heat spontaneously flows from the hotter object (X) to the colder one (Y). This corresponds to a loss of thermal energy by X and a gain of thermal energy by Y.

$$q_X < 0 \quad \text{and} \quad q_Y = -q_X > 0 \qquad (10.1.5)$$

From the perspective of this two-object system, there was no net gain or loss of thermal energy, rather the available thermal energy was redistributed among the two objects. This spontaneous process resulted in a *more uniform dispersal of energy*.



Figure **10.1.4**:When two objects at different temperatures come in contact, heat spontaneously flows from the hotter to the colder object.
Two separated blocks. One is labeled X and the other labeled Y. The diagram next to it shows the two blocks in contact with one another.

As illustrated by the two processes described, an important factor in determining the spontaneity of a process is the extent to which it changes the dispersal or distribution of matter and/or energy. In each case, a spontaneous process took place that resulted in a more uniform distribution of matter or energy.

Example 10.1.1: Redistribution of Matter during a Spontaneous Process

Describe how matter and energy are redistributed when the following spontaneous processes take place:

a. A solid sublimes.
b. A gas condenses.
c. A drop of food coloring added to a glass of water forms a solution with uniform color.

Solution



Figure **10.1.5**:(credit a: modification of work by Jenny Downing; credit b: modification of work by "Fuzzy Gerdes"/Flickr; credit c: modification of work by Sahar Atwa)
This figure has three photos labeled, "a," "b," and "c." Photo a shows a glass with dry ice in water. There is a thick vapor coming from the top of the glass. Photo b shows water forming outside of a glass containing cold beverage. Photo c shows a sealed container that holds a red liquid.

a. *Sublimation* is the conversion of a solid (relatively high density) to a gas (much lesser density). This process yields a much greater dispersal of matter, since the molecules will occupy a much greater volume after the solid-to-gas transition. However, an input of energy from the surroundings ss required for the molecules to leave the solid phase and enter the gas phase.
b. *Condensation* is the conversion of a gas (relatively low density) to a liquid (much greater density). This process yields a much lesser dispersal of matter, since the molecules will occupy a much lesser volume after the gas-to-liquid transition. As the gas molecules move together to form the droplets of liquid, they form intermolecular forces and thus release energy to the surroundings.
c. The process in question is *dilution*. The food dye molecules initially occupy a much smaller volume (the drop of dye solution) than they occupy once the process is complete (in the full glass of water). The process therefore entails a greater dispersal of matter. The process may also yield a more uniform dispersal of matter, since the initial state of the system involves two regions of different dye concentrations (high in the drop, zero in the water), and the final state of the system contains a single dye concentration throughout. This process can occur with out a change in energy because the molecules have kinetic energy relative to the temperature of the water, and so will be constantly in motion.

Exercise 10.1.1

Describe how matter and energy are redistributed when you empty a canister of compressed air into a room.

Answer

This process entails both a greater and more uniform dispersal of matter as the compressed air in the canister is permitted to expand into the lower-pressure air of the room. The process also requires an input of energy to disrupt the intermolecular forces between the closely-spaced gas molecules that are originally compressed into the container. If you were to touch the nozzle of the canister, you would notice that it is cold because the exiting molecules are taking energy away from their surroundings, and the canister is part of the surroundings.

Summary

Chemical and physical processes have a natural tendency to occur in one direction under certain conditions. A spontaneous process occurs without the need for a continual input of energy from some external source, while a nonspontaneous process requires such. Systems undergoing a spontaneous process may or may not experience a gain or loss of energy, but they will experience a change in the way matter and/or energy is distributed within the system. In this section we have only discussed nuclear decay, physical changes of pure substances, and macroscopic events such as water flowing downhill. In the following sections we will discuss mixtures and chemical reactions, situations in which the description of sponteneity becomes more challenging.

Glossary

nonspontaneous process
: process that requires continual input of energy from an external source

spontaneous change
: process that takes place without a continuous input of energy from an external source

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10.2: Entropy

Learning Objectives

- Define entropy
- Explain the relationship between entropy and the number of microstates
- Predict the sign of the entropy change for chemical and physical processes

In 1824, at the age of 28, Nicolas Léonard Sadi Carnot (Figure **10.2.2**) published the results of an extensive study regarding the efficiency of steam heat engines. In a later review of Carnot's findings, Rudolf Clausius introduced a new thermodynamic property that relates the spontaneous heat flow accompanying a process to the temperature at which the process takes place. This new property was expressed as the ratio of the *reversible* heat (q_{rev}) and the kelvin temperature (T). The term reversible process refers to a process that takes place at such a slow rate that it is always at equilibrium and its direction can be changed (it can be "reversed") by an infinitesimally small change is some condition. Note that the idea of a reversible process is a formalism required to support the development of various thermodynamic concepts; no real processes are truly reversible, rather they are classified as *irreversible*.

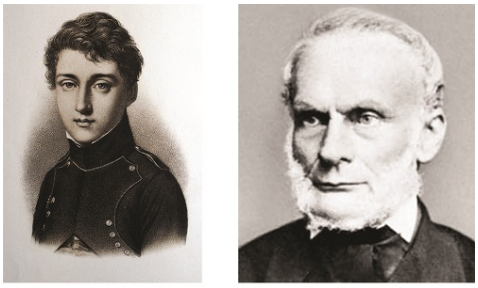


Figure **10.2.1**: (a) Nicholas Léonard Sadi Carnot's research into steam-powered machinery and (b) Rudolf Clausius's later study of those findings led to groundbreaking discoveries about spontaneous heat flow processes.

Similar to other thermodynamic properties, this new quantity is a state function, and so its change depends only upon the initial and final states of a system. In 1865, Clausius named this property entropy (S) and defined its change for any process as the following:

$$\Delta S = \frac{q_{rev}}{T} \tag{10.2.1}$$

The entropy change for a real, irreversible process is then equal to that for the theoretical reversible process that involves the same initial and final states.

Entropy and Microstates

Following the work of Carnot and Clausius, Ludwig Boltzmann developed a molecular-scale statistical model that related the entropy of a system to the number of *microstates* possible for the system. A microstate (Ω) is a specific configuration of the locations and energies of the atoms or molecules that comprise a system like the following:

$$S = k \ln \Omega \tag{10.2.2}$$

Here k is the Boltzmann constant and has a value of $1.38 \times 10^{-23}\ J/K$.

As for other state functions, the change in entropy for a process is the difference between its final (S_f) and initial (S_i) values:

$$\begin{aligned} \Delta S &= S_f - S_i \\ &= k \ln \Omega_f - k \ln \Omega_i \\ &= k \ln \frac{\Omega_f}{\Omega_i} \end{aligned} \tag{10.2.3}$$

For processes involving an increase in the number of microstates of the system, $\Omega_f > \Omega_i$, the entropy of the system increases, $\Delta S > 0$. Conversely, processes that reduce the number of microstates in the system, $\Omega_f < \Omega_i$, yield a decrease in system entropy, ΔS

< 0. This molecular-scale interpretation of entropy provides a link to the probability that a process will occur as illustrated in the next paragraphs.

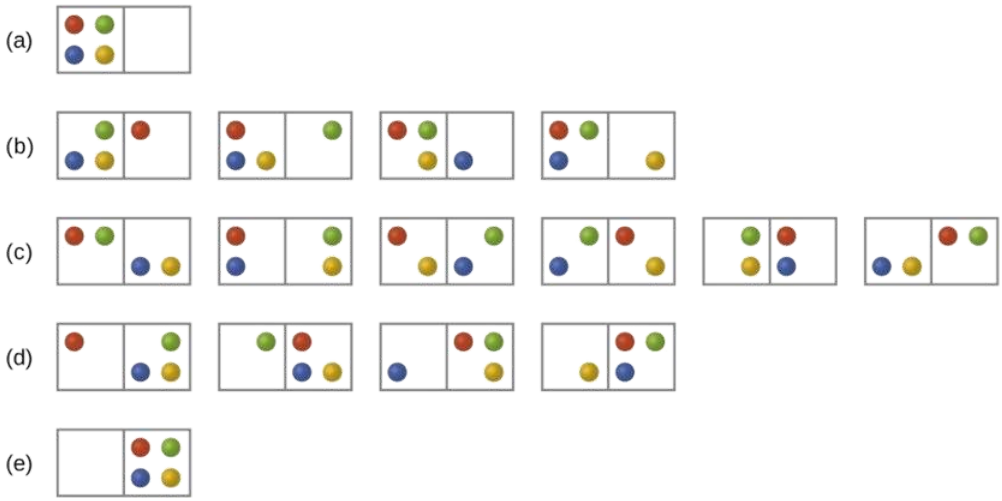


Figure **10.2.2**: The sixteen microstates associated with placing four particles in two boxes are shown. The microstates are collected into five distributions—(a), (b), (c), (d), and (e)—based on the numbers of particles in each box.

Five rows of diagrams that look like dominoes are shown and labeled a, b, c, d, and e. Row a has one "domino" that has four dots on the left side, red, green, blue and yellow in a clockwise pattern from the top left, and no dots on the right. Row b has four "dominos," each with three dots on the left and one dot on the right. The first shows a "domino" with green, yellow and blue on the left and red on the right. The second "domino" has yellow, blue and red on the left and green on the right. The third "domino" has red, green and yellow on the left and blue on the right while the fourth has red, green and blue on the left and yellow on the right. Row c has six "dominos", each with two dots on either side. The first has a red and green on the left and a blue and yellow on the right. The second has a red and blue on the left and a green and yellow on the right while the third has a yellow and red on the left and a green and blue on the right. The fourth has a green and blue on the left and a red and yellow on the right. The fifth has a green and yellow on the left and a red and blue on the right. The sixth has a blue and yellow on the left and a green and red on the right. Row d has four "dominos," each with one dot on the left and three on the right. The first "domino" has red on the left and a blue, green and yellow on the right. The second has a green on the left and a red, yellow and blue on the right. The third has a blue on the left and a red, green and yellow on the right. The fourth has a yellow on the left and a red, green and blue on the right. Row e has 1 "domino" with no dots on the left and four dots on the right that are red, green, blue and yellow.

Consider the general case of a system comprised of N particles distributed among n boxes. The number of microstates possible for such a system is n^N. For example, distributing four particles among two boxes will result in $2^4 = 16$ different microstates as illustrated in Figure **10.2.2**. Microstates with equivalent particle arrangements (not considering individual particle identities) are grouped together and are called *distributions* (sometimes called macrostates or configurations). The probability that a system will exist with its components in a given distribution is proportional to the number of microstates within the distribution. Since entropy increases logarithmically with the number of microstates, *the most probable distribution is therefore the one of greatest entropy*.

For this system, the most probable configuration is one of the six microstates associated with distribution (c) where the particles are evenly distributed between the boxes, that is, a configuration of two particles in each box. The probability of finding the system in this configuration is

$$\frac{6}{16} = \frac{3}{8}$$

The least probable configuration of the system is one in which all four particles are in one box, corresponding to distributions (a) and (e), each with a probability of

$$\frac{1}{16}$$

The probability of finding all particles in only one box (either the left box or right box) is then

$$\left(\frac{1}{16} + \frac{1}{16}\right) = \frac{2}{16} = \frac{1}{8}$$

As you add more particles to the system, the number of possible microstates increases exponentially (2^N). A macroscopic (laboratory-sized) system would typically consist of moles of particles ($N \sim 10^{23}$), and the corresponding number of microstates would be staggeringly huge. Regardless of the number of particles in the system, however, the distributions in which roughly equal numbers of particles are found in each box are always the most probable configurations.

> *The most probable distribution is therefore the one of greatest entropy.*

The previous description of an ideal gas expanding into a vacuum is a macroscopic example of this particle-in-a-box model. For this system, the most probable distribution is confirmed to be the one in which the matter is most uniformly dispersed or distributed between the two flasks. The spontaneous process whereby the gas contained initially in one flask expands to fill both flasks equally therefore yields an increase in entropy for the system.

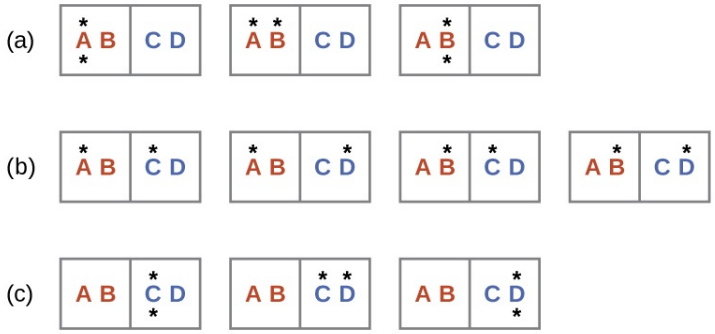


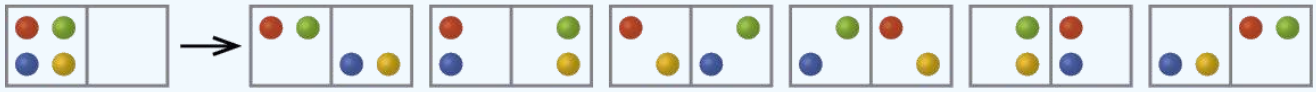
Figure **10.2.3**: This shows a microstate model describing the flow of heat from a hot object to a cold object. (a) Before the heat flow occurs, the object comprised of particles **A** and **B** contains both units of energy and as represented by a distribution of three microstates. (b) If the heat flow results in an even dispersal of energy (one energy unit transferred), a distribution of four microstates results. (c) If both energy units are transferred, the resulting distribution has three microstates.

Three rows labeled a, b, and c are shown and each contains rectangles with two sides where the left side is labeled, “A,” and “B,” and the right is labeled, “C,” and “D.” Row a has three rectangles where the first has a dot above and below the letter A, the second has a dot above the A and B, and the third which has a dot above and below the letter B. Row b has four rectangles; the first has a dot above A and C, the second has a dot above A and D, the third has a dot above B and C and the fourth has a dot above B and D. Row c has three rectangles; the first has a dot above and below the letter C, the second has a dot above C and D and the third has a dot above and below the letter D.

A similar approach may be used to describe the spontaneous flow of heat. Consider a system consisting of two objects, each containing two particles, and two units of energy (represented as “*”) in Figure **10.2.3**. The hot object is comprised of particles **A** and **B** and initially contains both energy units. The cold object is comprised of particles **C** and **D**, which initially has no energy units. Distribution (a) shows the three microstates possible for the initial state of the system, with both units of energy contained within the hot object. If one of the two energy units is transferred, the result is distribution (b) consisting of four microstates. If both energy units are transferred, the result is distribution (c) consisting of three microstates. And so, we may describe this system by a total of ten microstates. The probability that the heat does not flow when the two objects are brought into contact, that is, that the system remains in distribution (a), is $\frac{3}{10}$. More likely is the flow of heat to yield one of the other two distribution, the combined probability being $\frac{7}{10}$. The most likely result is the flow of heat to yield the uniform dispersal of energy represented by distribution (b), the probability of this configuration being $\frac{4}{10}$. As for the previous example of matter dispersal, extrapolating this treatment to macroscopic collections of particles dramatically increases the probability of the uniform distribution relative to the other distributions. This supports the common observation that placing hot and cold objects in contact results in spontaneous heat flow that ultimately equalizes the objects’ temperatures. And, again, this spontaneous process is also characterized by an increase in system entropy.

Example 10.2.1: Determination of ΔS

Consider the system shown here. What is the change in entropy for a process that converts the system from distribution (a) to (c)?



A diagram shows one rectangle with two sides that has four dots, red, green, yellow and blue written on the left side. A right-facing arrow leads to six more two-sided rectangles, each with two dots on the left and right sides. The first rectangle has a red and green dot on the left and a blue and yellow on the right, while the second shows a red and blue on the left and a green and yellow on the right. The third rectangle has a red and yellow dot on the left and a blue and green on the right, while the fourth shows a green and blue on the left and a red and yellow on the right. The fifth rectangle has a yellow and green dot on the left and a blue and red on the right, while the sixth shows a yellow and blue on the left and a green and red on the right.

Solution

We are interested in the following change:

The initial number of microstates is one, the final six:

$$\begin{aligned}\Delta S &= k \ln \frac{\Omega_c}{\Omega_a} \\ &= 1.38 \times 10^{-23}\ J/K \times \ln \frac{6}{1} \\ &= 2.47 \times 10^{-23}\ J/K\end{aligned}$$

The sign of this result is consistent with expectation; since there are more microstates possible for the final state than for the initial state, the change in entropy should be positive.

? Exercise 10.2.1

Consider the system shown in Figure **10.2.3**. What is the change in entropy for the process where *all* the energy is transferred from the hot object (**AB**) to the cold object (**CD**)?

Answer

0 J/K

Predicting the Sign of ΔS

The relationships between entropy, microstates, and matter/energy dispersal described previously allow us to make generalizations regarding the relative entropies of substances and to predict the sign of entropy changes for chemical and physical processes. Consider the phase changes illustrated in Figure **10.2.4**. In the solid phase, the atoms or molecules are restricted to nearly fixed positions with respect to each other and are capable of only modest oscillations about these positions. With essentially fixed locations for the system's component particles, the number of microstates is relatively small. In the liquid phase, the atoms or molecules are free to move over and around each other, though they remain in relatively close proximity to one another. This increased freedom of motion results in a greater variation in possible particle locations, so the number of microstates is correspondingly greater than for the solid. As a result, $S_{liquid} > S_{solid}$ and the process of converting a substance from solid to liquid (melting) is characterized by an increase in entropy, $\Delta S > 0$. By the same logic, the reciprocal process (freezing) exhibits a decrease in entropy, $\Delta S < 0$.

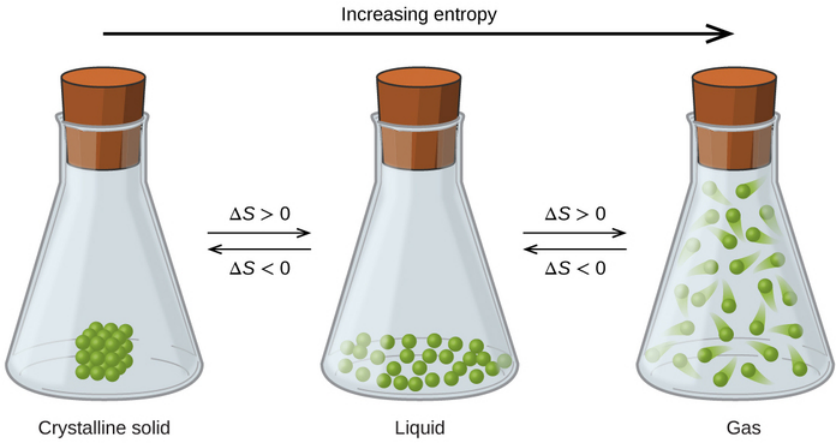


Figure **10.2.4**: The entropy of a substance increases (ΔS > 0) as it transforms from a relatively ordered solid, to a less-ordered liquid, and then to a still less-ordered gas. The entropy decreases (ΔS < 0) as the substance transforms from a gas to a liquid and then to a solid.

Three stoppered flasks are shown with right and left-facing arrows in between each; the first is labeled above as, “delta S greater than 0,” and below as, “delta S less than 0,” while the second is labeled above as, “delta S greater than 0,” and below as, “delta S less than 0.” A long, right-facing arrow is drawn above all the flasks and labeled, “Increasing entropy.” The left flask contains twenty-seven particles arranged in a cube in the bottom of the flask and is labeled, “Crystalline solid,” below. The middle flask contains twenty-seven particles dispersed randomly in the bottom of the flask and is labeled, “Liquid,” below. The right flask contains twenty-seven particles dispersed inside of the flask and moving rapidly and is labeled, “Gas,” below.

Now consider the vapor or gas phase. The atoms or molecules occupy a *much* greater volume than in the liquid phase; therefore each atom or molecule can be found in many more locations than in the liquid (or solid) phase. Consequently, for any substance, $S_{gas} > S_{liquid} > S_{solid}$, and the processes of vaporization and sublimation likewise involve increases in entropy, $\Delta S > 0$. Likewise, the reciprocal phase transitions, condensation and deposition, involve decreases in entropy, $\Delta S < 0$.

According to kinetic-molecular theory, the temperature of a substance is proportional to the average kinetic energy of its particles. Raising the temperature of a substance will result in more extensive vibrations of the particles in solids and more rapid translations of the particles in liquids and gases. At higher temperatures, the distribution of kinetic energies among the atoms or molecules of the substance is also broader (more dispersed) than at lower temperatures. Thus, the entropy for any substance increases with temperature (Figure **10.2.5**).

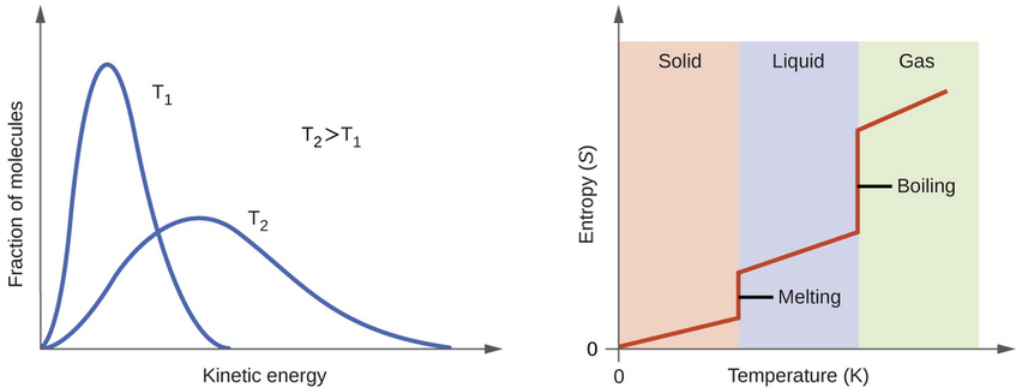


Figure 10.2.5: Entropy increases as the temperature of a substance is raised, which corresponds to the greater spread of kinetic energies. When a substance melts or vaporizes, it experiences a significant increase in entropy.

Two graphs are shown. The y-axis of the left graph is labeled, “Fraction of molecules,” while the x-axis is labeled, “Velocity, v (m / s),” and has values of 0 through 1,500 along the axis with increments of 500. Four lines are plotted on this graph. The first, labeled, “100 K,” peaks around 200 m / s while the second, labeled, “200 K,” peaks near 300 m / s and is slightly lower on the y-axis than the first. The third line, labeled, “500 K,” peaks around 550 m / s and is lower than the first two on the y-axis. The fourth line, labeled, “1000 K,” peaks around 750 m / s and is the lowest of the four on the y-axis. Each line get increasingly broad. The second graph has a y-axis labeled, “Entropy, S,” with an upward-facing arrow and an x-axis labeled, “Temperature (K),” and a right-facing arrow. The graph has three equally spaced columns in the background, labeled, “Solid,” “Liquid,” and, “Gas,” from left to right. A line extends slightly upward through the first column in a slight upward direction, then goes straight up in the transition between the first two columns. In then progresses in a slight upward direction through the second column, then goes up dramatically between the second and third columns, then continues in a slight upward direction once more. The first vertical region of this line is labeled, “Melting,” and the second is labeled, “Boiling.”

The entropy of a substance is influenced by structure of the particles (atoms or molecules) that comprise the substance. With regard to atomic substances, heavier atoms possess greater entropy at a given temperature than lighter atoms, which is a consequence of the relation between a particle’s mass and the spacing of quantized translational energy levels (which is a topic beyond the scope of our treatment). For molecules, greater numbers of atoms (regardless of their masses) increase the ways in which the molecules can vibrate and thus the number of possible microstates and the system entropy.

Finally, variations in the types of particles affects the entropy of a system. Compared to a pure substance, in which all particles are identical, the entropy of a mixture of two or more different particle types is greater. This is because of the additional orientations and interactions that are possible in a system comprised of nonidentical components. For example, when a solid dissolves in a liquid, the particles of the solid experience both a greater freedom of motion and additional interactions with the solvent particles. This corresponds to a more uniform dispersal of matter and energy and a greater number of microstates. The process of dissolution therefore involves an increase in entropy, $\Delta S > 0$.

Considering the various factors that affect entropy allows us to make informed predictions of the sign of ΔS for various chemical and physical processes as illustrated in Example .

Example 10.2.2: Predicting the Sign of ΔS

Predict the sign of the entropy change for the following processes. Indicate the reason for each of your predictions.

a. One mole liquid water at room temperature $\longrightarrow$ one mole liquid water at 50 °C

b. $\mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq) \longrightarrow \mathrm{AgCl}(s)$

c. $\mathrm{C_6H_6}(l) + \frac{15}{2}\mathrm{O_2}(g) \longrightarrow 6\,\mathrm{CO_2}(g) + 3\,\mathrm{H_2O}(l)$

d. $\mathrm{NH_3}(s) \longrightarrow \mathrm{NH_3}(l)$

Solution

a. positive, temperature increases

b. negative, reduction in the number of ions (particles) in solution, decreased dispersal of matter

c. negative, net decrease in the amount of gaseous species

d. positive, phase transition from solid to liquid, net increase in dispersal of matter

Exercise 10.2.2

Predict the sign of the enthalpy change for the following processes. Give a reason for your prediction.

a. $\mathrm{NaNO_3}(s) \longrightarrow \mathrm{Na^+}(aq) + \mathrm{NO_3^-}(aq)$
b. the freezing of liquid water
c. $\mathrm{CO_2}(s) \longrightarrow \mathrm{CO_2}(g)$
d. $\mathrm{CaCO}(s) \longrightarrow \mathrm{CaO}(s) + \mathrm{CO_2}(g)$

Answer a

Positive; The solid dissolves to give an increase of mobile ions in solution.

Answer b

Negative; The liquid becomes a more ordered solid.

Answer c

Positive; The relatively ordered solid becomes a gas

Answer d

Positive; There is a net production of one mole of gas.

Summary

Entropy (\(S\)) is a state function that can be related to the number of microstates for a system (the number of ways the system can be arranged) and to the ratio of reversible heat to kelvin temperature. It may be interpreted as a measure of the dispersal or distribution of matter and/or energy in a system, and it is often described as representing the “disorder” of the system. For a given substance, $S_{solid} < S_{liquid} \ll S_{gas}$ in a given physical state at a given temperature, entropy is typically greater for heavier atoms or more complex molecules. Entropy increases when a system is heated and when solutions form. Using these guidelines, the sign of entropy changes for some chemical reactions may be reliably predicted.

Key Equations

- $\Delta S = \frac{q_{\text{rev}}}{T}$
- $S = k \ln W$
- $\Delta S = k \ln \frac{W_\text{f}}{W_\text{i}}$

Glossary

entropy (S)
state function that is a measure of the matter and/or energy dispersal within a system, determined by the number of system microstates often described as a measure of the disorder of the system

microstate (W)
possible configuration or arrangement of matter and energy within a system

reversible process
process that takes place so slowly as to be capable of reversing direction in response to an infinitesimally small change in conditions; hypothetical construct that can only be approximated by real processes removed

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10.3: The Second and Third Laws of Thermodynamics

Learning Objectives

- State and explain the second and third laws of thermodynamics
- Calculate entropy changes for phase transitions and chemical reactions under standard conditions

The Second Law of Thermodynamics

In the quest to identify a property that may reliably predict the spontaneity of a process, we have identified a very promising candidate: entropy. Processes that involve an increase in entropy *of the system* ($\Delta S > 0$) are very often spontaneous; however, examples to the contrary are plentiful. By expanding consideration of entropy changes to include *the surroundings*, we may reach a significant conclusion regarding the relation between this property and spontaneity. In thermodynamic models, the system and surroundings comprise everything, that is, the universe, and so the following is true:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \tag{10.3.1}$$

To illustrate this relation, consider again the process of heat flow between two objects, one identified as the system and the other as the surroundings. There are three possibilities for such a process:

1. The objects are at different temperatures, and heat flows from the hotter to the cooler object. *This is always observed to occur spontaneously.* Designating the hotter object as the system and invoking the definition of entropy yields the following:

$$\Delta S_{\text{sys}} = \frac{-q_{\text{rev}}}{T_{\text{sys}}} \quad \text{and} \quad \Delta S_{\text{surr}} = \frac{q_{\text{rev}}}{T_{\text{surr}}} \tag{10.3.2}$$

   The arithmetic signs of q_{rev} denote the loss of heat by the system and the gain of heat by the surroundings. Since $T_{\text{sys}} > T_{\text{surr}}$ in this scenario, the magnitude of the entropy change for the surroundings will be greater than that for the system, and so the sum of ΔS_{sys} and ΔS_{surr} will yield a positive value for ΔS_{univ}. *This process involves an increase in the entropy of the universe.*
2. The objects are at different temperatures, and heat flows from the cooler to the hotter object. *This is never observed to occur spontaneously.* Again designating the hotter object as the system and invoking the definition of entropy yields the following:

$$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T_{\text{sys}}} \quad \text{and} \quad \Delta S_{\text{surr}} = \frac{-q_{\text{rev}}}{T_{\text{surr}}} \tag{10.3.3}$$

   The arithmetic signs of q_{rev} denote the gain of heat by the system and the loss of heat by the surroundings. The magnitude of the entropy change for the surroundings will again be greater than that for the system, but in this case, the signs of the heat changes will yield a negative value for ΔS_{univ}. *This process involves a decrease in the entropy of the universe.*
3. The temperature difference between the objects is infinitesimally small, $T_{\text{sys}} \approx T_{\text{surr}}$, and so the heat flow is thermodynamically reversible. See the previous section's discussion). In this case, the system and surroundings experience entropy changes that are equal in magnitude and therefore sum to yield a value of zero for ΔS_{univ}. *This process involves no change in the entropy of the universe.*

These results lead to a profound statement regarding the relation between entropy and spontaneity known as the second law of thermodynamics: *all spontaneous changes cause an increase in the entropy of the universe.* A summary of these three relations is provided in Table **10.3.1**.

Table **10.3.1**: The Second Law of Thermodynamics

$\Delta S_{\text{univ}} > 0$	spontaneous
$\Delta S_{\text{univ}} < 0$	nonspontaneous (spontaneous in opposite direction)
$\Delta S_{\text{univ}} = 0$	reversible (system is at equilibrium)

All spontaneous changes cause an increase in the entropy of the universe.

For many realistic applications, the surroundings are vast in comparison to the system. In such cases, the heat gained or lost by the surroundings as a result of some process represents a very small, nearly infinitesimal, fraction of its total thermal energy. For example, combustion of a fuel in air involves transfer of heat from a system (the fuel and oxygen molecules undergoing reaction) to surroundings that are infinitely more massive (the earth's atmosphere). As a result, q_{surr} is a good approximation of q_{rev}, and the second law may be stated as the following:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \tag{10.3.4}$$

We may use this equation to predict the spontaneity of a process as illustrated in Example **10.3.1**.

✔ Example 10.3.1: Will Ice Spontaneously Melt?

The entropy change for the process

$$\mathrm{H_2O}(s) \longrightarrow \mathrm{H_2O}(l)$$

is 22.1 J/K and requires that the surroundings transfer 6.00 kJ of heat to the system. Is the process spontaneous at −10.00 °C? Is it spontaneous at +10.00 °C?

Solution

We can assess the spontaneity of the process by calculating the entropy change of the universe. If ΔS_{univ} is positive, then the process is spontaneous. At both temperatures, ΔS_{sys} = 22.1 J/K and q_{surr} = −6.00 kJ.

At −10.00 °C (263.15 K), the following is true:

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \\ &= 22.1\ \text{J/K} + \frac{-6.00 \times 10^3\ \text{J}}{263.15\ \text{K}} = -0.7\ \text{J/K}\end{aligned}$$

$S_{univ} < 0$, so melting is nonspontaneous (*not* spontaneous) at **−10.0 °C**.

At 10.00 °C (283.15 K), the following is true:

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \\ &= 22.1\ J/K + \frac{-6.00 \times 10^3\ J}{283.15\ K} = +0.9\ J/K\end{aligned}$$

$S_{univ} > 0$, so melting *is* spontaneous at **10.00 °C.**

? Exercise 10.3.1

Using this information, determine if liquid water will spontaneously freeze at the same temperatures. What can you say about the values of S_{univ}?

Answer

Entropy is a state function, and freezing is the opposite of melting. At −10.00 °C spontaneous, +0.7 J/K; at +10.00 °C nonspontaneous, −0.9 J/K.

The Third Law of Thermodynamics

The previous section described the various contributions of matter and energy dispersal that contribute to the entropy of a system. With these contributions in mind, consider the entropy of a pure, perfectly crystalline solid possessing no kinetic energy (that is, at a temperature of absolute zero, 0 K). This system may be described by a single microstate, as its purity, perfect crystallinity and

complete lack of motion means there is but one possible location for each identical atom or molecule comprising the crystal (W = 1). According to the Boltzmann equation, the entropy of this system is zero.

$$S = k \ln W = k \ln(1) = 0 \tag{10.3.5}$$

This limiting condition for a system's entropy represents the third law of thermodynamics: *the entropy of a pure, perfect crystalline substance at 0 K is zero.*

Definition: Third Law of Thermodynamics

The entropy of a pure, perfect crystalline substance at 0 K is zero.

We can make careful calorimetric measurements to determine the temperature dependence of a substance's entropy and to derive absolute entropy values under specific conditions. Standard entropies are given the label S°_{298} for values determined for one mole of substance, isolated in its pure form in its own container, at a pressure of 1 bar and a temperature of 298 K.

Definition: Term

The thermodynamic standard state of a substance refers to an isolated sample of that substance, in its own container, at 1.000 bar (0.9869 atm) pressure. If the substance is a solute, the most common standard state is one in which the concentration of the solute is 1.000 molal (sometimes approximated with 1.000 M). There is no defined temperature for the standard state, but most discussions about standard state assume that the temperature is 298.15 K (25ºC) unless otherwise noted.

This may seem like a strange definition, because it requires that each of the reactants and each of the products of a reaction are kept separate from one another, unmixed. The entropy of mixing must be determined separately.

The standard entropy change ($\Delta S°$) for any process may be computed from the standard entropies of its reactant and product species like the following:

$$\Delta S^\circ = \sum \nu S^\circ_{298}(\text{products}) - \sum \nu S^\circ_{298}(\text{reactants}) \tag{10.3.6}$$

Here, ν represents stoichiometric coefficients in the balanced equation representing the process. For example, $\Delta S°$ for the following reaction at room temperature

$$m\text{A} + n\text{B} \longrightarrow x\text{C} + y\text{D} \tag{10.3.7}$$

is computed as the following:

$$= [xS^\circ_{298}(\text{C}) + yS^\circ_{298}(\text{D})] - [mS^\circ_{298}(\text{A}) + nS^\circ_{298}(\text{B})] \tag{10.3.8}$$

Table **10.3.2** lists some standard entropies at 298.15 K. You can find additional standard entropies in Tables T1 or T2.

Table **10.3.2**: Standard Entropies (at 298.15 K, 1 atm)

Substance	$S^\circ_{298}\ \frac{J}{mol\ K}$
carbon	
C(*s*, graphite)	5.740
C(*s*, diamond)	2.38
CO(*g*)	197.7
$CO_2(g)$	213.8
$CH_4(g)$	186.3
$C_2H_4(g)$	219.5
$C_2H_6(g)$	229.5
$CH_3OH(l)$	126.8
$C_2H_5OH(l)$	160.7
hydrogen	
$H_2(g)$	130.57
H(*g*)	114.6
$H_2O(g)$	188.71
$H_2O(l)$	69.91
HCI(*g*)	186.8
$H_2S(g)$	205.7
oxygen	
$O_2(g)$	205.03

Example 10.3.2: Determination of ΔS°

Calculate the standard entropy change for the following process:

$$\mathbf{H_2O}(g) \longrightarrow \mathbf{H_2O}(l)$$

Solution

The value of the standard entropy change at room temperature, ΔS°_{298}, is the difference between the standard entropy of the product, $H_2O(l)$, and the standard entropy of the reactant, $H_2O(g)$.

$$\begin{aligned}\Delta S^\circ_{298} &= S^\circ_{298}(\mathbf{H_2O}(l)) - S^\circ_{298}(\mathbf{H_2O}(g)) \\ &= (70.0\ J\ mol^{-1}K^{-1}) - (188.8\ Jmol^{-1}K^{-1}) = -118.8\ J\ mol^{-1}K^{-1}\end{aligned}$$

The value for ΔS°_{298} is negative, as expected for this phase transition (condensation), which the previous section discussed.

Exercise 10.3.2

Calculate the standard entropy change for the following process:

$$\mathbf{H_2}(g) + \mathbf{C_2H_4}(g) \longrightarrow \mathbf{C_2H_6}(g)$$

Answer

$-120.6\ \text{J mol}^{-1}\ \text{K}^{-1}$

Example 10.3.3: Determination of ΔS°

Calculate the standard entropy change for the combustion of methanol, CH_3OH at room temperature:

$$2\,\text{CH}_3\text{OH}(l) + 3\,\text{O}_2(g) \longrightarrow 2\,\text{CO}_2(g) + 4\,\text{H}_2\text{O}(l)$$

Solution

The value of the standard entropy change is equal to the difference between the standard entropies of the products and the entropies of the reactants scaled by their stoichiometric coefficients.

$$\begin{aligned}\Delta S^\circ = \Delta S^\circ_{298} &= \sum \nu S^\circ_{298}(\text{products}) - \sum \nu S^\circ_{298}(\text{reactants}) \\ &= [2S^\circ_{298}(\text{CO}_2(g)) + 4S^\circ_{298}(\text{H}_2\text{O}(l))] - [2S^\circ_{298}(\text{CH}_3\text{OH}(l)) + 3S^\circ_{298}(\text{O}_2(g))] \\ &= \{[2(213.8) + 4 \times 70.0] - [2(126.8) + 3(205.03)]\} = -161.1\ J/mol \cdot K\end{aligned}$$

Exercise 10.3.3

Calculate the standard entropy change for the following reaction:

$$\text{Ca(OH)}_2(s) \longrightarrow \text{CaO}(s) + \text{H}_2\text{O}(l)$$

Answer

24.7 J/mol•K

Summary

The second law of thermodynamics states that a spontaneous process increases the entropy of the universe, $S_{\text{univ}} > 0$. If $\Delta S_{\text{univ}} < 0$, the process is nonspontaneous, and if $\Delta S_{\text{univ}} = 0$, the system is at equilibrium. The third law of thermodynamics establishes the zero for entropy as that of a perfect, pure crystalline solid at 0 K. With only one possible microstate, the entropy is zero. We may compute the standard entropy change for a process by using standard entropy values for the reactants and products involved in the process.

Key Equations

- $\Delta S^\circ = \Delta S^\circ_{298} = \sum \nu S^\circ_{298}(\text{products}) - \sum \nu S^\circ_{298}(\text{reactants})$
- $\Delta S = \frac{q_{\text{rev}}}{T}$
- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$
- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T}$

Glossary

second law of thermodynamics
entropy of the universe increases for a spontaneous process

standard entropy (S°)
entropy for a substance at 1 bar pressure; tabulated values are usually determined at 298.15 K and denoted S°_{298}

standard entropy change (ΔS°)
change in entropy for a reaction calculated using the standard entropies, usually at room temperature and denoted ΔS°_{298}

third law of thermodynamics
entropy of a perfect crystal at absolute zero (0 K) is zero

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10.4: Gibbs Energy

Learning Objectives

- Define Gibbs free energy, and describe its relation to spontaneity
- Calculate the standard free energy change for a process using standard free energies of formation for its reactants and products
- Calculate standard free energy change for a process using senthalpies of formation and the entropies for its reactants and products
- Explain how temperature affects the spontaneity of some processes
- Relate standard free energy changes to equilibrium constants

One of the challenges of using the second law of thermodynamics to determine if a chemical reaction is spontaneous is that we must determine the entropy change for the system *and* the entropy change for the surroundings. A second challenge when working with a chemical reaction is that we need to take into account the mixing of the substances, an issue that does not occur when observing the phase change if a pure substance. An alternative approach involving a new thermodynamic property defined in terms of system properties only was introduced in the late nineteenth century by American mathematician Josiah Willard Gibbs. This new property is called the Gibbs free energy (G) (or simply the *free energy*), and it is defined in terms of a system's enthalpy and entropy as the following:

$$G = H - TS$$

Free energy is a state function, and at constant temperature and pressure, the standard free energy change (ΔG°) may be expressed as the following:

$$\Delta G^{\circ}_{\text{sys}} = \Delta H^{\circ}_{\text{sys}} - T\Delta S^{\circ}_{\text{sys}}$$

(For simplicity's sake, the subscript "sys" will be omitted henceforth.) We can understand the relationship between this system property and the spontaneity of a process by recalling the previously derived second law expression:

$$\Delta S_{\text{univ}} = \Delta S + \frac{q_{\text{surr}}}{T}$$

The first law requires that $q_{surr} = -q_{sys}$, and at constant pressure $q_{sys} = \Delta H$, and so this expression may be rewritten as the following:

$$\Delta S_{\text{univ}} = \Delta S - \frac{\Delta H}{T}$$

ΔH is the enthalpy change of the system. Multiplying both sides of this equation by −T, and rearranging yields the following:

$$-T\Delta S_{\text{univ}} = \Delta H - T\Delta S$$

Comparing this equation to the previous one for free energy change shows the following relation:

$$\Delta G = -T\Delta S_{\text{univ}} \tag{10.4.1}$$

The free energy change is therefore a reliable indicator of the spontaneity of a process, being directly related to the previously identified spontaneity indicator, ΔS_{univ}. Table **10.4.1** summarizes the relation between the spontaneity of a process and the arithmetic signs of these indicators.

Table **10.4.1**: Relation between Process Spontaneity and Signs of Thermodynamic Properties

$\Delta S_{univ} > 0$	$\Delta G < 0$	moves spontaneously in the forward direction, as written, to reach equilibrium
$\Delta S_{univ} < 0$	$\Delta G > 0$	nonspontaneous in the forward direction, as written, but moves spontaneously in the reverse direction, as written, to reach equilibrium
$\Delta S_{univ} = 0$	$\Delta G = 0$	reversible (at equilibrium)

Calculating Free Energy Change

Free energy is a state function, so its value depends only on the conditions of the initial and final states of the system that have undergone some change. A convenient and common approach to the calculation of free energy changes for physical changes and chemical reactions is by use of widely available compilations of standard state thermodynamic data. One method involves the use of standard enthalpies and entropies to compute standard free energy changes according to the following relation as demonstrated in Example **10.4.1**.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{10.4.2}$$

It is important to understand that for phase changes, ΔG° tells you if the phase change is spontaneous or not; will it happen, or not happen. For chemical reactions, ΔG° tells you the **extent** of a reaction. In other words, ΔG° for a reaction tells you how much product will be present at equilibrium. A reaction with $\Delta G^\circ < 0$ is considered **product-favored at equilibrium**; there will be more products than reactants when the reaction reaches equilibrium. A reaction with $\Delta G^\circ > 0$ is considered **reactant-favored at equilibrium**; there will be more reactants than products when the reaction reaches equilibrium.

Example 10.4.1: Evaluation of ΔG° for a Phase Change of a Pure Substance

Use standard enthalpy and entropy data from Tables T1 or T2 to calculate the standard free energy change for the vaporization of water at room temperature (298 K). What does the computed value for ΔG° say about the spontaneity of this physical change for a pure substance?

Solution

The process of interest is the following:

$$\mathrm{H_2O}(l) \longrightarrow \mathrm{H_2O}(g) \tag{10.4.3}$$

The standard change in free energy may be calculated using the following equation:

$$\Delta G^\circ_{298} = \Delta H^\circ - T\Delta S^\circ \tag{10.4.4}$$

From Tables T1 or T2, here are the data:

Data from Tables T1 or T2

Substance	ΔH_f° (kJ/mol)	S°_{298} (J/K·mol)
$H_2O(l)$	−286.83	70.0
$H_2O(g)$	−241.82	188.8

Combining at 298 K:

$$\begin{aligned}\Delta H^\circ = \Delta H^\circ_{298} &= \Delta H^\circ_f(\mathrm{H_2O}(g)) - \Delta H^\circ_f(\mathrm{H_2O}(l)) \\ &= [-241.82\ kJ - (-285.83)]\ kJ/mol \\ &= 44.01\ kJ/mol \\ \Delta S^\circ = \Delta S^\circ_{298} &= S^\circ_{298}(\mathrm{H_2O}(g)) - S^\circ_{298}(\mathrm{H_2O}(l)) \\ &= 188.8\ J/mol \cdot K - 70.0\ J/K \\ &= 118.8\ J/mol \cdot K\end{aligned}$$

then use Equation 10.4.2:

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

Converting everything into kJ and combining at 298 K:

$$\begin{aligned}\Delta G^\circ_{298} &= \Delta H^\circ - T\Delta S^\circ \\ &= 44.01\ kJ/mol - (298\ K \times 118.8\ J/mol \cdot K) \times \frac{1\ kJ}{1000\ J} \\ &\mathrm{44.01\ kJ/mol - 35.4\ kJ/mol = 8.6\ kJ/mol}\end{aligned}$$

At 298 K (25 °C) $\Delta G^\circ_{298} > 0$, and so boiling is nonspontaneous (not spontaneous) at 298 K.

? Exercise 10.4.1: Evaluation of ΔG° for a Chemical Reaction

Use standard enthalpy and entropy data from Tables T1 or T2 to calculate the standard free energy change for the reaction shown here (298 K). What does the computed value for ΔG° say about the extent of this reaction at 298 K?

$$\mathrm{C_2H_6}(g) \longrightarrow \mathrm{H_2}(g) + \mathrm{C_2H_4}(g)$$

Answer

$\Delta G^\circ_{298} = \mathrm{102.0\ kJ/mol}$; the reaction is reactant-favored at equilibrium at 25 °C. There will be more $\mathrm{C_2H_6}(g)$ than $\mathrm{H_2}(g)$ and $\mathrm{C_2H_4}(g)$ at equilibrium

Free energy changes may also use the standard free energy of formation (ΔG°_f), for each of the reactants and products involved in the reaction. The standard free energy of formation is the free energy change that accompanies the formation of one mole of a substance from its elements in their standard states. Similar to the standard enthalpies of formation, (ΔG°_f) is by definition zero for elemental substances under standard state conditions. The approach to computing the free energy change for a reaction using this approach is the same as that demonstrated previously for enthalpy and entropy changes. For the reaction

$$m\mathrm{A} + n\mathrm{B} \longrightarrow x\mathrm{C} + y\mathrm{D},$$

the standard free energy change at room temperature may be calculated as

$$\Delta G^\circ_{298} = \Delta G^\circ \tag{10.4.5}$$

$$= \sum \nu \Delta G^\circ_{298}(\mathrm{products}) - \sum \nu \Delta G^\circ_{298}(\mathrm{reactants}) \tag{10.4.6}$$

$$= [x\Delta G^\circ_f(\mathrm{C}) + y\Delta G^\circ_f(\mathrm{D})] - [m\Delta G^\circ_f(\mathrm{A}) + n\Delta G^\circ_f(\mathrm{B})]. \tag{10.4.7}$$

✓ Example 10.4.2: Calculation of ΔG°_{298}

Consider the decomposition of yellow mercury(II) oxide.

$$\mathrm{HgO}(s,\ \mathrm{yellow}) \longrightarrow \mathrm{Hg}(l) + \tfrac{1}{2}\,\mathrm{O_2}\,(\mathrm{g})$$

Calculate the standard free energy change at room temperature, ΔG°_{298}, using:

a. standard free energies of formation and
b. standard enthalpies of formation and standard entropies.

Do the results indicate the reaction to be product-favored or reactant-favored at equilibrium?

Solution

The required data are available in Tables T1 or T2 and are shown here.

Required data for Tables T1 or T2

Compound	ΔG_f° (kJ/mol)	ΔH_f° (kJ/mol)	S_{298}° (J/K·mol)
HgO (*s*, yellow)	−58.43	−90.46	71.13
Hg(*l*)	0	0	75.9
$O_2(g)$	0	0	205.2

(a) Using free energies of formation:

$$\begin{aligned}\Delta G_{298}^\circ &= \sum \nu G S_{298}^\circ(\text{products}) - \sum \nu \Delta G_{298}^\circ(\text{reactants}) \\ &= \left[1\Delta G_{298}^\circ \text{Hg}(l) + \frac{1}{2}\Delta G_{298}^\circ \text{O}_2(g)\right] - 1\Delta G_{298}^\circ \text{HgO}(s,\text{ yellow}) \\ &= \left[1\text{ mol}(0\text{ kJ/mol}) + \frac{1}{2}\text{mol}(0\text{ kJ/mol})\right] - 1\text{ mol}(-58.43\text{ kJ/mol}) = 58.43\text{ kJ/mol}\end{aligned}$$

(b) Using enthalpies and entropies of formation:

$$\begin{aligned}\Delta H_{298}^\circ &= \sum \nu \Delta H_{298}^\circ(\text{products}) - \sum \nu \Delta H_{298}^\circ(\text{reactants}) \\ &= \left[1\Delta H_{298}^\circ \text{Hg}(l) + \frac{1}{2}\Delta H_{298}^\circ \text{O}_2(g)\right] - 1\Delta H_{298}^\circ \text{HgO}(s,\text{ yellow}) \\ &= [1\text{ mol}(0\text{ kJ/mol}) + \frac{1}{2}\text{mol}(0\text{ kJ/mol})] - 1\text{ mol}(-90.46\text{ kJ/mol}) = 90.46\text{ kJ/mol} \\ \Delta S_{298}^\circ &= \sum \nu \Delta S_{298}^\circ(\text{products}) - \sum \nu \Delta S_{298}^\circ(\text{reactants}) \\ &= \left[1\Delta S_{298}^\circ \text{Hg}(l) + \frac{1}{2}\Delta S_{298}^\circ \text{O}_2(g)\right] - 1\Delta S_{298}^\circ \text{HgO}(s,\text{ yellow}) \\ &= \left[1\text{ mol}(75.9\text{ J/mol K}) + \frac{1}{2}\text{mol}(205.2\text{ J/mol K})\right] - 1\text{ mol}(71.13\text{ J/mol K}) \\ &= 107.4\text{ J/mol K}\end{aligned}$$

then we can use Equation \ref7} directly:

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= 90.46\text{ kJ} - 298.15\text{ K} \times 107.4\text{ J/K}\cdot\text{mol} \times \frac{1\text{ kJ}}{1000\text{ J}} \\ &= (90.46 - 32.01)\text{ kJ/mol} = 58.45\text{ kJ/mol}\end{aligned}$$

Both ways to calculate the standard free energy change at 25 °C give the same numerical value (to three significant figures), and both predict that the process is reactant-favored at equilibrium at room temperature.

? Exercise 10.4.2

Calculate ΔG° using (a) free energies of formation and (b) enthalpies of formation and entropies (Tables T1 or T2). Do the results indicate the reaction to be product-favored or reactant-favored at equilibrium at 25 °C?

$$C_2H_4(g) \longrightarrow H_2(g) + C_2H_2(g)$$

Answer

141.5 kJ/mol, reactant-favored at equilibrium

Temperature Dependence of Spontaneity and Extent of Reaction

As was previously demonstrated in this chapter's section on entropy, the spontaneity of a process may depend upon the temperature of the system. Phase transitions, for example, will proceed spontaneously in one direction or the other depending upon the temperature of the substance in question. In a similar, but not identical fashion, some chemical reactions can switch from being product-favored at equilibrium, to being reactant-favored at equilibrium, depending on the temperature.

> **Note**
>
> The numerical value of ΔG° is always dependent on the temperature. In this section we are determining whether or not the **sign** of ΔG° is dependent on the temperature.

To illustrate this concept, the equation relating free energy change to the enthalpy and entropy changes for the process is considered:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

The extent of a process, as reflected in the arithmetic sign of its standard free energy change, is then determined by the signs of the enthalpy and entropy changes and, in some cases, the absolute temperature. Since T is the absolute (Kelvin) temperature, it can only have positive values. Four possibilities therefore exist with regard to the signs of the enthalpy and entropy changes:

1. **Both ΔH^{o} and ΔS^{o} are positive.** This condition describes an endothermic process that involves an increase in system entropy. In this case, ΔG^{o} will be negative if the magnitude of the $T\Delta S^{o}$ term is greater than ΔH^{o}. If the $T\Delta S^{o}$ term is less than ΔH^{o}, the free energy change will be positive. Such a process is *product-favored at equilibrium at high temperatures and reactant-favored at equilibrium at low temperatures.*
2. **Both ΔH^{o} and ΔS^{o} are negative.** This condition describes an exothermic process that involves a decrease in system entropy. In this case, ΔG^{o} will be negative if the magnitude of the $T\Delta S^{o}$ term is less than ΔH^{o}. If the $T\Delta S^{o}$ term's magnitude is greater than ΔH^{o}, the free energy change will be positive. Such a process is *product-favored at equilibrium at low temperatures* and *reactant-favored at equilibrium at high temperatures.*
3. **ΔH^{o} is positive and ΔS^{o} is negative.** This condition describes an endothermic process that involves a decrease in system entropy. In this case, ΔG^{o} will be positive regardless of the temperature. Such a process is *reactant-favored at equilibrium at all temperatures.*
4. **ΔH^{o} is negative and ΔS^{o} is positive.** This condition describes an exothermic process that involves an increase in system entropy. In this case, ΔG^{o} will be negative regardless of the temperature. Such a process is *product-favored at equilibrium at all temperatures.*

These four scenarios are summarized in Table **10.4.1**

Table **10.4.1**

Sign of ΔH^o	Sign of ΔS^o	Sign of ΔG^o	Temperature Dependence of ΔG^o
-	+	-	The sign of ΔG^o does not depend on the temperature.The reaction is product-favored at equilibrium at all temperatures.
+	-	+	The sign of ΔG^o does not depend on the temperature.The reaction is reactant-favored at equilibrium at all temperatures.
-	-	- or +	The sign of ΔG^o **does** depend on the temperature. The reaction will be product-favored at equilibrium at lower temperatures.
+	+	- or +	The sign of ΔG^o **does** depend on the temperature. The reaction will be product-favored at equilibrium at lower temperatures.

Example 10.4.3: Predicting the Temperature Dependence of Spontaneity

The incomplete combustion of carbon is described by the following equation:

$$2\,C(s) + O_2(g) \longrightarrow 2\,CO(g)$$

Does the sign of ΔG^o of this process depend upon temperature?

Solution

Combustion processes are exothermic ($\Delta H^o < 0$). This particular reaction involves an increase in entropy due to the accompanying increase in the amount of gaseous species (net gain of one mole of gas, $\Delta S^o > 0$). The reaction is therefore product-favored at equilibrium ($\Delta G^o < 0$) at all temperatures.

Exercise 10.4.3

Popular chemical hand warmers generate heat by the air-oxidation of iron:

$$4\,Fe(s) + 3\,O_2(g) \longrightarrow 2\,Fe_2O_3(s)$$

Does the sign of ΔG^o of this process depend upon temperature?

Answer

ΔH^o and ΔS^o are both negative; the reaction is product-favored at equilibrium at low temperatures.

When considering the conclusions drawn regarding the temperature dependence of the sign of ΔG^o, it is important to keep in mind what the terms “high” and “low” mean. Since these terms are adjectives, the temperatures in question are deemed high or low relative to some reference temperature. A process that is reactant-favored at equilibrium at one temperature but product-favored at equilibrium at another temperature will necessarily undergo a change in “extent” (as reflected by its ΔG^o) as temperature varies.

This is clearly illustrated by a graphical presentation of the free energy change equation, in which ΔG^o is plotted on the *y* axis versus *T* on the *x* axis:

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

$$y = b + mx$$

Such a plot is shown in Figure **10.4.2**. A process whose enthalpy and entropy changes are of the same arithmetic sign will exhibit a temperature-dependence for the sign of ΔG^o as depicted by the two yellow lines in the plot. Each line crosses from one spontaneity domain (positive or negative ΔG^o) to the other at a temperature that is characteristic of the process in question. This temperature is represented by the *x*-intercept of the line, that is, the value of *T* for which ΔG^o is zero:

$$\Delta G^o = 0 = \Delta H^o - T\Delta S^o$$

$$T = \frac{\Delta H^o}{\Delta S^o}$$

Thus, saying a process is product-favored at equilibrium at “high” or “low” temperatures means the temperature is above or below, respectively, that temperature at which ΔG^o for the process is zero.

Note

In this discussion, we have used two different descriptions for the meaning of the sign of ΔG^o. You should be aware of the meaning of each description.

a) **Extent of Reaction:** This description is used to predict the ratio of the product and reactant concentrations at equilibrium. In this description, we use the thermodynamic term ΔG^o to tell us the same information as the equilibrium constant, K. When $\Delta G^o < 0$, K > 1, and the reaction will be product-favored at equilibrium. When $\Delta G^o > 0$, K< 1, and the reaction is reactant-favored at equilibrium. When $\Delta G^o = 0$, K =1, and the reaction will have roughly equal amounts of products and reactants at equilibrium. In all cases, the reaction will form a mixture of products and reactants at equilibrium. We use the sign and magnitude of ΔG^o to tell us how much product will be made if the reaction is allowed to reach equilibrium.

b) **Spontaneity:** This description is much more complicated because it involves two different interpretations of how a reaction at standard state occurs. One interpretation involves the hypothetical process in which the reaction proceeds from a starting point of pure reactants to a finishing point of pure products, with all substances isolated in their own containers under standard state conditions. In the second, more realistic interpretation, the reaction starts with all reactants and all products in their standard state in one container. We then allow this specific mixture to react an infinitesimally small amount so that we can obtain a rate of change in free energy with respect to the extent of reaction when all reactants and products are mixed and (essentially) in their standard states. Although each interpretation describes a different reaction scenario, the value of the difference in free energy and the value of the rate of change in free energy are the same number. If $\Delta G^o < 0$, we say that the reaction is spontaneous, meaning that the reaction would proceed in the forward direction, as written, to form pure products in their standard state. If $\Delta G^o > 0$, we say that the reaction is nonspontaneous, meaning that the reaction would proceed in the reverse direction, as written, to form pure reactants in their standard state. If $\Delta G^o = 0$, we say that the neither the reactants nor the products are favored to be formed.

A detailed treatment of the meaning of ΔG^o can be found in the paper, "Free Energy versus Extent of Reaction" by Richard S. Treptow, Journal of Chemical Education, **1996**, Volume 73 (1), 51-54.

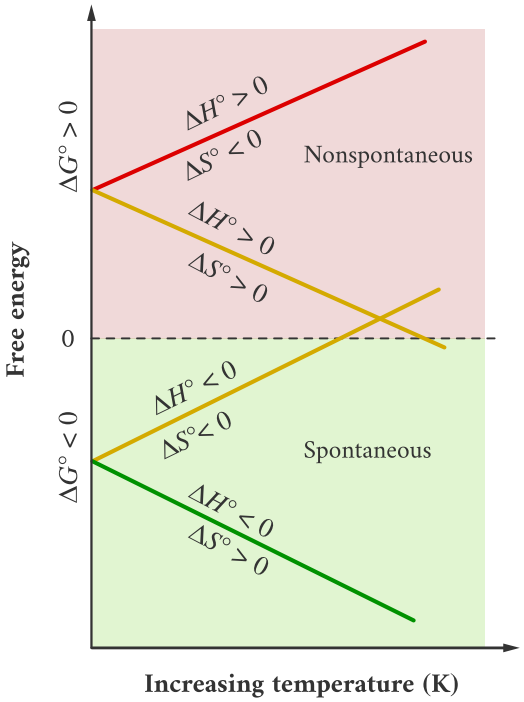


Figure **10.4.2**: These plots show the variation in ΔGº with temperature for the four possible combinations of arithmetic sign for ΔHº and ΔSº. Note that in this graph of ΔGº, "spontaneous" is synonymous with "product-favored at equilibrium", and "nonspontaneous" is synonymous with "reactant-favored at equilibrium".

Example 10.4.4: Equilibrium Temperature for a Phase Transition

As defined in the chapter on liquids and solids, the boiling point of a liquid is the temperature at which its solid and liquid phases are in equilibrium (that is, when vaporization and condensation occur at equal rates). Use the information in Tables T1 or T2 to estimate the boiling point of water.

Solution

The process of interest is the following phase change:

$$\mathrm{H_2O}(l) \longrightarrow \mathrm{H_2O}(g)$$

When this process is at equilibrium, $\Delta G = 0$, so the following is true:

$$0 = \Delta H^\circ - T\Delta S^\circ \qquad \text{or} \qquad T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

Using the standard thermodynamic data from Tables T1 or T2,

$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ(\mathrm{H_2O}(g)) - \Delta H_f^\circ(\mathrm{H_2O}(l)) \\ &= -241.82\ \mathrm{kJ/mol} - (-285.83\ \mathrm{kJ/mol}) = 44.01\ \mathrm{kJ/mol}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= \Delta S_{298}^\circ(\mathrm{H_2O}(g)) - \Delta S_{298}^\circ(\mathrm{H_2O}(l)) \\ &= 188.8\ \mathrm{J/K \cdot mol} - 70.0\ \mathrm{J/K \cdot mol} = 118.8\ \mathrm{J/K \cdot mol}\end{aligned}$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{44.01 \times 10^3\ \mathrm{J/mol}}{118.8\ \mathrm{J/K \cdot mol}} = 370.5\ \mathrm{K} = 97.3\ ^\circ\mathrm{C}$$

The accepted value for water's normal boiling point is 373.2 K (100.0 °C), and so this calculation is in reasonable agreement. Note that the values for enthalpy and entropy changes data used were derived from standard data at 298 K (Tables T1 or T2.). If desired, you could obtain more accurate results by using enthalpy and entropy changes determined at (or at least closer to) the actual boiling point.

? Exercise 10.4.4

Use the information in Tables T1 or T2 to estimate the boiling point of CS_2.

Answer

313 K (accepted value 319 K).

Free Energy and Equilibrium

The free energy change for a process may be viewed as a measure of its driving force. A negative value for ΔG represents a finite driving force for the process in the forward direction, while a positive value represents a driving force for the process in the reverse direction. When ΔG is zero, the forward and reverse driving forces are equal, and so the process occurs in both directions at the same rate (the system is at equilibrium).

In the chapter on equilibrium the *reaction quotient*, Q, was introduced as a convenient measure of the status of an equilibrium system. Recall that Q is the numerical value of the mass action expression for the system, and that you may use its value to identify the direction in which a reaction will proceed in order to achieve equilibrium. When Q is lesser than the equilibrium constant, K, the reaction will proceed in the forward direction until equilibrium is reached and $Q = K$. Conversely, if $Q > K$, the process will proceed in the reverse direction until equilibrium is achieved.

The free energy change for a process taking place with reactants and products present under nonstandard conditions, ΔG, is related to the standard free energy change, $\Delta G°$, according to this equation:

$$\Delta G = \Delta G° + RT \ln Q \tag{10.4.8}$$

R is the gas constant (8.314 J/K mol), T is the kelvin or absolute temperature, and Q is the reaction quotient. We may use this equation to predict the spontaneity for a process under any given set of conditions as illustrated in Example 10.4.1.

✓ Example 10.4.5: Calculating ΔG under Nonstandard Conditions

What is the free energy change for the process shown here under the specified conditions?

T = 25 °C, $P_{N_2} = 0.870\ \text{atm}$, $P_{H_2} = 0.250\ \text{atm}$, and $P_{NH_3} = 12.9\ \text{atm}$

$$2\,NH_3(g) \longrightarrow 3\,H_2(g) + N_2(g) \quad \Delta G° = 33.0\ \text{kJ/mol}$$

Solution

Equation 10.4.8 relates free energy change to standard free energy change and reaction quotient and may be used directly:

$$\begin{aligned}\Delta G &= \Delta G° + RT \ln Q \\ &= 33.0\ \frac{\text{kJ}}{\text{mol}} + \left(8.314\ \frac{\text{J}}{\text{mol K}} \times 298\ \text{K} \times \ln \frac{(0.250^3) \times 0.870}{12.9^2}\right) \\ &= 9680\ \frac{\text{J}}{\text{mol}}\ \text{or}\ 9.68\ \text{kJ/mol}\end{aligned}$$

Since the computed value for ΔG is positive, the reaction is nonspontaneous under these conditions. The reaction will proceed in the reverse direction to reach equilibrium.

? Exercise 10.4.5

Calculate the free energy change for this same reaction at 875 °C in a 5.00 L mixture containing 0.100 mol of each gas. Is the reaction spontaneous under these conditions?

Answer

ΔG = −47 kJ; yes, the reaction proceeds in the forward direction, as written, to reach equilibrium.

For a system at equilibrium, $Q = K$ and $\Delta G = 0$, and the Equation 10.4.8 may be written as

$$\underbrace{0 = \Delta G^\circ + RT\ln K}_{\text{at equilibrium}}$$

$$\Delta G^\circ = -RT\ln K \tag{10.4.9}$$

or alternatively

$$K = e^{-\frac{\Delta G^\circ}{RT}} \tag{10.4.10}$$

This form of the equation provides a useful link between these two essential thermodynamic properties, and it can be used to derive equilibrium constants from standard free energy changes and vice versa. The relations between standard free energy changes and equilibrium constants are summarized in Table 10.4.1.

Table 10.4.1: Relations between Standard Free Energy Changes and Equilibrium Constants

K	ΔG°	Comments
< 1	> 0	Reactants are more abundant at equilibrium.
= 1	= 0	Reactants and products are equally abundant at equilibrium.
> 1	< 0	Products are more abundant at equilibrium.

Example 10.4.6: Equilibrium Constant using Standard Free Energy Change

Given that the standard free energies of formation of $Ag^+(aq)$, $Cl^-(aq)$, and $AgCl(s)$ are 77.1 kJ/mol, −131.2 kJ/mol, and −109.8 kJ/mol, respectively, calculate the solubility product, K_{sp}, for AgCl.

Solution

The reaction of interest is the following:

$$\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq) \quad K_{sp} = [\mathrm{Ag^+}][\mathrm{Cl^-}]$$

The standard free energy change for this reaction is first computed using standard free energies of formation for its reactants and products:

$$\begin{aligned}\Delta G^\circ = \Delta G^\circ_{298} &= [\Delta G^\circ_f(\mathrm{Ag^+}(aq)) + \Delta G^\circ_f(\mathrm{Cl^-}(aq))] - [\Delta G^\circ_f(\mathrm{AgCl}(s))] \\ &= [77.1\ kJ/mol - 131.2\ kJ/mol] - [-109.8\ kJ/mol] \\ &= 55.7\ kJ/mol\end{aligned}$$

The equilibrium constant for the reaction may then be derived from its standard free energy change via Equation 10.4.10:

$$\begin{aligned}K_{sp} = e^{-\frac{\Delta G^\circ}{RT}} &= \exp\left(-\frac{\Delta G^\circ}{RT}\right) \\ &= \exp\left(-\frac{55.7 \times 10^3\ \mathrm{J/mol}}{8.314\ \mathrm{J/mol \cdot K} \times 298.15\ \mathrm{K}}\right) \\ &= \exp(-22.470) = e^{-22.470} = 1.74 \times 10^{-10}\end{aligned}$$

Exercise 10.4.6: dissociation of dinitrogen tetroxide

Use the thermodynamic data provided in Tables T1 or T2 to calculate the equilibrium constant for the dissociation of dinitrogen tetroxide at 25 °C.

$$\mathrm{NO_{2(g)}} \rightleftharpoons \mathrm{N_2O_{4(g)}}$$

Answer

K = 6.9

To further illustrate the relation between these two essential thermodynamic concepts, consider the observation that reactions spontaneously proceed in a direction that ultimately establishes equilibrium. As may be shown by plotting the free energy change versus the extent of the reaction (for example, as reflected in the value of Q), equilibrium is established when the system's free energy is minimized (Figure **10.4.3**). If a system is present with reactants and products present in nonequilibrium amounts ($Q \neq K$), the reaction will proceed spontaneously in the direction necessary to establish equilibrium.

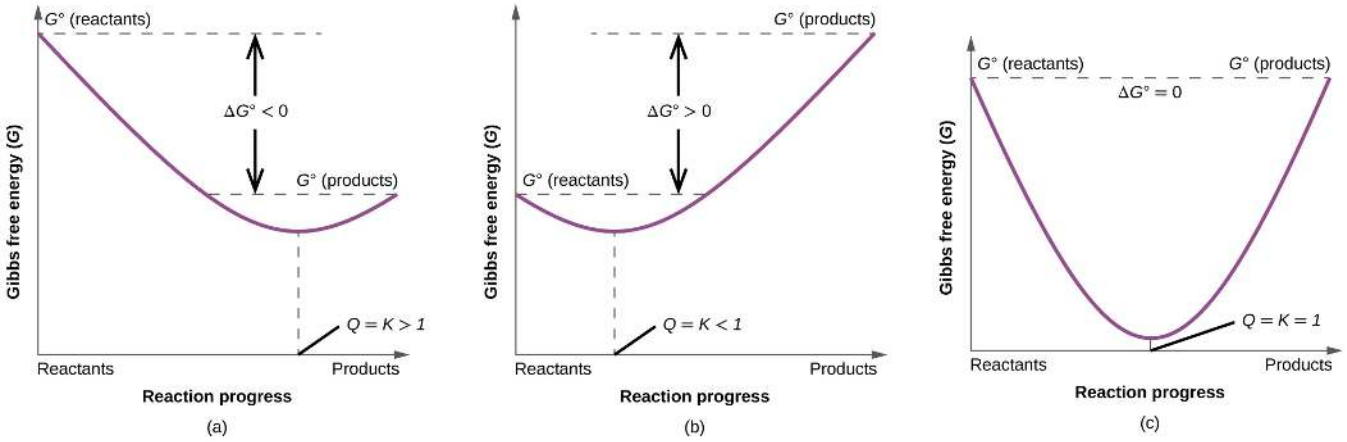


Figure **10.4.3**: These plots show the free energy versus reaction progress for systems whose standard free changes are (a) negative, (b) positive, and (c) zero. Nonequilibrium systems will proceed spontaneously in whatever direction is necessary to minimize free energy and establish equilibrium. Note that reactions with K equal to exactly 1.000 are rare.

Summary

Gibbs free energy (G) is a state function defined with regard to system quantities only and may be used to predict the spontaneity of a process. A negative value for ΔG indicates that the process will proceed in the forward direction to reach equilibrium; a positive ΔG indicates that the process will proceed in the reverse direction to reach equilibrium ; and a ΔG of zero indicates that the system is at equilibrium. A negative value for ΔG^o means that the reaction is product-favored at equilibrium. A positive value for ΔG^o means that the reaction is reactant-favored at equilibrium. If ΔG^o equals 0 (a rare occurrence), the reaction has roughly equal amounts of reactants and products at equilibrium.A number of approaches to the computation of free energy changes are possible.

Key Equations

- $\Delta G = \Delta H - T\Delta S$
- $\Delta G = \Delta G° + RT \ln Q$
- $\Delta G° = -RT \ln K$

Glossary

Gibbs free energy change (G)
thermodynamic property defined in terms of system enthalpy and entropy; all spontaneous processes involve a decrease in G

standard free energy change ($\Delta G°$)
change in free energy for a process occurring under standard conditions (1 bar pressure for gases, 1 M concentration for solutions)

standard free energy of formation (ΔG_f°)
change in free energy accompanying the formation of one mole of substance from its elements in their standard states

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10.E: Thermodynamics (Exercises)

16.1: Spontaneity Exercises

Q16.1.1

What is a spontaneous reaction?

S16.1.1

A reaction has a natural tendency to occur and takes place without the continual input of energy from an external source.

Q16.1.2

What is a nonspontaneous reaction?

Q16.1.3

Indicate whether the following processes are spontaneous or nonspontaneous.

a. Liquid water freezing at a temperature below its freezing point
b. Liquid water freezing at a temperature above its freezing point
c. The combustion of gasoline
d. A ball thrown into the air
e. A raindrop falling to the ground
f. Iron rusting in a moist atmosphere

S16.1.2

spontaneous; nonspontaneous; spontaneous; nonspontaneous; spontaneous; spontaneous

Q16.1.4

A helium-filled balloon spontaneously deflates overnight as He atoms diffuse through the wall of the balloon. Describe the redistribution of matter and/or energy that accompanies this process.

Q16.1.5

Many plastic materials are organic polymers that contain carbon and hydrogen. The oxidation of these plastics in air to form carbon dioxide and water is a spontaneous process; however, plastic materials tend to persist in the environment. Explain.

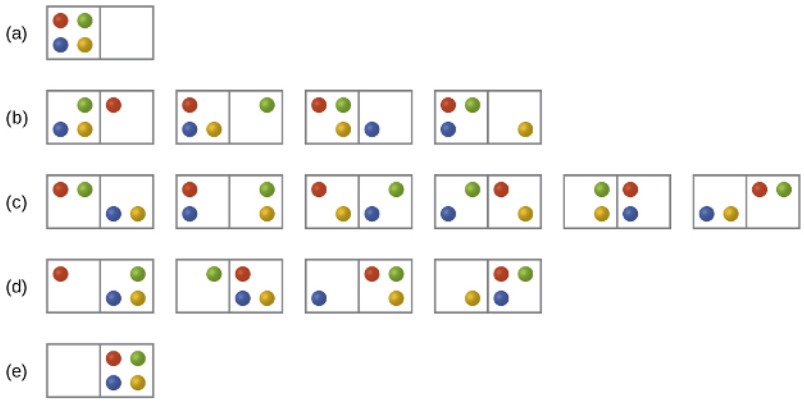
S16.1.5

Although the oxidation of plastics is spontaneous, the rate of oxidation is very slow. Plastics are therefore kinetically stable and do not decompose appreciably even over relatively long periods of time.

16.2: Entropy Exercises

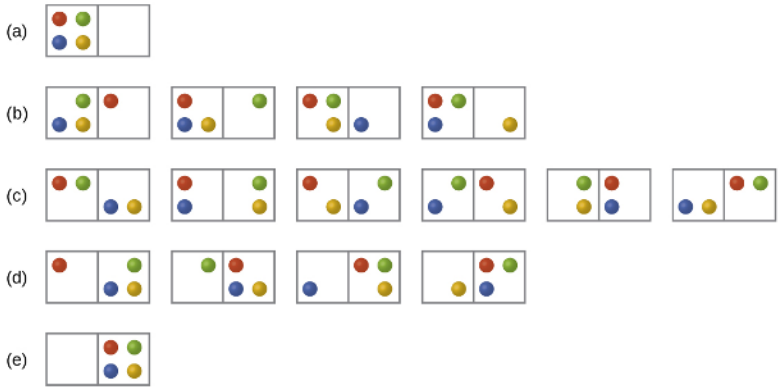
Q16.2.1

In the below Figure all possible distributions and microstates are shown for four different particles shared between two boxes. Determine the entropy change, ΔS, if the particles are initially evenly distributed between the two boxes, but upon redistribution all end up in Box (b).



Q16.2.2

In Figure all of the possible distributions and microstates are shown for four different particles shared between two boxes. Determine the entropy change, ΔS, for the system when it is converted from distribution to distribution (d).



S16.2.2

There are four initial microstates and four final microstates.

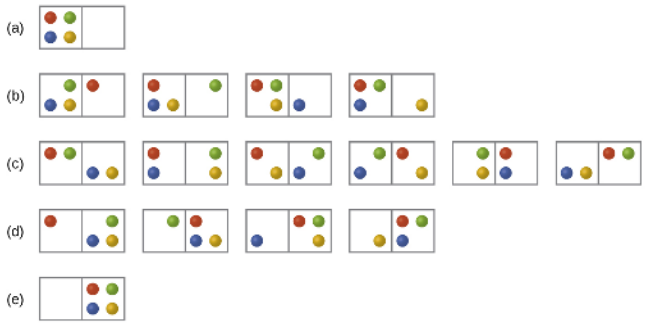
$$\Delta S = k \ln \frac{W_\mathrm{f}}{W_\mathrm{i}} = 1.38 \times 10^{-23}\ \mathrm{J/K} \times \ln \frac{4}{4} = 0 \tag{10.E.1}$$

Q16.2.3

How does the process described in the previous item relate to the system shown in [link]?

Q16.2.4

Consider a system similar to the one below, except that it contains six particles instead of four. What is the probability of having all the particles in only one of the two boxes in the case? Compare this with the similar probability for the system of four particles that we have derived to be equal to $\frac{1}{8}$. What does this comparison tell us about even larger systems?

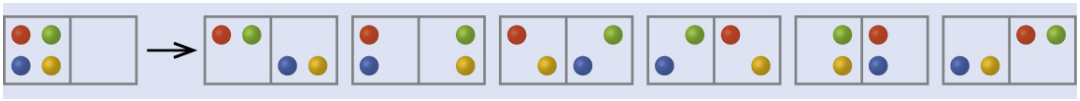


S16.2.4

The probability for all the particles to be on one side is $\frac{1}{32}$. This probability is noticeably lower than the $\frac{1}{8}$ result for the four-particle system. The conclusion we can make is that the probability for all the particles to stay in only one part of the system will decrease rapidly as the number of particles increases, and, for instance, the probability for all molecules of gas to gather in only one side of a room at room temperature and pressure is negligible since the number of gas molecules in the room is very large.

Q16.2.5

Consider the system shown in Figure. What is the change in entropy for the process where the energy is initially associated only with particle A, but in the final state the energy is distributed between two different particles?



Q16.2.6

Consider the system shown in Figure. What is the change in entropy for the process where the energy is initially associated with particles A and B, and the energy is distributed between two particles in different boxes (one in A-B, the other in C-D)?

S16.2.6

There is only one initial state. For the final state, the energy can be contained in pairs A-C, A-D, B-C, or B-D. Thus, there are four final possible states.

$$\Delta S = k \ln \left(\frac{W_f}{W_i} \right) = 1.38 \times 10^{-23}\ \text{J/K} \times \ln \left(\frac{4}{1} \right) = 1.91 \times 10^{-23}\ \text{J/K} \tag{10.E.2}$$

Q16.2.7

Arrange the following sets of systems in order of increasing entropy. Assume one mole of each substance and the same temperature for each member of a set.

a. $H_2(g)$, $HBrO_4(g)$, $HBr(g)$
b. $H_2O(l)$, $H_2O(g)$, $H_2O(s)$
c. $He(g)$, $Cl_2(g)$, $P_4(g)$

Q16.2.8

At room temperature, the entropy of the halogens increases from I_2 to Br_2 to Cl_2. Explain.

S16.2.8

The masses of these molecules would suggest the opposite trend in their entropies. The observed trend is a result of the more significant variation of entropy with a physical state. At room temperature, I_2 is a solid, Br_2 is a liquid, and Cl_2 is a gas.

Q16.2.9

Consider two processes: sublimation of $I_2(s)$ and melting of $I_2(s)$ (Note: the latter process can occur at the same temperature but somewhat higher pressure).

$$\mathrm{I_2}(s) \longrightarrow \mathrm{I_2}(g) \tag{10.E.3}$$

$$\mathrm{I_2}(s) \longrightarrow \mathrm{I_2}(l) \tag{10.E.4}$$

Is ΔS positive or negative in these processes? In which of the processes will the magnitude of the entropy change be greater?

Q16.2.11

Indicate which substance in the given pairs has the higher entropy value. Explain your choices.

a. $C_2H_5OH(l)$ or $C_3H_7OH(l)$
b. $C_2H_5OH(l)$ or $C_2H_5OH(g)$
c. 2Hor $H(g)$

S16.2.11

$C_3H_7OH(l)$ as it is a larger molecule (more complex and more massive), and so more microstates describing its motions are available at any given temperature. $C_2H_5OH(g)$ as it is in the gaseous state. $2H(g)$, since entropy is an extensive property, and so two H atoms (or two moles of H atoms) possess twice as much entropy as one atom (or one mole of atoms).

Q16.2.11

Predict the sign of the entropy change for the following processes:

a. An ice cube is warmed to near its melting point.
b. Exhaled breath forms fog on a cold morning.
c. Snow melts.

Q16.2.12

Predict the sign of the enthalpy change for the following processes. Give a reason for your prediction.

a. $\mathrm{Pb^{2+}}(aq) + \mathrm{S^{2-}}(aq) \longrightarrow \mathrm{PbS}(s)$
b. $2\,\mathrm{Fe}(s) + 3\,\mathrm{O_2}(g) \longrightarrow \mathrm{Fe_2O_3}(s)$
c. $2\,\mathrm{C_6H_{14}}(l) + 19\,\mathrm{O_2}(g) \longrightarrow 14\,\mathrm{H_2O}(g) + 12\,\mathrm{CO_2}(g)$

S16.2.12

Negative. The relatively ordered solid precipitating decreases the number of mobile ions in solution. Negative. There is a net loss of three moles of gas from reactants to products. Positive. There is a net increase of seven moles of gas from reactants to products.

Q16.2.13

Write the balanced chemical equation for the combustion of methane, $CH_4(g)$, to give carbon dioxide and water vapor. Explain why it is difficult to predict whether ΔS is positive or negative for this chemical reaction.

Q16.2.14

Write the balanced chemical equation for the combustion of benzene, $C_6H_6(l)$, to give carbon dioxide and water vapor. Would you expect ΔS to be positive or negative in this process?

S16.2.14

$$\mathrm{C_6H_6}(l) + 7.5\mathrm{O_2}(g) \longrightarrow 3\,\mathrm{H_2O}(g) + 6\,\mathrm{CO_2}(g) \tag{10.E.5}$$

There are 7.5 moles of gas initially, and 3 + 6 = 9 moles of gas in the end. Therefore, it is likely that the entropy increases as a result of this reaction, and ΔS is positive.

16.3: The Second and Third law

Q16.3.0

What is the difference between ΔS, $\Delta S°$, and ΔS°_{298} for a chemical change?

Q16.3.1

Calculate ΔS°_{298} for the following changes.

a. $\mathrm{SnCl_4}(l) \longrightarrow \mathrm{SnCl_4}(g)$
b. $\mathrm{CS_2}(g) \longrightarrow \mathrm{CS_2}(l)$
c. $\mathrm{Cu}(s) \longrightarrow \mathrm{Cu}(g)$
d. $\mathrm{H_2O}(l) \longrightarrow \mathrm{H_2O}(g)$
e. $2\,\mathrm{H_2}(g) + \mathrm{O_2}(g) \longrightarrow 2\,\mathrm{H_2O}(l)$
f. $2\,\mathrm{HCl}(g) + \mathrm{Pb}(s) \longrightarrow \mathrm{PbCl_2}(s) + \mathrm{H_2}(g)$
g. $\mathrm{Zn}(s) + \mathrm{CuSO_4}(s) \longrightarrow \mathrm{Cu}(s) + \mathrm{ZnSO_4}(s)$

S16.3.1

107 J/K; −86.4 J/K; 133.2 J/K; 118.8 J/K; −326.6 J/K; −171.9 J/K; (g) −7.2 J/K

Q16.3.2

Determine the entropy change for the combustion of liquid ethanol, C_2H_5OH, under standard state conditions to give gaseous carbon dioxide and liquid water.

Q16.3.3

Determine the entropy change for the combustion of gaseous propane, C_3H_8, under standard state conditions to give gaseous carbon dioxide and water.

S16.3.3

100.6 J/K

Q16.3.4

“Thermite” reactions have been used for welding metal parts such as railway rails and in metal refining. One such thermite reaction is:

$$\mathrm{Fe_2O_3}(s) + 2\,\mathrm{Al}(s) \longrightarrow \mathrm{Al_2O_3}(s) + 2\,\mathrm{Fe}(s) \tag{10.E.6}$$

Is the reaction spontaneous at room temperature under standard conditions? During the reaction, the surroundings absorb 851.8 kJ/mol of heat.

Q16.3.5

Using the relevant S°_{298} values listed in Appendix G, calculate S°_{298} for the following changes:

a. $\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \longrightarrow 2\,\mathrm{NH_3}(g)$
b. $\mathrm{N_2}(g) + \frac{5}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{N_2O_5}(g)$

S16.3.5

−198.1 J/K; −348.9 J/K

Q16.3.6

From the following information, determine ΔS°_{298} for the following:

a. $\mathrm{N}(g) + \mathrm{O}(g) \longrightarrow \mathrm{NO}(g) \quad \Delta S^\circ_{298} = ?$
b. $\mathrm{N_2}(g) + \mathrm{O_2}(g) \longrightarrow 2\,\mathrm{NO}(g) \quad \Delta S^\circ_{298} = 24.8\ \mathrm{J/K}$
c. $\mathrm{N_2}(g) \longrightarrow 2\,\mathrm{N}(g) \quad \Delta S^\circ_{298} = 115.0\ \mathrm{J/K}$
d. $\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{O}(g) \quad \Delta S^\circ_{298} = 117.0\ \mathrm{J/K}$

Q16.3.7

By calculating ΔS_{univ} at each temperature, determine if the melting of 1 mole of NaCl(s) is spontaneous at 500 °C and at 700 °C.

\[S^\circ_{\ce{NaCl}(s)}=\mathrm{72.11\:\dfrac{J}{mol·K}}\hspace{40px} S^\circ_{\ce{NaCl}(l)}=\mathrm{95.06\:\dfrac{J}{mol·K}}\hspace{40px} \Delta H^\circ_\ce{fusion}=\mathrm{27.95\: kJ/mol}\]

What assumptions are made about the thermodynamic information (entropy and enthalpy values) used to solve this problem?

S16.3.7

As $\Delta S_{\text{univ}} < 0$ at each of these temperatures, melting is not spontaneous at either of them. The given values for entropy and enthalpy are for NaCl at 298 K. It is assumed that these do not change significantly at the higher temperatures used in the problem.

Q16.3.8

Use the standard entropy data in Appendix G to determine the change in entropy for each of the reactions listed in [link]. All are run under standard state conditions and 25 °C.

Q16.3.8

2.86 J/K; 24.8 J/K; −113.2 J/K; −24.7 J/K; 15.5 J/K; 290.0 J/K

16.4: Free Energy

Q16.4.1

What is the difference between ΔG, $\Delta G°$, and ΔG°_{298} for a chemical change?

Q16.4.2

A reactions has ΔH°_{298} = 100 kJ/mol and $\Delta S^\circ_{298} = 250\ \text{J/mol·K}$. Is the reaction spontaneous at room temperature? If not, under what temperature conditions will it become spontaneous?

S16.4.2

The reaction is nonspontaneous at room temperature. Above 400 K, ΔG will become negative, and the reaction will become spontaneous.

Q16.4.3

Explain what happens as a reaction starts with $\Delta G < 0$ (negative) and reaches the point where $\Delta G = 0$.

Use the standard free energy of formation data in Appendix G to determine the free energy change for each of the following reactions, which are run under standard state conditions and 25 °C. Identify each as either spontaneous or nonspontaneous at these conditions.

a. $\ce{MnO2}(s) \longrightarrow \ce{Mn}(s) + \ce{O2}(g)$
b. $\ce{H2}(g) + \ce{Br2}(l) \longrightarrow 2\,\ce{HBr}(g)$
c. $\ce{Cu}(s) + \ce{S}(g) \longrightarrow \ce{CuS}(s)$
d. $2\,\ce{LiOH}(s) + \ce{CO2}(g) \longrightarrow \ce{Li2CO3}(s) + \ce{H2O}(g)$
e. $\ce{CH4}(g) + \ce{O2}(g) \longrightarrow \ce{C}(s,\ \text{graphite}) + 2\,\ce{H2O}(g)$
f. $\ce{CS2}(g) + 3\,\ce{Cl2}(g) \longrightarrow \ce{CCl4}(g) + \ce{S2Cl2}(g)$

S16.4.3

465.1 kJ nonspontaneous; −106.86 kJ spontaneous; −53.6 kJ spontaneous; −83.4 kJ spontaneous; −406.7 kJ spontaneous; −30.0 kJ spontaneous

Q16.4.4

Use the standard free energy data in Appendix G to determine the free energy change for each of the following reactions, which are run under standard state conditions and 25 °C. Identify each as either spontaneous or nonspontaneous at these conditions.

a. $\ce{C}(s,\ \text{graphite}) + \ce{O2}(g) \longrightarrow \ce{CO2}(g)$
b. $\ce{O2}(g) + \ce{N2}(g) \longrightarrow 2\,\ce{NO}(g)$
c. $2\,\ce{Cu}(s) + \ce{S}(g) \longrightarrow \ce{Cu2S}(s)$

d. $\mathrm{CaO}(s) + \mathrm{H_2O}(l) \longrightarrow \mathrm{Ca(OH)_2}(s)$
e. $\mathrm{Fe_2O_3}(s) + 3\,\mathrm{CO}(g) \longrightarrow 2\,\mathrm{Fe}(s) + 3\,\mathrm{CO_2}(g)$
f. $\mathrm{CaSO_4 \cdot 2\,H_2O}(s) \longrightarrow \mathrm{CaSO_4}(s) + 2\,\mathrm{H_2O}(g)$

Given:

$$\mathrm{P_4}(s) + 5\,\mathrm{O_2}(g) \longrightarrow \mathrm{P_4O_{10}}(s) \quad \Delta G^\circ_{298} = -2697.0\ \mathrm{kJ/mol} \tag{10.E.7}$$

$$2\,\mathrm{H_2}(g) + \mathrm{O_2}(g) \longrightarrow 2\,\mathrm{H_2O}(g) \quad \Delta G^\circ_{298} = -457.18\ \mathrm{kJ/mol} \tag{10.E.8}$$

$$6\,\mathrm{H_2O}(g) + \mathrm{P_4O_{10}}(g) \longrightarrow 4\,\mathrm{H_3PO_4}(l) \quad \Delta G^\circ_{298} = -428.66\ \mathrm{kJ/mol} \tag{10.E.9}$$

Q16.4.5

a. Determine the standard free energy of formation, ΔG°_f, for phosphoric acid.
b. How does your calculated result compare to the value in Appendix G? Explain.

S16.4.5

−1124.3 kJ/mol for the standard free energy change. The calculation agrees with the value in Appendix G because free energy is a state function (just like the enthalpy and entropy), so its change depends only on the initial and final states, not the path between them.

Q16.4.6

Is the formation of ozone ($O_3(g)$) from oxygen ($O_2(g)$) spontaneous at room temperature under standard state conditions?

Q16.4.7

Consider the decomposition of red mercury(II) oxide under standard state conditions.

$$2\,\mathrm{HgO}(s,\ \mathrm{red}) \longrightarrow 2\,\mathrm{Hg}(l) + \mathrm{O_2}(g) \tag{10.E.10}$$

a. Is the decomposition spontaneous under standard state conditions?
b. Above what temperature does the reaction become spontaneous?

S16.4.7

The reaction is nonspontaneous; Above 566 °C the process is spontaneous.

Q16.4.8

Among other things, an ideal fuel for the control thrusters of a space vehicle should decompose in a spontaneous exothermic reaction when exposed to the appropriate catalyst. Evaluate the following substances under standard state conditions as suitable candidates for fuels.

a. Ammonia: $2\,\mathrm{NH_3}(g) \longrightarrow \mathrm{N_2}(g) + 3\,\mathrm{H_2}(g)$
b. Diborane: $\mathrm{B_2H_6}(g) \longrightarrow 2\,\mathrm{B}(g) + 3\,\mathrm{H_2}(g)$
c. Hydrazine: $\mathrm{N_2H_4}(g) \longrightarrow \mathrm{N_2}(g) + 2\,\mathrm{H_2}(g)$
d. Hydrogen peroxide: $\mathrm{H_2O_2}(l) \longrightarrow \mathrm{H_2O}(g) + \frac{1}{2}\mathrm{O_2}(g)$

Q16.4.9

Calculate ΔG° for each of the following reactions from the equilibrium constant at the temperature given.

a. $\mathrm{N_2}(g) + \mathrm{O_2}(g) \longrightarrow 2\,\mathrm{NO}(g) \quad \mathrm{T} = 2000\ ^\circ\mathrm{C} \quad K_p = 4.1 \times 10^{-4}$
b. $\mathrm{H_2}(g) + \mathrm{I_2}(g) \longrightarrow 2\,\mathrm{HI}(g) \quad \mathrm{T} = 400\ ^\circ\mathrm{C} \quad K_p = 50.0$
c. $\mathrm{CO_2}(g) + \mathrm{H_2}(g) \longrightarrow \mathrm{CO}(g) + \mathrm{H_2O}(g) \quad \mathrm{T} = 980\ ^\circ\mathrm{C} \quad K_p = 1.67$
d. $\mathrm{CaCO_3}(s) \longrightarrow \mathrm{CaO}(s) + \mathrm{CO_2}(g) \quad \mathrm{T} = 900\ ^\circ\mathrm{C} \quad K_p = 1.04$
e. $\mathrm{HF}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{H_3O^+}(aq) + \mathrm{F^-}(aq) \quad \mathrm{T} = 25\ ^\circ\mathrm{C} \quad K_p = 7.2 \times 10^{-4}$
f. $\mathrm{AgBr}(s) \longrightarrow \mathrm{Ag^+}(aq) + \mathrm{Br^-}(aq) \quad \mathrm{T} = 25\ ^\circ\mathrm{C} \quad K_p = 3.3 \times 10^{-13}$

S16.4.9

1.5×10^2 kJ; −21.9 kJ; −5.34 kJ; −0.383 kJ; 18 kJ; 71 kJ

Q16.4.10

Calculate $\Delta G°$ for each of the following reactions from the equilibrium constant at the temperature given.

a. $\mathrm{Cl_2}(g) + \mathrm{Br_2}(g) \longrightarrow 2\,\mathrm{BrCl}(g) \quad \mathrm{T} = 25\ °\mathrm{C} \quad K_p = 4.7 \times 10^{-2}$
b. $2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{SO_3}(g) \quad \mathrm{T} = 500\ °\mathrm{C} \quad K_p = 48.2$
c. $\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2O}(g) \quad \mathrm{T} = 60\ °\mathrm{C} \quad K_p = 0.196\ \mathrm{atm}$
d. $\mathrm{CoO}(s) + \mathrm{CO}(g) \rightleftharpoons \mathrm{Co}(s) + \mathrm{CO_2}(g) \quad \mathrm{T} = 550\ °\mathrm{C} \quad K_p = 4.90 \times 10^2$
e. $\mathrm{CH_3NH_2}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{CH_3NH_3^+}(aq) + \mathrm{OH^-}(aq) \quad \mathrm{T} = 25\ °\mathrm{C} \quad K_p = 4.4 \times 10^{-4}$
f. $\mathrm{PbI_2}(s) \longrightarrow \mathrm{Pb^{2+}}(aq) + 2\,\mathrm{I^-}(aq) \quad \mathrm{T} = 25\ °\mathrm{C} \quad K_p = 8.7 \times 10^{-9}$

Q16.4.11

Calculate the equilibrium constant at 25 °C for each of the following reactions from the value of $\Delta G°$ given.

a. $\mathrm{O_2}(g) + 2\,\mathrm{F_2}(g) \longrightarrow 2\,\mathrm{OF_2}(g) \quad \Delta G° = -9.2\ \mathrm{kJ}$
b. $\mathrm{I_2}(s) + \mathrm{Br_2}(l) \longrightarrow 2\,\mathrm{IBr}(g) \quad \Delta G° = 7.3\ \mathrm{kJ}$
c. $2\,\mathrm{LiOH}(s) + \mathrm{CO_2}(g) \longrightarrow \mathrm{Li_2CO_3}(s) + \mathrm{H_2O}(g) \quad \Delta G° = -79\ \mathrm{kJ}$
d. $\mathrm{N_2O_3}(g) \longrightarrow \mathrm{NO}(g) + \mathrm{NO_2}(g) \quad \Delta G° = -1.6\ \mathrm{kJ}$
e. $\mathrm{SnCl_4}(l) \longrightarrow \mathrm{SnCl_4}(l) \quad \Delta G° = 8.0\ \mathrm{kJ}$

S16.4.11

K = 41; K = 0.053; $K = 6.9 \times 10^{13}$; K = 1.9; K = 0.04

Q16.4.2

Calculate the equilibrium constant at 25 °C for each of the following reactions from the value of $\Delta G°$ given.

a. $\mathrm{I_2}(s) + \mathrm{Cl_2}(g) \longrightarrow 2\,\mathrm{ICl}(g) \quad \Delta G° = -10.88\ \mathrm{kJ}$
b. $\mathrm{H_2}(g) + \mathrm{I_2}(s) \longrightarrow 2\,\mathrm{HI}(g) \quad \Delta G° = 3.4\ \mathrm{kJ}$
c. $\mathrm{CS_2}(g) + 3\,\mathrm{Cl_2}(g) \longrightarrow \mathrm{CCl_4}(g) + \mathrm{S_2Cl_2}(g) \quad \Delta G° = -39\ \mathrm{kJ}$
d. $2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g) \longrightarrow 2\,\mathrm{SO_3}(g) \quad \Delta G° = -141.82\ \mathrm{kJ}$
e. $\mathrm{CS_2}(g) \longrightarrow \mathrm{CS_2}(l) \quad \Delta G° = -1.88\ \mathrm{kJ}$

Q16.4.13

Calculate the equilibrium constant at the temperature given.

a. (a) $\mathrm{O_2}(g) + 2\,\mathrm{F_2}(g) \longrightarrow 2\,\mathrm{F_2O}(g) \quad (\mathrm{T} = 100\ °\mathrm{C})$
b. $\mathrm{I_2}(s) + \mathrm{Br_2}(l) \longrightarrow 2\,\mathrm{IBr}(g) \quad (\mathrm{T} = 0.0\ °\mathrm{C})$
c. $2\,\mathrm{LiOH}(s) + \mathrm{CO_2}(g) \longrightarrow \mathrm{Li_2CO_3}(s) + \mathrm{H_2O}(g) \quad (\mathrm{T} = 575\ °\mathrm{C})$
d. $\mathrm{N_2O_3}(g) \longrightarrow \mathrm{NO}(g) + \mathrm{NO_2}(g) \quad (\mathrm{T} = -10.0\ °\mathrm{C})$
e. $\mathrm{SnCl_4}(l) \longrightarrow \mathrm{SnCl_4}(g) \quad (\mathrm{T} = 200\ °\mathrm{C})$

S16.4.13

In each of the following, the value of ΔG is not given at the temperature of the reaction. Therefore, we must calculate $\Delta G°$ from the values $\Delta H°$ and $\Delta S°$ and then calculate ΔG from the relation $\Delta G° = \Delta H° - T\Delta S°$.

a. K = 1.29
b. $K = 2.51 \times 10^{-3}$
c. $K = 4.83 \times 10^3$
d. K = 0.219
e. K = 16.1

Q16.4.14

Calculate the equilibrium constant at the temperature given.

a. (a) $\mathrm{I_2}(s) + \mathrm{Cl_2}(g) \longrightarrow 2\,\mathrm{ICl}(g)$ $(\mathrm{T} = 100\ ^\circ\mathrm{C})$
b. $\mathrm{H_2}(g) + \mathrm{I_2}(s) \longrightarrow 2\,\mathrm{HI}(g)$ $(\mathrm{T} = 0.0\ ^\circ\mathrm{C})$
c. $\mathrm{CS_2}(g) + 3\,\mathrm{Cl_2}(g) \longrightarrow \mathrm{CCl_4}(g) + \mathrm{S_2Cl_2}(g)$ $(\mathrm{T} = 125\ ^\circ\mathrm{C})$
d. $2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g) \longrightarrow 2\,\mathrm{SO_3}(g)$ $(\mathrm{T} = 675\ ^\circ\mathrm{C})$
e. $\mathrm{CS_2}(g) \longrightarrow \mathrm{CS_2}(l)$ $(\mathrm{T} = 90\ ^\circ\mathrm{C})$

Q16.4.15

Consider the following reaction at 298 K:

$$\mathrm{N_2O_4}(g) \rightleftharpoons 2\,\mathrm{NO_2}(g) \quad K_P = 0.142 \tag{10.E.11}$$

What is the standard free energy change at this temperature? Describe what happens to the initial system, where the reactants and products are in standard states, as it approaches equilibrium.

S16.4.16

The standard free energy change is $\Delta G^\circ_{298} = -RT\ln K = 4.84\ \mathrm{kJ/mol}$. When reactants and products are in their standard states (1 bar or 1 atm), Q = 1. As the reaction proceeds toward equilibrium, the reaction shifts left (the amount of products drops while the amount of reactants increases): $Q < 1$, and ΔG_{298} becomes less positive as it approaches zero. At equilibrium, $Q = K$, and $\Delta G = 0$.

Q16.4.17

Determine the normal boiling point (in kelvin) of dichloroethane, CH_2Cl_2. Find the actual boiling point using the Internet or some other source, and calculate the percent error in the temperature. Explain the differences, if any, between the two values.

Q16.4.18

Under what conditions is $\mathrm{N_2O_3}(g) \longrightarrow \mathrm{NO}(g) + \mathrm{NO_2}(g)$ spontaneous?

S16.4.18

The reaction will be spontaneous at temperatures greater than 287 K.

Q16.4.19

At room temperature, the equilibrium constant (K_w) for the self-ionization of water is 1.00×10^{-14}. Using this information, calculate the standard free energy change for the aqueous reaction of hydrogen ion with hydroxide ion to produce water. (Hint: The reaction is the reverse of the self-ionization reaction.)

Q16.4.20

Hydrogen sulfide is a pollutant found in natural gas. Following its removal, it is converted to sulfur by the reaction $2\,\mathrm{H_2S}(g) + \mathrm{SO_2}(g) \rightleftharpoons \frac{3}{8}\mathrm{S_8}(s,\ \text{rhombic}) + 2\,\mathrm{H_2O}(l)$. What is the equilibrium constant for this reaction? Is the reaction endothermic or exothermic?

S16.4.20

$K = 5.35 \times 10^{15}$

The process is exothermic.

Q16.4.21

Consider the decomposition of $CaCO_3(s)$ into $CaO(s)$ and $CO_2(g)$. What is the equilibrium partial pressure of CO_2 at room temperature?

Q16.4.22

In the laboratory, hydrogen chloride ($HCl(g)$) and ammonia ($NH_3(g)$) often escape from bottles of their solutions and react to form the ammonium chloride ($NH_4Cl(s)$), the white glaze often seen on glassware. Assuming that the number of moles of each gas that escapes into the room is the same, what is the maximum partial pressure of HCl and NH_3 in the laboratory at room temperature? (Hint: The partial pressures will be equal and are at their maximum value when at equilibrium.)

S16.4.22

1.0×10^{-8} atm. This is the maximum pressure of the gases under the stated conditions.

Q16.4.23

Benzene can be prepared from acetylene. $\mathbf{3\,C_2H_2}(g) \rightleftharpoons \mathbf{C_6H_6}(g)$. Determine the equilibrium constant at 25 °C and at 850 °C. Is the reaction spontaneous at either of these temperatures? Why is all acetylene not found as benzene?

Q16.4.24

Carbon dioxide decomposes into CO and O_2 at elevated temperatures. What is the equilibrium partial pressure of oxygen in a sample at 1000 °C for which the initial pressure of CO_2 was 1.15 atm?

$$x = 1.29 \times 10^{-5}\ \text{atm} = P_{O_2} \tag{10.E.12}$$

Q16.4.25

Carbon tetrachloride, an important industrial solvent, is prepared by the chlorination of methane at 850 K.

$$\mathbf{CH_4}(g) + \mathbf{4\,Cl_2}(g) \longrightarrow \mathbf{CCl_4}(g) + \mathbf{4\,HCl}(g) \tag{10.E.13}$$

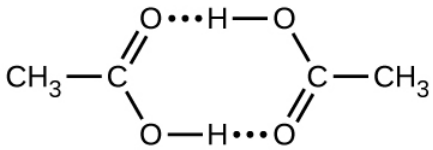
What is the equilibrium constant for the reaction at 850 K? Would the reaction vessel need to be heated or cooled to keep the temperature of the reaction constant?

Q16.4.25B

Acetic acid, CH_3CO_2H, can form a dimer, $(CH_3CO_2H)_2$, in the gas phase.

$$\mathbf{2\,CH_3CO_2H}(g) \longrightarrow \mathbf{(CH_3CO_2H)_2}(g) \tag{10.E.14}$$

The dimer is held together by two hydrogen bonds with a total strength of 66.5 kJ per mole of dimer.



At 25 °C, the equilibrium constant for the dimerization is 1.3×10^3 (pressure in atm). What is $\Delta S°$ for the reaction?

S16.4.25B

−0.16 kJ

Q16.4.26

Nitric acid, HNO_3, can be prepared by the following sequence of reactions:

$$\mathbf{4\,NH_3}(g) + \mathbf{5\,O_2}(g) \longrightarrow \mathbf{4\,NO}(g) + \mathbf{6\,H_2O}(g) \tag{10.E.15}$$

$$\mathbf{2\,NO}(g) + \mathbf{O_2}(g) \longrightarrow \mathbf{2\,NO_2}(g) \tag{10.E.16}$$

$$\mathbf{3\,NO_2}(g) + \mathbf{H_2O}(l) \longrightarrow \mathbf{2\,HNO_3}(l) + \mathbf{NO}(g) \tag{10.E.17}$$

How much heat is evolved when 1 mol of $NH_3(g)$ is converted to $HNO_3(l)$? Assume standard states at 25 °C.

Q16.4.27A

Determine ΔG for the following reactions.

(a) Antimony pentachloride decomposes at 448 °C. The reaction is:

$$\mathrm{SbCl_5}(g) \longrightarrow \mathrm{SbCl_3}(g) + \mathrm{Cl_2}(g) \tag{10.E.18}$$

An equilibrium mixture in a 5.00 L flask at 448 °C contains 3.85 g of $SbCl_5$, 9.14 g of $SbCl_3$, and 2.84 g of Cl_2.

Chlorine molecules dissociate according to this reaction:

$$\mathrm{Cl_2}(g) \longrightarrow 2\,\mathrm{Cl}(g) \tag{10.E.19}$$

1.00% of Cl_2 molecules dissociate at 975 K and a pressure of 1.00 atm.

S16.4.27A

a. (a) −22.1 kJ;
b. 61.6 kJ/mol

Q16.4.27

Given that the ΔG_f° for $Pb^{2+}(aq)$ and $Cl^-(aq)$ is −24.3 kJ/mole and −131.2 kJ/mole respectively, determine the solubility product, K_{sp}, for $PbCl_2(s)$.

Q16.4.28

Determine the standard free energy change, ΔG_f°, for the formation of $S^{2-}(aq)$ given that the ΔG_f° for $Ag^+(aq)$ and $Ag_2S(s)$ are 77.1 k/mole and −39.5 kJ/mole respectively, and the solubility product for $Ag_2S(s)$ is 8×10^{-51}.

S16.4.28

90 kJ/mol

Q16.4.29

Determine the standard enthalpy change, entropy change, and free energy change for the conversion of diamond to graphite. Discuss the spontaneity of the conversion with respect to the enthalpy and entropy changes. Explain why diamond spontaneously changing into graphite is not observed.

Q16.4.30

The evaporation of one mole of water at 298 K has a standard free energy change of 8.58 kJ.

$$\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2O}(g) \quad \Delta G^\circ_{298} = 8.58\ \mathrm{kJ} \tag{10.E.20}$$

a. (a) Is the evaporation of water under standard thermodynamic conditions spontaneous?
b. Determine the equilibrium constant, K_P, for this physical process.
c. By calculating ΔG, determine if the evaporation of water at 298 K is spontaneous when the partial pressure of water, P_{H_2O}, is 0.011 atm.
d. If the evaporation of water were always nonspontaneous at room temperature, wet laundry would never dry when placed outside. In order for laundry to dry, what must be the value of P_{H_2O} in the air?

S16.4.30

(a) Under standard thermodynamic conditions, the evaporation is nonspontaneous; K_p = 0.031; The evaporation of water is spontaneous; P_{H_2O} must always be less than K_p or less than 0.031 atm. 0.031 atm represents air saturated with water vapor at 25 °C, or 100% humidity.

Q16.4.31

In glycolysis, the reaction of glucose (Glu) to form glucose-6-phosphate (G6P) requires ATP to be present as described by the following equation:

$$\mathrm{Glu + ATP \longrightarrow G6P + ADP} \quad \Delta G^\circ_{298} = -17\ \mathrm{kJ} \tag{10.E.21}$$

In this process, ATP becomes ADP summarized by the following equation:

$$\mathrm{ATP \longrightarrow ADP} \quad \Delta G^\circ_{298} = -30\ \mathrm{kJ} \tag{10.E.22}$$

Determine the standard free energy change for the following reaction, and explain why ATP is necessary to drive this process:

$$\mathrm{Glu \longrightarrow G6P} \quad \Delta G^\circ_{298} = ? \tag{10.E.23}$$

Q16.4.32

One of the important reactions in the biochemical pathway glycolysis is the reaction of glucose-6-phosphate (G6P) to form fructose-6-phosphate (F6P):

$$\mathrm{G6P \rightleftharpoons F6P} \quad \Delta G^\circ_{298} = 1.7\ \mathrm{kJ} \tag{10.E.24}$$

a. (a) Is the reaction spontaneous or nonspontaneous under standard thermodynamic conditions?
b. Standard thermodynamic conditions imply the concentrations of G6P and F6P to be 1 *M*, however, in a typical cell, they are not even close to these values. Calculate ΔG when the concentrations of G6P and F6P are 120 μ*M* and 28 μ*M* respectively, and discuss the spontaneity of the forward reaction under these conditions. Assume the temperature is 37 °C.

S16.4.32

(a) Nonspontaneous as $\Delta G^\circ_{298} > 0$; $\Delta G^\circ_{298} = -RT\ln K$, $\Delta G = 1.7 \times 10^3 + \left(8.314 \times 335 \times \ln\frac{28}{128}\right) = -2.5\ \mathrm{kJ}$. The forward reaction to produce F6P is spontaneous under these conditions.

Q16.4.33

Without doing a numerical calculation, determine which of the following will reduce the free energy change for the reaction, that is, make it less positive or more negative, when the temperature is increased. Explain.

a. (a) $\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \longrightarrow 2\,\mathrm{NH_3}(g)$
b. $\mathrm{HCl}(g) + \mathrm{NH_3}(g) \longrightarrow \mathrm{NH_4Cl}(s)$
c. $\mathrm{(NH_4)_2Cr_2O_7}(s) \longrightarrow \mathrm{Cr_2O_3}(s) + 4\,\mathrm{H_2O}(g) + \mathrm{N_2}(g)$
d. $2\,\mathrm{Fe}(s) + 3\,\mathrm{O_2}(g) \longrightarrow \mathrm{Fe_2O_3}(s)$

When ammonium chloride is added to water and stirred, it dissolves spontaneously and the resulting solution feels cold. Without doing any calculations, deduce the signs of ΔG, ΔH, and ΔS for this process, and justify your choices.

S16.4.33

ΔG is negative as the process is spontaneous. ΔH is positive as with the solution becoming cold, the dissolving must be endothermic. ΔS must be positive as this drives the process, and it is expected for the dissolution of any soluble ionic compound.

Q16.4.34

An important source of copper is from the copper ore, chalcocite, a form of copper(I) sulfide. When heated, the Cu_2S decomposes to form copper and sulfur described by the following equation:

$$\mathrm{Cu_2S}(s) \longrightarrow \mathrm{Cu}(s) + \mathrm{S}(s) \tag{10.E.25}$$

a. (a) Determine ΔG°_{298} for the decomposition of $Cu_2S(s)$.
b. The reaction of sulfur with oxygen yields sulfur dioxide as the only product. Write an equation that describes this reaction, and determine ΔG°_{298} for the process.
c. The production of copper from chalcocite is performed by roasting the Cu_2S in air to produce the Cu. By combining the equations from Parts (a) and (b), write the equation that describes the roasting of the chalcocite, and explain why coupling these reactions together makes for a more efficient process for the production of the copper.

Q16.4.35

What happens to ΔG°_{298} (becomes more negative or more positive) for the following chemical reactions when the partial pressure of oxygen is increased?

a. (a) $\mathrm{S}(s) + \mathrm{O_2}(g) \longrightarrow \mathrm{SO_2}(g)$
b. $2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g) \longrightarrow \mathrm{SO_3}(g)$
c. $\mathrm{HgO}(s) \longrightarrow \mathrm{Hg}(l) + \mathrm{O_2}(g)$

S16.4.35

a. (a) Increasing $P_{\mathrm{O_2}}$ will shift the equilibrium toward the products, which increases the value of K. ΔG°_{298} therefore becomes more negative.
b. Increasing $P_{\mathrm{O_2}}$ will shift the equilibrium toward the products, which increases the value of K. ΔG°_{298} therefore becomes more negative.
c. Increasing $P_{\mathrm{O_2}}$ will shift the equilibrium the reactants, which decreases the value of K. ΔG°_{298} therefore becomes more positive.

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Glossary

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