



Chemistry

The Core Concepts

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KONA

PUBLISHING & MEDIA GROUP

CHEMISTRY

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ABOUT THIS E-TEXT

This textbook is an attempt to provide a rigorous but learner-friendly introduction to Chemistry. This textbook should serve the needs of science and non-science majors alike.

1. the very first concepts are defined in simple terms that even someone with a minimal background in science can understand
2. the order of presentation of topics is meticulously chosen so that sufficient background has been provided by the time each new concept is introduced
3. examples are immediately provided to illustrate and/or apply each new concept
4. “test yourself” questions provide additional reinforcement
5. useful physics and math background/review, often relegated to appendices in typical textbooks, are integrated into the development of the topics
6. A companion website (i-assign.com) provides:
 - a. links to videos explaining answers to “test yourself” questions
 - b. study tips and links to useful and entertaining web resources
 - c. additional study questions that can be assigned as computer-graded homework.

For alternative sequencing of topics (for a typical first-semester course), it is useful to organize the chapters into the following learning units:

Unit 1: Introductory Concepts (Ch. 1–8)

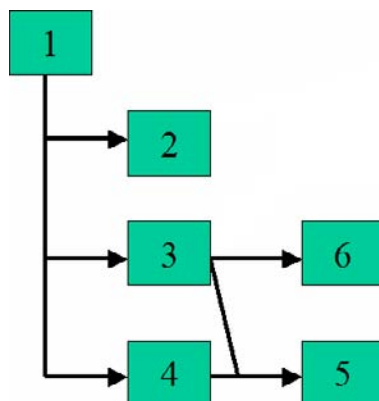
Unit 2: Atomic and Molecular Structure and Properties (Ch. 9–16)


Unit 3: Counting Atoms, Molecules, and Ions (Ch. 17–20)

Unit 4: Reactions in Aqueous Solutions (Ch. 21)

Unit 5: Molarity and solution stoichiometry (Ch. 22)

Unit 6: Ideal gas behavior and gas stoichiometry (Ch. 23–26)





Units 2, 3, and 4 may be covered in any order after Unit 1. Units 3 and 4 must be covered before Unit 5. Unit 3 must be covered before Unit 6 or 8. Units 2 and 6 must be covered before Unit 7. Units 5 and 6 must be covered before Unit 9.

The companion website, i-Assign.com, is a web-based homework delivery and collection system, as well as a test bank authoring system and test generator. The automation afforded by i-Assign reduces a teacher's workload while providing the following benefits.

1. By setting periodic deadlines for graded homework, teachers are able to encourage students to study on a regular basis and focus on a manageable amount of material.
2. Teachers can set up practice homework to give students more opportunities for mastery.
3. Homework and test individualization minimizes cheating.
4. Teachers can add their own questions.
5. Multiple versions of a test, which can be printed or delivered online, can be easily generated.



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What is Chemistry?

1.1 Science

Chemistry is a science, so we begin by defining science. *Science* is a study that seeks to understand something based on empirical (or factual) information. Major ideas in science are consistent with unbiased and verifiable facts; they are not mere opinions. A more thorough way of defining science is to describe what scientists do. Scientists:

- conduct research to acquire knowledge or solve problems.
- summarize knowledge into laws and theories.
- disseminate knowledge.


1.1.1 Scientific Research

Scientists engage in research to acquire knowledge. In doing so, they follow a procedure called the *Scientific Method*. It involves the following:

- Formulating the question or problem.
- Formulating a hypothesis.
- Conducting experiments to test a hypothesis.
- Analyzing experimental results and making a conclusion.

A *hypothesis* is a tentative answer to a question or problem and is defined as an educated guess. What makes it educated? A scientist tries to find out as much of what is known or related to the problem before making a hypothesis. This is done by reading scientific publications (the scientific *literature*), making observations, and relating the observations to what is already known from experience. *Observations* or *data* are factual information based on what is sensed (seen, touched, heard, tasted, smelled) or measured.

A hypothesis must be testable. It is tested by doing an *experiment*. Observations made or data collected in an experiment should be reproducible. Performing *replicate measurements* (multiple trials) is standard procedure in scientific work. Things that could affect the outcome of an experiment are called *variables*. A common type of research attempts to establish relationships between two variables. In this case, a series of



experiments is performed where one variable (the *independent variable*) is deliberately chosen as another variable is measured (*dependent variable*). When doing this type of research, it is important to try to identify all the other possible independent variables and hold all of those variables constant.

The *analysis of experimental results* should attempt to determine if they support the hypothesis. The experimental results may be inconsistent with the hypothesis and lead one to a *conclusion* that the hypothesis needs to be rejected or revised. If the hypothesis is revised, further experiments obviously need to be done.

► Example

A patient comes into a doctor's office with an illness. The first question that a doctor might try to answer is "what is the illness".

- (a) What would the doctor have to do to formulate a hypothesis?
- (b) Suppose the doctor's hypothesis is that the illness is something due to a certain type of bacteria. What experiment could be done to test the hypothesis?

Answers:

- (a) The doctor could examine the symptoms (patient's temperature, rashes, etc.) and ask the patient about other symptoms, previous illnesses, medication the patient may be currently taking, etc. The doctor could then relate the information to what he has learned from medical school and his experiences with previous patients. The doctor could also refer to medical publications.
- (b) There may be established laboratory procedures for detecting the presence of the bacteria in a blood or urine sample. If the test turns out to be negative, then the doctor will have to come up with another hypothesis.

1.1.2 Disseminating Knowledge

Sharing of information is important for the advancement of knowledge. Once a scientist reaches a conclusion about a novel problem that others could find useful, it is important that the information be disseminated. One way this is done is by writing a paper that describes the work. The paper should not only present the results, but should also describe the procedures in sufficient detail so that other scientists can duplicate the experiments and verify the results. The paper is then submitted for *publication* in scientific journals. Reputable journals use a *peer review* process; articles submitted for publication are sent to other scientists to examine for reliability.



1.1.3 Laws and Theories

Organizing and summarizing information are important for the advancement of knowledge. Scientists do these by formulating laws and theories.


A pattern tends to emerge when *numerous* related observations are examined. A statement that summarizes the pattern is called a *law* (of nature). For example, the statement “heat naturally flows from a hot object to a colder one” is a law of nature. For us to be able to say that this is a law, we must have made this observation numerous times. Laws generally have no known exceptions *at the time they are formulated*. Over time, exceptions might be found, but it is customary to still refer to the original statement as a law. Oftentimes, the statement of a law specifies exceptions; such a law is called a *limiting law*. A law can be written in the form of a mathematical equation; an example is the so-called ideal gas law, $PV = nRT$. The ideal gas law is an example of a limiting law; it is only valid as P approaches zero.

The word *theory* is often mistakenly used when referring to a hypothesis. This may be fine in layman’s terms, but not in science. In science, theory and hypothesis are not the same. A theory is a set of fundamental ideas that is consistent with everything (observations and laws) that is known about a subject. These fundamental ideas are called *postulates*. The postulates of a theory are *assumptions*; they *cannot* be proven to be true but they are accepted for as long as there are no known exceptions. Laws with no known exceptions could be among the postulates of a theory. A theory becomes widely accepted (or *well-established*) if there is overwhelming evidence to support it. All one needs to disprove a theory is one fact that contradicts one of the postulates of the theory. However, should such an exception be found, it is typically not necessary to discard a theory; rather, one or more postulates is/are modified in order to account for the exception. The more a theory has been modified, the more reliable it becomes. So what is the difference between a hypothesis and a theory? A hypothesis is an educated attempt to explain or predict something. A good way to come up with an educated explanation or prediction is to examine the known facts in light of a well-established theory. If you do that, you could say that your hypothesis is a *theoretical explanation* or a *theoretical prediction* but it is not the theory.

1.2 Chemistry and Related Disciplines

Chemistry is an example of a natural science. In a *natural science*, the “thing” that we seek to understand is nature itself. Other examples of natural sciences are physics, biology, geology, and astronomy.

Physics and Chemistry, the *physical sciences*, are both defined as the study of matter and its properties. *Matter* is the stuff that the universe is made of; anything that has mass



and occupies space. The term *property* refers to characteristics of matter, such as color, taste, melting point, boiling point, etc. Physics focuses on the mathematical description of the most basic property of matter, motion. Physicists precisely define concepts such as force, energy, heat, light, and electric charge to summarize everything that is known about motion into a few fundamental equations. Chemistry, on the other hand, focuses on transformations of matter; we call these transformations *chemical changes* or *chemical reactions*. Chemists try to understand matter in terms of the idea that all matter is made up of tiny particles called *atoms*, and in terms of theories about how these particles behave. We could say that *chemists study matter from an atomic perspective*. Chemists study *macroscopic* or bulk systems (things we can see) and interpret the results from a *microscopic* standpoint. In Chemistry, the word microscopic refers to atomic sizes, which are much smaller than cells in living things. You could say that what a chemist calls microscopic, a biologist would call sub-microscopic.

Why study Chemistry? By understanding atoms, we are better able to make matter behave the way we want it to. A strong motivation for studying science is that it allows us to develop technology that would make our lives better; the word *technology* refers to the practical application of science. Here are some examples of practical applications of Chemistry: how to make a drug more potent and have fewer side effects, how to make something taste more like sugar but less fattening, how to make a battery produce more current over a shorter period of time, how to make touch-sensitive computer screens, how to make computer chips process information faster, how to counteract the effect of a poison, how to make less expensive, sturdier, lighter building materials, etc.

Most modern scientific work is interdisciplinary or multidisciplinary. A *discipline* is a field of study. When something is interdisciplinary, it involves two or more fields. For example, Mathematics and Physics are used extensively in Chemistry to characterize the behavior of matter (in bulk samples or at the atomic level); work involving these may be classified as Physical Chemistry or Chemical Physics. Chemistry and Physics are the most basic of all the sciences. Both are used extensively in the other sciences, such as Biology (which deals with life) and Geology (which deals with the earth). Much of the progress in modern biology is due to (and relies on) an understanding of Chemistry. Living things are made up of atoms! Biochemists and molecular biologists are primarily concerned with studies of things associated with life from an atomic perspective (or chemical perspective); they deal with molecules such as proteins, carbohydrates, lipids, nucleic acids, which are found in living things. The word *molecule* refers to two or more atoms that are bound together.



TEST YOURSELF

For answers and other study resources, see:

<http://i-assign.com/ebook/answers/chapter1.htm>.

1. Consider the following statements: “A drop of alcohol on a lab bench disappears after 5 minutes. The drop disappeared because molecules of alcohol moved apart and spread into the entire room.” These statements, respectively, are:
A. hypothesis and theory B. observation and hypothesis
C. observation and theory D. law and theory
2. Consider the following statement: “Matter expands when heated.” This statement is an example of:
A. a law B. a theory C. a hypothesis D. an observation
3. Which of these statements is/are true?
 1. It is good to do research on a problem or question before formulating a hypothesis.
 2. It is not possible to prove a theory.A. 1 only B. 2 only C. both D. neither

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Measurements

A measurement is a quantitative comparison. It usually (not always!) has two parts: a number and a unit. The unit tells us what the basis is for the comparison. For example, when we say that something has a mass of 5 kg, we mean that its mass is 5 times that of the metallic cylinder stored in a vault at the BIPM (*Bureau International des Poids et Mesures*, www.bipm.org, or *International Bureau of Weights and Measures*) in Sevres, France. The cylinder in BIPM is defined to have a mass of 1 kg and is an example of what is called a *standard reference*. By *reference*, we mean that it is the basis for comparison. By *standard*, we mean that people (governments) agree to use it as the reference; as a matter of convenience and necessity people have to agree on a reference.

2.1 Reliability of Measurements

There are two characteristics of a measurement that we use to assess its reliability: accuracy and precision. Although often used interchangeably, accuracy and precision are two different things. *Accuracy* refers to the “correctness” of a measured value, while *precision* refers to its reproducibility or consistency. Precision is necessary in order to be accurate; it is difficult to be correct if you are inconsistent. However, good precision does not necessarily lead to high accuracy; it is possible to be consistently wrong (precisely inaccurate).

2.1.1 Accuracy

We can determine the accuracy of a measured value by comparing it with the expected (correct or true) value. To assess the accuracy of a measured value, we calculate either the *absolute error*:

$$\text{Absolute Error} = \text{Measured value} - \text{Correct value}$$

or the *relative error*:

$$\text{Relative Error} = \text{Absolute Error} / \text{Correct Value}$$

Relative error is often expressed as a percentage; in this case it is referred to as the percent error. The smaller the absolute or relative error is, the more accurate the measurement.



► Example

On a laboratory exam, students were asked to determine the amount of ascorbic acid in an “unknown” tablet. One student determined the amount to be 225.0 mg. The correct value is 250.0 mg. Calculate the absolute error and the relative error.

Answer:

$$\text{Absolute Error} = 225.0 \text{ mg} - 250.0 \text{ mg} = -25.0 \text{ mg}$$

$$\text{Relative Error} = -25.0 \text{ mg} / 250.0 \text{ mg} = -0.100, \text{ or } -10.0\%$$


A negative error means that the measured value is less than the correct value. Similarly, a positive error means that the measured value is larger than the correct value.

Why should we bother measuring something if we already know what it is? In a teaching laboratory, it would be a way for the teacher to check if a student has learned the skills pertinent to the course (as illustrated in the preceding example). In general, the reason is to check if the instrument or method that we would be using for subsequent measurements is reliable. Checking if an instrument is giving correct values and adjusting it so that it gives correct values, or figuring out how to calculate the correct values, is called *calibration* or *standardization*. We do this using *standard reference materials* and/or *standard operating procedures*. For something to be considered a “standard” its validity should ultimately be traceable to an authorized agency; in the United States, this agency is the NIST (National Institutes of Standards and Technology, www.nist.gov). In cases where a standard is not defined, the “correct” value is assumed to be one that is predicted by a well-established theory (the *theoretical value*), or one previously reported in a peer-reviewed publication (the *literature value*).

We can tell there is a problem with the accuracy of a measurement if we repeat it several times and find that the errors are “one-sided” (that is, consistently positive or consistently negative). This type of error is called a *systematic* or *determinate* error and is avoidable. It could, for example, be due to an improper calibration of the instrument; to avoid it, we re-calibrate. It could be due to a shortcoming of the method used; to avoid it, we modify the method.

2.1.2 Precision

In general, it is *not* possible to obtain *exactly* the same result every time we repeat a measurement regardless of how carefully we try to replicate the procedure. This is due to natural fluctuations in the property being measured and in the response of measuring instrument to the property. Errors associated with these natural fluctuations are called *indeterminate* or *random errors*. Random errors *cannot* be avoided, but can be minimized



by doing multiple trials. If errors are truly random, positive and negative errors tend to be equally probable. Thus, it is good practice to perform multiple trials and take the average as *the* measured value; errors in the individual trial values will tend to cancel each other out when we calculate the average. The simplest way of assessing the precision the measured value is to calculate the *range*, the difference between the highest and lowest trial values:

$$\text{Range} = \text{highest value} - \text{lowest value}$$

The smaller the range is, the more precise the measured value.

► Example

A student determined the time it takes for rock to fall from the top of a building to the ground below. Based on the following results, calculate the range.

Trial 1: 3.12 s

Trial 2: 3.15 s

Trial 3: 3.20 s

Trial 4: 3.22 s

Answer: 0.10 s

The range is the difference between the highest and lowest trial values. In this case, the highest value is 3.22 s and the lowest value is 3.12 s. Therefore:

$$\text{Range} = 3.22 \text{ s} - 3.12 \text{ s} = 0.10 \text{ s}$$


2.2 Reporting Measured Values

Measurements should be reported in a manner that informs the reader about its precision. The best way is to specify the *uncertainty* along with the measured value. If we report a measurement as “525.26 ± 0.21 g,” we are saying that our best estimate is 525.26 g, but if the measurement were repeated, we are likely to get a value that can be up to 0.21 g smaller, or up to 0.21 g larger. The uncertainty is “± 0.21 g,” which is read as “plus-or-minus 0.21 g.”

The uncertainty should be rounded off to the first nonzero digit; one additional digit may be kept if the first nonzero digit is less than 3. The measured value should be reported so that the last decimal place is the same as that of the uncertainty.

► Example

The length of an object is measured several times and the average was found to be 24.3828 mm, with an uncertainty of ± 0.0286 mm. How should the measured value and uncertainty be reported?



Answer: 24.38 ± 0.03 mm, or 24.383 ± 0.029 mm
The first nonzero digit in the uncertainty is the 2 in the hundredth's place. Therefore, uncertainty should be rounded off to the hundredth's place: $\pm 0.0286 \rightarrow \pm 0.03$. The average should also be rounded off the hundredth's place: $24.3828 \rightarrow 24.38$.
Since the first nonzero digit in the uncertainty is less than 3, we may keep an extra digit: $\pm 0.0286 \rightarrow \pm 0.029$. If we write our uncertainty to the thousandth's place, then we also write our average to the thousandth's place: $24.3828 \rightarrow 24.383$.

How do we determine the uncertainty? The simplest way is to take half of the range.

► Example

The percentage of calcium in a tablet was determined four times, and the following results were obtained:

Trial 1: 27.530%

Trial 2: 20.894%

Trial 3: 29.227%

Trial 4: 21.187%

How should the average be reported?

Answer: 25%

We can calculate the average by adding up the values from the four trials and dividing by the number of trials (4). If we do this, our calculator should give us 24.71%

The range is the difference between the highest and lowest value.

$$\text{Range} = 29.227\% - 20.894\% = 8.333\%$$

The uncertainty is approximately equal to half the range:

$$\text{Uncertainty} = \pm 8.333/2 = \pm 4.167 \rightarrow \pm 4 \text{ (round off to the first nonzero digit)}$$

Therefore, the level of uncertainty is in the ones place; the average should be reported to the nearest unit: $24.71 \rightarrow 25$.

A more sophisticated method of determining uncertainty is to calculate the *standard error of the mean* or *standard deviation of the mean*. The formula for standard deviation of the mean is:

$$\sqrt{\frac{\sum_{i=1}^N (x_i - \langle x \rangle)^2}{N(N-1)}}$$



In this expression:

- N is the number of trials.
- x_i is the measured value for the i^{th} trial.
- $\langle x \rangle$ is the average or mean of all the x_i values.
- $x_i - \langle x \rangle$ is called the deviation of x_i from the mean.

Basically, what we do is square each deviation, add up all the squared deviations, divide the sum by $N(N-1)$, then take the square root of the result. If we calculate the standard error of the mean for the data in the preceding example, we find it to be 2.1. Thus, the uncertainty is $\pm 2.1\%$ or $\pm 2\%$. The estimated uncertainty based on the range is generally larger than the standard error of the mean; we could say that it is a more conservative estimate of the uncertainty.

We do not always have to quote the uncertainty when reporting measurements. If we do leave out the uncertainty we should still give the reader an indication of what the magnitude of the uncertainty is. The last digit in the reported value should be in the same decimal place as the first nonzero digit of the uncertainty.

► Example

How should 25.03 ± 0.27 mg be reported if the uncertainty is left out?

Answer: 25.0 mg

The magnitude of the uncertainty is in tenth's place since the first nonzero digit of the uncertainty (± 0.27) is in the **tenth's** place. So, if we were to leave out the uncertainty, we report the measured value to the nearest tenth. We say that this last digit (in this case, in tenths place) is the last *significant* digit; given the magnitude of the uncertainty, there is no good reason for us to report additional digits.

How should we report values for each trial? If the measuring instrument has a *digital* readout, the fluctuations in the readout should give us an estimate of the uncertainty. If the reading does not seem to fluctuate, it suggests that our instrument is not sensitive enough to detect the natural fluctuations in whatever it is we are trying to measure; in this case, we use all the digits shown on the readout and we say that the instrument's sensitivity limits the precision. If the instrument has an *analog* scale, it is customary to take the uncertainty as $1/10$ of the difference between adjacent marks.

► Example

Adjacent marks on a meter stick are 1 mm apart. How should readings from this scale be reported?

Answer: We estimate the uncertainty to be 1/10 of 1 mm, or 0.1 mm. Therefore, we should report readings from this scale to the nearest tenth of a millimeter.

2.3 Significant Figures

Significant figures or significant digits refer to the “meaningful” digits in a measurement. The last significant digit gives us information about the precision of the measurement. The significant figures in a reported measurement are determined as follows:

Rule 1. If the number is written in scientific notation, all the digits in the coefficient are significant. (A number is said to be written in scientific notation if it is written as a number between 1 and 10 times a power of 10.)

Rule 2. If the number is not written in scientific notation and has a decimal point, the *first nonzero digit* is the first significant digit and all digits to the right of the first nonzero digit are significant. **EXCEPTION:** if the number *does not have a decimal point*, trailing zeros may or may not be significant; unless otherwise specified, it is customary to assume that they are not significant.


► Example

How many significant digits are in the following:

- (a) 1.50×10^{-3} kg (b) 2.835×10^4 mm (c) 0.00250 m
(d) 73.00 km (e) 385 mL (f) 3800 mg

Answers:

- (a) 1.50×10^{-3} kg has 3 significant digits (the 1, 5, and 0 in 1.50); rule 1
(b) 2.835×10^4 mm has 4 significant digits (the 2, 8, 3 and 5 in 2.835); rule 1
(c) 0.00250 m has 3 significant digits (2, 5, and 0); rule 2
(d) 73.00 km has 4 significant digits (7, 3, 0, and 0); rule 2
(e) 385 mL has 3 significant digits (3, 8, and 5); rule 2
(f) 3800 mg can have 2, 3, or 4 significant digits; rule 2 exception



The 3 and 8 in 3800 are significant. The trailing zeros may or may not be significant because there is no decimal point. Unless otherwise specified, assume that they are not significant; therefore 3800 mg has only 2 significant digits. This is an example of a measurement that is *not properly reported* but is, unfortunately, commonly encountered. To avoid ambiguity, it is best to write a number like this in scientific notation:

- Write 3800 as 3.8×10^3 if the trailing zeros are not significant.
- Write 3800 as 3.80×10^3 if the first zero is significant and the second is not.
- Write 3800 as 3.800×10^3 if both zeros are significant.

2.4 Calculations Involving Measurements

2.4.1 Dealing with Units

When performing calculations involving measurements, units are treated like any algebraic quantity. When a unit is attached to a number, multiplication is implied. As a consequence:

- numerical values of measurements can only be added or subtracted if they have the same unit.
- when using measured quantities in multiplication, division, or exponentiation, the units must be manipulated accordingly.

► Example

Calculate: $5\ m + 2\ m = ?$

Answer: $7\ m$

Since both measurements have the same units, we can add the numerical values: $5\ m + 2\ m = (5 + 2)\ m$, or $7\ m$

The unit (m) can be factored out just like x can be factored out of an algebraic expression like $(5x + 2x)$:

$$5x + 2x = (5 + 2)x, \text{ or } 7x.$$

► Example

Calculate: $(2 \text{ cm})(3 \text{ cm}) = ?$

Answer: 6 cm^2

The unit (cm) is treated just like x in the algebraic expression “ $(2x)(3x)$ ”:

$$(2x)(3x) = 6x^2$$

► Example

Calculate: $(6 \text{ m}) / (2 \text{ min}) = ?$

Answer: 3 m/min , or 3 m min^{-1}

Dividing by min is the same as multiplying by the reciprocal of min , which is the same as min raised to the -1 power (min^{-1}).

2.4.2 Significant Digits in Calculated Values

The result of a calculation should be written in a manner that reflects the level of uncertainty in the numbers used in the calculation.

Rule for Addition and/or Subtraction. Determine the least precise term, the term with the largest uncertainty. Express the answer to as many decimal places as the least precise term.

► Example

Calculate: $25.0 \text{ g} + 1.003 \text{ g} = ?$

Answer: 26.0 g

The uncertainty in 25.0 g is at least $\pm 0.1 \text{ g}$.

The uncertainty in 1.003 is at least $\pm 0.001 \text{ g}$.

The term 25.0 g is less precise than 1.003 g ; its uncertainty is larger.

Therefore, the answer needs to be expressed to the nearest tenth, since the less precise term (25.0) is expressed to the nearest tenth.

The sum is (26.003 g) should be rounded off to 26.0 g .

► Example

Calculate: $4.2 \times 10^{-3} \text{ m} + 4.4 \times 10^{-4} \text{ m} - 3.50 \times 10^{-5} \text{ m} = ?$

Answer: $4.6 \times 10^{-3} \text{ m}$

The best thing to do in this case is to first make the powers of 10 the same. Choose the largest power (-3).

- $4.4 \times 10^{-4} \rightarrow 0.44 \times 10^{-3}$ [Math review: move decimal point in coefficient one place to the left while adding one to the exponent. Note that $-4 + 1 = -3$.]
- $3.5 \times 10^{-5} \rightarrow 0.0350 \times 10^{-3}$

Then add and/or subtract the coefficients:

$$\begin{aligned} & 4.2 \times 10^{-3} + 0.44 \times 10^{-3} - 0.0350 \times 10^{-3} \\ & = (4.2 + 0.44 - 0.0350) \times 10^{-3} \\ & = (4.605) \times 10^{-3} \end{aligned}$$

Here, we round off the coefficient to the nearest tenth since 4.2 has the largest uncertainty (at least ± 0.1). Therefore, the answer is $4.6 \times 10^{-3} \text{ m}$

Rule for Multiplication and/or Division. Determine the least precise term, the term with the fewest number of significant digits. Express result to as many significant digits as the least precise term.

► Example

Calculate: $(16.00 \text{ g}) / (2.00 \text{ mL}) = ?$

Answer: 8.00 g/mL

The term 16.00 g has 4 significant digits.

The term 2.00 mL has 3 significant digits.

The term 2.00 mL has fewer significant digits (3) and is considered as less precise. Therefore, the answer should have 3 significant digits, the same as the less precise term (2.00 mL).

Multi-step Calculation. Apply the appropriate rule for each step, but keep an extra digit in the intermediate steps in order to avoid build-up of round off errors. It would be helpful to mark the last significant digit for the intermediate result so that you can easily keep track of it.

► Example

Calculate: $(25.1)(1.0) + 2.5$

Answer: 28

Step 1. Multiply $(25.1)(1.0)$

- 25.1 has three significant digits
- 1.0 has two significant digits
- Therefore: $(25.1)(1.0) = 25.1$; should only have 2 significant digits (5 is the last significant digit; the “1” after that is not significant, but we keep it since we will use the result for the next step)

Step 2. Add: $25.1 + 2.5$

- 25.1 has an uncertainty of at least ± 1 because 5 is the last significant digit here; we are just keeping the extra digit to avoid round-off error
- 2.5 has an uncertainty of at least ± 0.1
- The less precise term has an uncertainty of at least ± 1
- $25.1 + 2.5 = 27.6 \rightarrow 28$; the answer should have an uncertainty of at least ± 1

Calculations Involving Exact Numbers. Exact numbers do not have any uncertainty. They are, therefore, considered to be perfectly precise and have an “infinite” number of significant figures for as long as they are not rounded off. They can never be the least precise term in a calculation. Exact numbers include small counts (as in 13 pencils) and numbers that are defined to be exact. In the context of the definition “1 inch = 2.54 cm”, the numbers 1 and 2.54 are exact and are considered as having an infinite number of significant digits.

► Example

Consider the following formula where 1.8 and 32 are exact:

$$F = 1.8C + 32.$$

Calculate F if $C = 20.0$.

Answer: 68.0

First we multiply 1.8×20.0

- 20.0 has 3 significant figures
- 1.8 has an infinite number of significant figures
- $20.0 \times 1.8 = 36.0$, should have 3 significant figures

Then we add 32 to the result:

- 36.0 has an uncertainty of at least ± 0.1
- 32 has zero uncertainty since it is exact

- 36.0 is the less precise term with an uncertainty of at least ± 0.1
- the answer should have an uncertainty of at least ± 0.1 :
 $36.0 + 32 = 68.0$

Rounding Off Precisely Known Numbers. There are quantities that are known to a much greater precision than others. We could round these off to fewer digits, but the rounded value must still be more precise than the least precise term in the calculation.

► Example

The speed of light, c , in the formula $E=mc^2$, is defined to be exactly 2.99792458×10^8 m/s. If, in a calculation, $m = 10.0$ kg, to what extent can we round off the value of c ?

Answer: For multiplication, the less precise term is the term with the fewer number of significant figures. In this calculation m , which is 10.0 kg, is the less precise term with only 3 significant figures. The value of c should have at least 4 significant figures: 2.998×10^8 m/s is acceptable.

Significant Figures Involving Logarithms. When we calculate the logarithm of another number, it is useful to write it in scientific notation in order to determine the number of significant digits needed for the result. The number of decimal places in the result should be the same as the number of significant digits in the coefficient of the original number.

► Example


Express $\log(2.7 \times 10^4)$ to the correct number of significant figures.

Answer: 4.43

If we take the logarithm of this number, we get:

$$\begin{aligned}\log(2.7 \times 10^4) &= \log(2.7) + \log(10^4) \\ &= 0.431 + 4 \\ &= 4.43\end{aligned}$$

The number 2.7 has two significant digits; the logarithm of 2.7 should be rounded to 0.43 (also two significant digits).



The integer part of the answer (4) essentially comes from the power of 10, which is an exact number; it has an infinite number of significant digits; we could have written it as 4.0000000...

Similarly, if we reverse the process, the number of significant digits in the antilog should be the same as the number of decimal places (after the decimal point) in the original number.

► Example

Express $10^{-2.699}$ to the correct number of significant figures.

Answer: 2.00×10^{-3}

There are **3 decimal places** in the original number (-2.699). The antilog should have 3 significant digits.


2.5 SI Units

Numerous units have been defined over the years. Different countries have adopted different sets of standards. In the English system, still widely used in the US and UK, the units used include inches, feet, yard and miles for length, pounds and ounces for mass, etc. Nowadays, however, the only system that is acceptable for scientific work and for international trade is the International System of Units, which is generally referred to as SI (from the French name: Le Systeme International d'Unites).

The SI system defines seven *fundamental quantities* and a *base unit* for each of these fundamental quantities. The fundamental quantities are: length, mass, time, temperature, amount of substance, electric current, and luminous intensity. The corresponding base units are meter (m), kilogram (kg), second (s), kelvin (K), mole (mol), ampere (A), and candela (cd). The abbreviations for the units, indicated in parentheses in the preceding sentence, are also well defined. The official abbreviation for second is s (lower case), not “sec.” The temperature unit is “Kelvin” (K), not “degrees Kelvin” ($^{\circ}\text{K}$).

Units for quantities that can be thought of as obtainable from measurements of two or more fundamental quantities are called derived units. For example, speed is a ratio of distance traveled (a measurement of length) to the elapsed time (a measurement of time). Therefore, the unit for speed — m/s or m s^{-1} (meters per second) — is a derived unit. Some derived units have special names. For example, the unit for force, kg m s^{-2} , is called a Newton (official abbreviation: N).

One reason why numerous units have been invented is convenience. It is more convenient to express the height of a person as 6 ft rather than, say, 0.0011 miles. We do not



lose this convenience when using SI because the system also defines official prefixes that can be used to scale a unit up or down. For example, the SI prefix *centi* (official abbreviation: c) means 10^{-2} , or one one-hundredth. Therefore, 1.5×10^{-2} m is equivalent to 1.5 cm. Similarly, 1,500,000 g (or 1.5×10^6 g) is equivalent to 1.5 Mg; M (upper case) is the official abbreviation for the prefix mega, which means 10^6 (or one million). The most commonly used SI prefixes are:

Prefix: Giga, Mega, Kilo, Hecto, Deca, Deci, Centi, Milli, Micro, Nano, Pico

Official abbreviation: G, M, k, h, da, d, c, m, μ (Greek letter mu), n, p

Meaning: 10^9 , 10^6 , 10^3 , 10^2 , 10^1 , 10^{-1} , 10^{-2} , 10^{-3} , 10^{-6} , 10^{-9} , 10^{-12}

The prefix micro (μ) is also commonly abbreviated using mc. For example, you'll find microgram abbreviated as mcg in vitamin bottles; however, μg is the official abbreviation.

Some commonly used units that were defined before the SI system was adopted have been officially redefined in terms of SI units. A Liter (L) is now defined as exactly 0.001 cubic meters ($1\text{L} = 10^{-3}\text{ m}^3$). A milliliter (mL) is one cubic centimeter ($1\text{ mL} = 1\text{ cm}^3$). One teaspoon is now 5 mL or 5 cm^3 ; one tablespoon is now 15 mL. One inch is now defined to be exactly 2.54 cm.

2.6 Unit Conversions

2.6.1 Algebraic Substitution

Quantities given in one unit can be expressed in another unit if we know equivalent quantities for both units. Simply treat units like any algebraic term and make appropriate substitutions.

In general, numbers used in defining equivalent quantities are defined to be exact. Therefore, converting measurements from one unit to another should not affect the number of significant figures. In other words, the number of significant figures in the answer should be the same as in the original measurement.

► Example

Convert 3.5 mm to m.

Answer: 3.5×10^{-3} m

Since $1\text{ mm} = 10^{-3}\text{ m}$, we simply replace mm in the 3.5 mm by 10^{-3} m .

$3.5\text{ mm} = 3.5 (10^{-3}\text{ m})$, or $3.5 \times 10^{-3}\text{ m}$

► Example

Convert 9.8×10^{-4} m to mm

Answer: 9.8×10^{-1} mm

Since $1 \text{ mm} = 10^{-3} \text{ m}$, $(1/10^{-3}) \text{ mm} = 1 \text{ m}$, or

$$10^3 \text{ mm} = 1 \text{ m}$$

Replace **m** by 10^3 mm :

$$9.8 \times 10^{-4} \text{ m} = 9.8 \times 10^{-4} (10^3 \text{ mm}), \text{ or } 9.8 \times 10^{-1} \text{ mm}$$

► Example

The gas constant R is $0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$. Express R in $\text{m}^3 \text{ Pa mol}^{-1} \text{ K}^{-1}$.

Given: $1 \text{ L} = 10^{-3} \text{ m}^3$, $1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa}$

Answer: $8.314 \text{ m}^3 \text{ Pa mol}^{-1} \text{ K}^{-1}$

$$R = 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

$$= 0.08206 (10^{-3} \text{ m}^3) (1.01325 \times 10^5 \text{ Pa}) \text{ mol}^{-1} \text{ K}^{-1}$$

$$= 8.314 \text{ m}^3 \text{ Pa mol}^{-1} \text{ K}^{-1}$$

► Example

A house has a floor area of $1.500 \times 10^3 \text{ ft}^2$. What is the floor area in in^2 ?

Given: $1 \text{ ft} = 12 \text{ in}$

Answer: $2.160 \times 10^5 \text{ in}^2$

$$\text{Area} = 1.500 \times 10^3 \text{ ft}^2 = 1.500 \times 10^3 (12 \text{ in})^2 = 2.160 \times 10^5 \text{ in}^2$$

► Example


Convert 658 nm to μm .

Answer: $0.658 \mu\text{m}$

We are not likely to find the relationship between nm and μm listed anywhere. However, we know that the SI prefix nano (n) means 10^{-9} and the SI prefix micro (μ) means 10^{-6} . Therefore, we know that:

- $1 \text{ nm} = 10^{-9} \text{ m}$

- $1 \mu\text{m} = 10^{-6} \text{ m}$, or $10^6 \mu\text{m} = 1 \text{ m}$



These relationships suggest a strategy for doing the needed conversion. First, we convert nm to m, then convert m to μm .

$$\begin{aligned} 658 \text{ nm} &= 658 (10^{-9} \text{ m}) = 658 \times 10^{-9} \text{ m} \\ &= 658 \times 10^{-9} (10^6 \mu\text{m}) = 658 \times 10^{-3} \mu\text{m}, \text{ or } 0.658 \mu\text{m} \end{aligned}$$

2.6.2 Factor Label Method

A popular method for converting units involves the use of conversion factors. This method is often referred to as “factor label” or “dimensional analysis.” A conversion factor is just a ratio of equivalent amounts in two different units. For example, since

$$1 \text{ mm} = 10^{-3} \text{ m},$$

we can set up two possible conversion factors:

$$\frac{1 \text{ mm}}{10^{-3} \text{ m}} \quad \text{or} \quad \frac{10^{-3} \text{ m}}{1 \text{ mm}}$$

We multiply whatever it is we want to convert by one of these so that the original unit cancels out.

► Example

Convert 3.5 mm to m.

Answer: $3.5 \times 10^{-3} \text{ m}$

We multiply it 3.5 mm by the conversion factor that has mm in the denominator.

$$3.5 \cancel{\text{ mm}} \times \frac{10^{-3} \text{ m}}{1 \cancel{\text{ mm}}} = 3.5 \times 10^{-3} \text{ m}$$

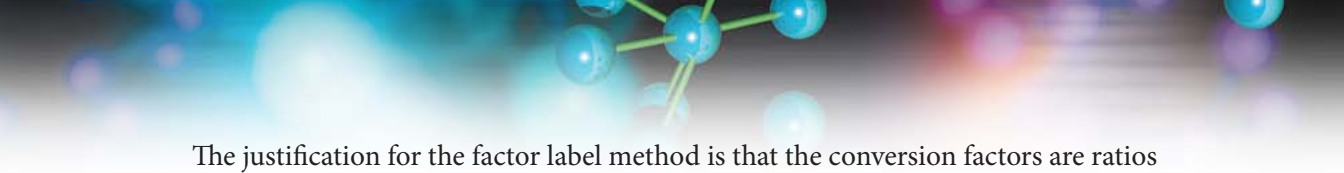
► Example

Convert 2.5 g/mm to g/m.

Answer: $2.5 \times 10^3 \text{ g/m}$

We multiply 2.5 g/mm by the conversion factor that has mm in the numerator because mm is in the denominator of the original measurement.

$$2.5 \frac{\text{g}}{\cancel{\text{ mm}}} \times \frac{1 \cancel{\text{ mm}}}{10^{-3} \text{ m}} = 2.5 \times 10^{-3} \frac{\text{g}}{\text{m}}$$



The justification for the factor label method is that the conversion factors are ratios of equivalent quantities and are therefore equal to one. Multiplying anything by one does not change its value. Quantities expressed in different units are also *directly proportional*. When two quantities are directly proportional, their ratio is constant. Put another way: if one is zero, so is the other; when one changes, the other changes by the same factor. For example, the ratio of (length in meters) to (length in millimeters) is a constant. Therefore:

$$\frac{\text{length in m}}{\text{length in mm}} = \frac{10^{-3} \text{ m}}{1 \text{ mm}}$$

So, if we know the length in millimeters, we can solve for the length in meters by multiplying both sides of the equation by the length in millimeters:

$$\text{length in m} = (\text{length in mm}) \times \frac{10^{-3} \text{ m}}{1 \text{ mm}}$$

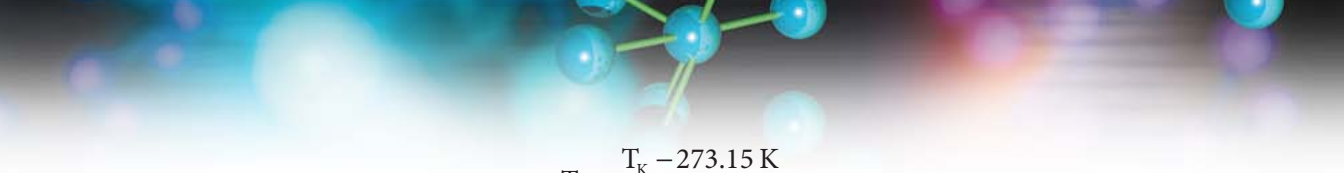
2.6.3 Temperature Conversions

One exception to the unit conversion methods described above involves temperature readings. Readings on the Celsius, Fahrenheit, and Kelvin scales are, by definition, not directly proportional. We can easily tell that this is the case since a zero reading on one scale does not correspond to a zero reading on the other scales. In fact, 0°C is equivalent to 32°F and 273.15K . In these cases, it is best to just use the defining formulas. Let T_{F} , T_{C} , and T_{K} be the temperature readings in Fahrenheit, Celsius and Kelvin. If we know T_{C} , then:

$$T_{\text{F}} = \left(\frac{1.8^{\circ}\text{F}}{1^{\circ}\text{C}} \right) T_{\text{C}} + 32^{\circ}\text{F}$$
$$T_{\text{K}} = \left(\frac{1 \text{ K}}{1^{\circ}\text{C}} \right) T_{\text{C}} + 273.15 \text{ K}$$

In other words, multiply the Celsius reading by 1.8, then add 32 to get the Fahrenheit reading, and add 273.15 to the Celsius reading to get the Kelvin temperature. Similarly, if we know T_{F} or T_{K} , then we can solve for T_{C} .

$$T_{\text{C}} = \frac{T_{\text{F}} - 32^{\circ}\text{F}}{\left(\frac{1.8^{\circ}\text{F}}{1^{\circ}\text{C}} \right)}$$


$$T_C = \frac{T_K - 273.15 \text{ K}}{\left(\frac{1 \text{ K}}{1^\circ\text{C}}\right)}$$

Note: All the numbers (1, 1.8, 32, and 273.15) in these formulas are exact numbers by definition.

► Example

What are the Fahrenheit and Kelvin readings equivalent to 25.000°C ?

Answer: 77.000°F and 298.15K

$$T_F = \left(\frac{1.8^\circ\text{F}}{1^\circ\text{C}}\right)(25.000^\circ\text{C}) + 32^\circ\text{F} = 77.000^\circ\text{F}$$

$$T_K = \left(\frac{1\text{K}}{1^\circ\text{C}}\right)(25.000^\circ\text{C}) + 273.15 \text{ K} = 298.150 \text{ K}$$

While temperature readings on the different scales are not directly proportional, temperature differences or changes on these scales are. Based on the definitions above, a one degree *change* on the Celsius scale is equivalent to a 1.8 degree *change* on the Fahrenheit scale and also equivalent to a one unit *change* on the Kelvin scale. Let ΔT_F , ΔT_C , and ΔT_K be the corresponding changes in temperature on the three scales. Then:

$$\frac{\Delta T_K}{\Delta T_C} = \frac{1\text{K}}{1^\circ\text{C}}$$
$$\frac{\Delta T_F}{\Delta T_C} = \frac{1.8^\circ\text{F}}{1^\circ\text{C}}$$

In other words, we can use algebraic substitution or the factor label method when dealing with temperature changes or temperature differences.

▶ Example

If the temperature goes up from 25°C to 34°C, by how much did the temperature change in Kelvin?

Answer: 9K

$$\Delta T_K = \Delta T_C \times \frac{1K}{1^\circ C} = (34^\circ C - 25^\circ C) \times \frac{1K}{1^\circ C} = (9^\circ C) \times \frac{1K}{1^\circ C} = 9K$$

Here's another way of solving this problem. We convert 34°C and 25°C to Kelvin first, then take the difference:

$$\Delta T_K = \left(34^\circ C \times \frac{1K}{1^\circ C} + 273.15K \right) - \left(25^\circ C \times \frac{1K}{1^\circ C} + 273.15K \right)$$

Note that when we take the difference, the 273.15K terms cancel out.

▶ Example

If the temperature changes from 50.0°F to 62.0°F, by how much did the temperature change in degrees Celsius.

Answer: 6.67°C


$$\begin{aligned} \Delta T_C &= \Delta T_F \times \frac{1^\circ C}{1.8^\circ F} = (62.0^\circ F - 50.0^\circ F) \times \frac{1^\circ C}{1.8^\circ F} \\ &= 12.0^\circ F \times \frac{1^\circ C}{1.8^\circ F} = 6.67^\circ C \end{aligned}$$

Here is a longer way of solving this problem. We could convert the Fahrenheit readings to Celsius first, then take the difference:

$$\Delta T_C = \left[\frac{62.0^\circ F - 32^\circ F}{\left(\frac{1.8^\circ F}{1^\circ C} \right)} \right] - \left[\frac{50.0^\circ F - 32^\circ F}{\left(\frac{1.8^\circ F}{1^\circ C} \right)} \right]$$

Since the two fractions above have the same denominator, we can combine the numerator and get

$$\Delta T_C = \frac{(62.0^\circ F - 32^\circ F) - (50.0^\circ F - 32^\circ F)}{\left(\frac{1.8^\circ F}{1^\circ C} \right)}$$


$$= (62.0^{\circ}\text{F} - 50.0^{\circ}\text{F}) \times \frac{1^{\circ}\text{C}}{1.8^{\circ}\text{F}} = 12.0^{\circ}\text{F} \times \frac{1^{\circ}\text{C}}{1.8^{\circ}\text{F}} = 6.67^{\circ}\text{C}$$

which is equivalent to the expression we have earlier. Note that the 32°F terms in the numerator cancel out.

2.7 Unitless Quantities

Not all measurements have a unit. The basis of comparison for those that do not have units is implied in the definition of the quantity being measured. Some of these quantities are defined as ratios of two quantities that have the same unit. When we calculate the ratio, the units cancel out. For example, *specific gravity* is a unitless quantity. It is defined as the ratio of the density of an object to the density of a reference material (such as water). Another example is *transmittance*. It is defined as the ratio of the intensity of light that passes through a solution to the intensity of light that passes through a reference solution.

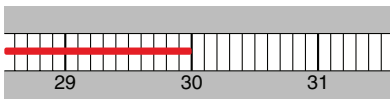
Other unitless quantities are defined as logarithms of unitless quantities. *Absorbance* is the negative of the logarithm of transmittance. *pH* is the negative of the logarithm of the *activity* of hydrogen ions; activity is a unitless quantity.

TEST YOURSELF

For answers and other study resources, see:

<http://i-assign.com/ebook/answers/chapter2.htm>.


- Which of the following has the fewest number of significant figures?
A. 10.50 mg B. 20700 mL C. 0.003100 g D. 1.500×10^{-3} m
- The amount of acid present in a sample was measured several times and the average value was determined to be 3601.2 mg, with an uncertainty of ± 30 mg. To how many significant figures should the average be reported?
A. 2 B. 3 C. 4 D. 5
- Five replicate measurements of the calcium content of a sample yielded the following results:
5.042%, 5.131%, 5.434%, 4.852%, 4.728%.
To how many significant digits should the average be reported?
A. 1 B. 2 C. 3 D. 4
- What is the proper way of reporting the temperature shown on the thermometer scale (Celsius) below?
A. 30°C B. 30.0°C C. 30.00°C D. $3.0 \times 10^1^\circ\text{C}$



- To how many significant figures should the result of the following calculation be reported: $2500.0 + 25$ g?
A. 2 B. 3 C. 4 D. 5
- To how many significant figures should the result of the following calculation be reported?
 $2500 \text{ mL} + 25 \text{ mL}$?
A. 2 B. 3 C. 4 D. 5

7. How should the result of the following calculation be reported?
80.00 g / 10.0 mL ?
A. 8 g/mL B. 8.0 g/mL C. 8.00 g/mL D. 8.000 g/mL
8. How should the result of the following calculation be reported?
0.800 m / 0.010 s
A. 80 m/s B. 80.0 m/s C. 8.0×10^1 m/s D. 8×10^1 m/s
9. How should the result of the following calculation be reported?
 $0.0072 + (0.0050)(39.0)$?
A. 0.20 B. 0.21 C. 0.202 D. 0.2022
10. How should the result of the following calculation be reported, assuming that 1.8 and 32 are exact numbers: $32 + (1.8)(2.37)$?
A. 36 B. 36.3 C. 36.27 D. 36.266
11. The volume of a sphere of radius r is given by the formula:
$$V = \frac{4}{3} \pi r^3$$

The radius of a sphere is measured to be 5.00 cm. What is the proper way to report the volume? Note: $\pi = 3.141592653589793238462643383279\dots$
A. 520 cm³ B. 523 cm³ C. 524 cm³
12. Which of the following is equivalent to 101.9 MHz?
A. 1.019×10^6 Hz B. 1.019×10^8 Hz, C. 1.019×10^4 Hz D. 1.019×10^{-5} Hz
13. Which of the following is not equivalent to 10^{-3} mg?
A. 10^{-6} g B. 1 μ g C. 10^{-4} cg D. 10^6 ng
14. Given: 1 inch is exactly equivalent to 2.54 cm. A measurement of 7.00 cm is equivalent to how many inches?
A. 2.76 in B. 3 in C. 17.8 in D. 20 in
15. Given: 1 inch is exactly equivalent to 2.54 cm, and 12 inches is exactly 1 foot. A measurement of 7.0 cm is equivalent to how many feet?

- 
16. A measurement of 2.50 mm is equivalent to ?
A. 2.50×10^6 nm B. 2.50×10^{-9} nm C. 2.50×10^{-6} nm D. 2.50×10^9 nm
17. A car is traveling at a speed of 40.0 km hr^{-1} .
How fast is the car moving in km min^{-1} ?
A. $2.40 \times 10^3 \text{ km min}^{-1}$ B. $6.67 \times 10^{-1} \text{ km min}^{-1}$ C. 1.50 km min^{-1}
18. The density of air is $1.29 \times 10^{-3} \text{ g/L}$. What is the density of air in mg/mL ?
A. $1.29 \times 10^{-3} \text{ mg/mL}$ B. 1.29 mg/mL C. $1.29 \times 10^{-6} \text{ mg/mL}$
19. The area of a circle is found to be 2.4 cm^2 . What is the area in m^2 ?
A. $2.4 \times 10^2 \text{ m}^2$ B. $2.4 \times 10^{-2} \text{ m}^2$ C. $2.4 \times 10^{-4} \text{ m}^2$ D. $5.8 \times 10^4 \text{ m}^2$
20. What temperature reading on the Fahrenheit scale corresponds to 20.0°C ?
A. 20.0°F B. 68.0°F C. 36.0°F D. -6.67°F
21. What temperature reading on the Celsius scale corresponds to 20.0°F ?
A. 20.0°C B. 68.0°C C. 36.0°C D. -6.67°C
22. At what temperature are the Celsius and Fahrenheit readings equal?
A. -40° B. 32° C. 100° D. 212°
23. What is the Kelvin temperature equivalent to 25.00°C ?
A. 298K B. 298.15K C. -248.15K
24. What is the Kelvin temperature equivalent to 50.00°F ?
A. 323.15K B. 283.15K C. 263.15K D. 395.15K
25. If the temperature increases by 20.0 degrees Celsius, by how much did it increase in degrees Fahrenheit?
A. 36.0° B. 68.0° C. 6.67° D. 20.0°
26. During a chemical reaction, the temperature of a mixture dropped by 10.0°C . By how much did the temperature drop in Kelvin?
A. 10.0K B. 283.15K C. 263.15K

Atoms, Ions, and Molecules

Chemistry is about understanding the behavior of matter in terms of atoms. Matter is what makes up our universe. Matter is made up of atoms, which are too small to see.

3.1 Subatomic Particles

An atom is made up of even smaller particles: *protons*, *neutrons*, and *electrons*. Protons and neutrons are in the nucleus, a very tiny spot in the middle of an atom. Protons and neutrons are collectively called *nucleons*.


Electrons are much smaller than protons and neutrons and they are found around the nucleus. Electrons move so fast that it is convenient to imagine electrons as a cloud around the nucleus.

An atom is mostly empty space. The typical diameter of a nucleus is $10^{-14} - 10^{-13}$ m, while the diameter of the rest of the atom (the “electron cloud”) is typically around 10^{-10} m. The diameter of each individual electron is estimated to be less than 10^{-18} m. To imagine the relative magnitudes of these numbers, imagine you are in a giant world where a typical atomic nucleus is 1 cm instead of about 10^{-13} m. In this magnified world, the diameter of a typical electron cloud would be at least 1000 cm and each individual electron would be a tiny speck. Put another way, if you put two atoms “side by side,” the distance between the nuclei would be at least 1000 times larger than the diameter of the nuclei themselves. Between the nuclei, where electrons are roaming about, is mostly empty space, which would be at least 1,000,000,000 times larger than the space actually occupied by the nuclei.

► Example

A tennis ball has a diameter of 6.5 cm. If the nuclei of two neighboring atoms were the size of tennis balls, how far away from each other would the nuclei be?

Answer: About 1000 times compared to the diameter:
 $1000 \times 6.5 \text{ cm} = 6.5 \times 10^3 \text{ cm}$, or 65 m.



Note: protons and neutrons are made up of even smaller particles called quarks. In the so-called “standard model”, all matter in our universe is said to be made up of quarks and leptons; there are 6 kinds of quarks and 6 kinds of leptons. An electron is a lepton. In Chemistry, we are generally not concerned about quarks and leptons (other than the electron).

3.2 Atoms and Elements

In general, samples of matter that we encounter in nature can be separated into two or more components with different properties. (The word “property” refers to characteristics of matter such as color, melting point, etc.) However, there are samples that cannot be separated into components with different properties. These samples are called *elements*. We explain why these samples cannot be separated into distinct components by assuming that an element is made up of only one kind of atom.

There are a little over a hundred known elements to date; less than one hundred are naturally-occurring. Newly discovered elements are generally created in the laboratory and are not stable. Differences in properties of elements are due to differences in their atoms.

3.3 The Atomic Number

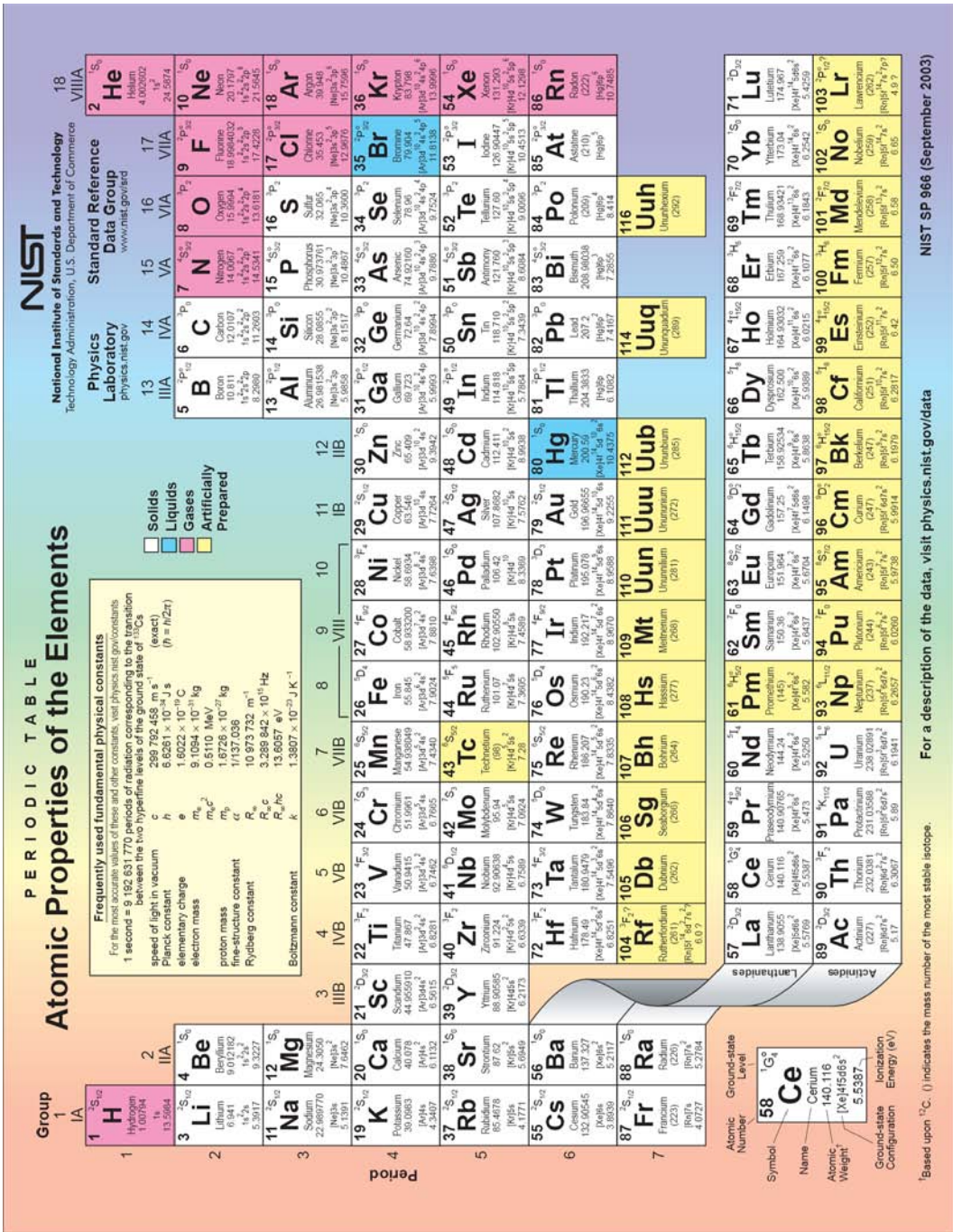
All atoms of the same element have the same number of protons; atoms of different elements have different number of protons. An element’s *atomic number* is defined as the number of protons in the each of the atoms of that element. Elements are listed in a chart called a *periodic table* (see Figure 1) in increasing atomic number (left-to-right, top-to-bottom). As a matter of convenience, elements are assigned symbols that are derived from their names. The first letter of the symbol is capitalized and the second letter, if there is one, must be written in lower case. For example, the symbol for oxygen is O. For magnesium, the symbol is Mg.

► Example

What is the symbol for an element whose atoms have 10 protons in their nucleus?

Answer: If the atoms of an element have 10 protons in their nucleus, then this element has an atomic number of 10. Referring to a periodic table, we find that the element with atomic number of 10 is neon (Ne).

Figure 1. Periodic Table



► Example

How many protons are found in the nucleus of a magnesium (Mg) atom?

Answer: Referring to a periodic table, we find that the atomic number of magnesium is 12. Therefore, any atom of magnesium has 12 protons.

3.4 Isotopes

All the atoms of an element have the same number of protons. But they may have different number of neutrons. Atoms of the same element that have different numbers of neutrons are called *isotopes*. To make a distinction between isotopes, we specify the total number of nucleons (protons and neutrons) next to the symbol for the element. This number is called the *mass number* and is written either a superscript to the left of the symbol or following a dash after the symbol for the element.

► Example

How many protons and neutrons are found in the nucleus of an atom of O-16 or ^{16}O ?

Answer: 8 protons and 8 neutrons

The number 16 in O-16 or ^{16}O is the mass number, which is the total number of protons and neutrons. Referring to a periodic table, we find that the atomic number of oxygen is 8; this means that any oxygen atom has 8 protons. Therefore, every atom of O-16 must have 8 neutrons in its nucleus.

In general, naturally-occurring samples of matter are *not isotopically pure*. For example, a typical sample containing oxygen atoms will be found to have:

- 99.757% O-16,
- 0.038% O-17, and
- 0.205% O-18.

These percentages are called the *natural abundance* of the oxygen isotopes. What these mean is that out of every 100,000 O atoms, we would expect 99,757 to be O-16, 38 would be O-17, and 205 would be O-18. A modern instrument that is used to separate isotopes and measure isotopic abundance is a mass spectrometer.

3.5 Mass of Protons, Neutrons, and Electrons

Not only are electrons very small in size, they also contribute very little to the mass of an atom. The currently accepted masses of protons, neutrons, and electrons are given below:

- Mass of proton: 1.6726×10^{-27} kg or 1.0073 u
- Mass of neutron: 1.6749×10^{-27} kg or 1.0087 u
- Mass of electron: 0.00091×10^{-27} kg or 0.0005486 u

The unit *u* is an abbreviation for *atomic mass unit*, which is also frequently abbreviated as *amu*; this unit is also called the *Dalton* (D). We can see from the numbers given above that a proton's mass is about 2000 times that of an electron (1836 times to be more precise). On the other hand, a neutron and a proton have almost the same mass. To the nearest tenth of an atomic mass unit, we can say that the mass of proton or neutron is 1.0 u, while that of an electron is 0.0 u. This is why the number of electrons is ignored in the defining the mass number of an atom. To the nearest atomic mass unit, the mass of an atom is equal to its mass number.

► Example

Which of these has the largest total mass: 1 proton, 3 electrons, or 2 neutrons?

Answer: 2 neutrons

- The mass of one proton is 1.0 u.
- Three electrons have a total mass of 3×0.0 u, or 0.0 u.
- Two neutrons have a total mass of 2×1.0 u, or 2.0 u.

3.6 Mass of Atoms

We cannot get the most precise value for the mass of an atom by simply adding the precise masses of protons, neutrons, and electrons that make it up. The actual mass of an atom is slightly different and needs to be looked up. The discrepancy is called the *mass defect* (*m*) and is related to the *binding energy* (*E*), the energy needed to separate all protons and neutrons from one another, according to Einstein's equation:

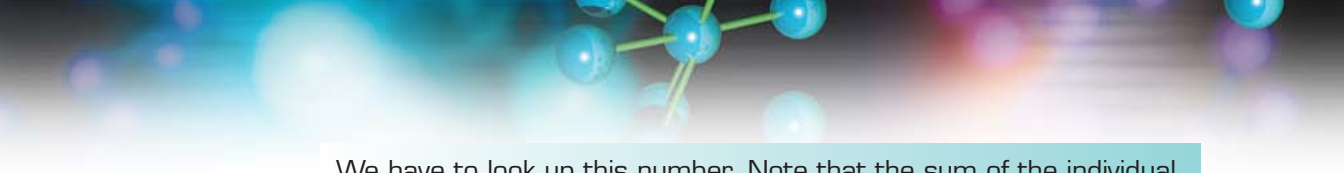
$$E = mc^2.$$

In this equation *c* is the speed of light, 2.998×10^8 m/s.

► Example

What is the most precisely known mass of an atom of ^{18}O ?

Answer: 17.9991603 u



We have to look up this number. Note that the sum of the individual masses of 8 protons and 10 neutrons alone should be larger than 18 u, but an actual O-18 atom has a mass slightly less than 18 u.

Most elements have two or more naturally-occurring isotopes. The masses of specific isotopes are typically not listed in simple periodic tables; what is typically listed is the *average* mass of atoms in a naturally-occurring sample. The numerical value of the average mass (in u) is called the *atomic weight*. For example, the atomic weight of Mg is often listed as 24.305. This means that, in a naturally-occurring sample of Mg, the average mass of the atoms is 24.305 u; there is *not* a single Mg atom that actually has a mass of 24.305 u.

If we want information about specific isotopes of an element, we need to look it up from more extensive data sources. For example, we can look up the following information about naturally-occurring isotopes of Mg from webelements.com:

(<http://webelements.com/magnesium/isotopes.html>)

- Mg-24, mass = 23.99 u, natural abundance = 78.99%.
- Mg-25, mass = 24.99 u, natural abundance = 10.00%.
- Mg-26, mass = 25.98 u, natural abundance = 11.01%.

A natural abundance of 78.99% for Mg-24 means that about 79 out of every 100 atoms have a mass of 23.99 u. The average mass of can be calculated from the information above using the formula:

Average Mass = Sum of (relative abundance \times mass)

In other words,

$$\begin{aligned}\text{Average Mass of Mg} &= (78.99\%)(23.99 \text{ u}) + (10.00\%)(24.99 \text{ u}) + (11.01\%)(25.98 \text{ u}) \\ &= 24.31 \text{ u}\end{aligned}$$

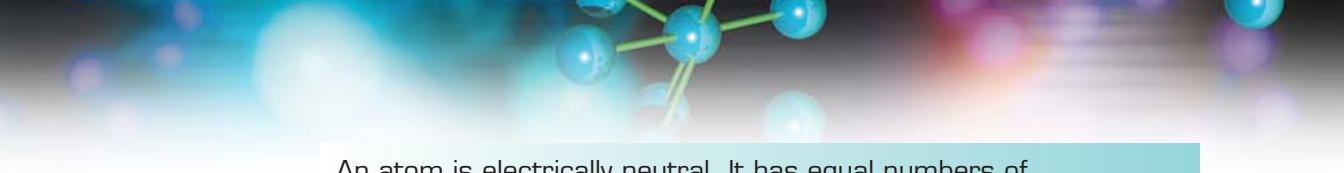
3.7 Electrical Charge

Electrons and protons are said to be *electrically-charged*, while neutrons are *electrically-neutral*. The unit for electric charge is the Coulomb (official abbreviation: C). Electrons carry the smallest magnitude of charge known, which is -1.602×10^{-19} C. This amount of charge is usually assigned a value of “-1” (atomic units). Protons have a charge of $+1.602 \times 10^{-19}$ C, or “+1” (atomic units). Neutrons are not charged (charge = 0). All atoms are electrically neutral. This means that they have equal numbers of protons and electrons.

► Example

An atom has 10 protons. How many electrons does it have?

Answer: 10 electrons



An atom is electrically neutral. It has equal numbers of protons and electrons. If an atom has 10 protons, it also has 10 electrons.

► Example

What is the nuclear charge of a magnesium atom?

Answer: +12 (atomic units), or $(12)(+1.602 \times 10^{-19} \text{ C})$

By nuclear charge, we mean the total charge of the nucleus.

The charge of the nucleus is due to the protons. Referring to a periodic table, we find that the atomic number of magnesium is 12. Therefore, any magnesium atom has 12 protons in its nucleus. Since each proton carries a charge of +1 atomic unit, the charge of the nucleus is +12. In Coulombs, the charge is $(12)(+1.602 \times 10^{-19} \text{ C})$

Particles with like charges are known to repel each other, while those with unlike charges attract each other. Therefore, electrons repel each other, and protons repel each other, but a proton and an electron attract each other. The attraction and repulsion forces due to charge are called Coulombic or electrostatic forces. But if protons repel each other, why are they clustered very close together in the nucleus? A much stronger force, which works only at very short distances, called the *strong* force (or strong nuclear force), holds the protons and neutrons together in the nucleus. The attractions due to the strong force counteract the repulsive Coulombic forces among the protons in the nucleus.

3.8 Radioactivity

Neutrons are needed to stabilize a nucleus that has more than one proton. If there are too many or too few neutrons, the atom would be unstable. The nuclei of unstable atoms tend to break up over time; the break up of a nucleus is called nuclear *fission*. These unstable atoms are said to be *radioactive*.

It is tempting to think that there would be no naturally-occurring radioisotopes since they are unstable. In fact, there are naturally-occurring radioisotopes. These are the ones that have extremely long half-lives. The half-life of a radioactive atom is the time it takes for half of the atoms to decay (transform into something else). For example, U-238 has a half-life of 4.46 billion years. This means that half of U-238 that existed 4.46 billion years ago are still here. Less stable radioisotopes can be created in the laboratory by bombarding atoms with energetic (very fast moving) particles, such as neutrons from a nuclear reactor, or charged particles accelerated within a cyclotron.

3.9 Formation of Ions and Molecules

Most naturally-occurring atoms have a stable nucleus (non-radioactive). For most everyday phenomena, the nuclei of atoms remain intact. However, atoms may:

- lose electrons to other atoms.
- gain electrons from other atoms.
- share electrons with other atoms.

These lead to the formation of ions and molecules.

3.10 Cations and Anions

Every atom is electrically neutral; each one has an equal number of protons and electrons. An ion has an unequal number of electrons and protons. We define the charge of an ion as the number of protons minus the number of electrons.

$$\text{Charge of ion} = (\text{Number of protons}) - (\text{Number of electrons})$$

Note that the charge of an atom, which has an equal number of protons and electrons, is zero.

An ion with more protons is positively charged and is called a cation (pronounced as *cat eye on*). An ion with more electrons is negatively charged and is called an anion (pronounced as *an eye on*).

► Example

What is the charge of an ion with 12 protons and 10 electrons?
Is it a cation or anion?

Answer: +2, cation

The charge of the ion is:

$$\begin{aligned}\text{Charge} &= (\text{Number of protons}) - (\text{Number of electrons}) \\ &= 12 - 10 = +2.\end{aligned}$$

Since the charge is positive, the ion is a cation.

3.11 Monatomic Ions

When an atom loses or gains one or more electrons, the result is a *monatomic ion*.

When writing symbols or formulas of ions, the charge must be indicated as a superscript (upper right-hand corner). The standard way of indicating charges is to put the magnitude in front of the algebraic sign. If the magnitude of the charge is 1, the number is omitted.

► Example

What type of ion (cation or anion) is formed when a magnesium atom loses two electrons? Write the symbol for the ion.

Answer: cation, Mg^{2+}

Loss of two electrons means that there will be two fewer electrons (compared to protons).

$$\begin{aligned}\text{Charge} &= (\text{Number of protons}) \text{ minus } (\text{Number of electrons}) \\ &= +2\end{aligned}$$

Loss of electron(s) leads to the formation of a positively charged ion, a cation. Since the charge is +2, the symbol for the ion is Mg^{2+} . Note that the 2 is written in front of the + sign. In very old textbooks, you may see the symbol written as Mg^{+2} or Mg^{++} .

► Example

What type of ion (cation or anion) is one that has 7 protons and 10 electrons? Write the symbol for the ion.

Answer: anion, N^{3-}

The charge is (Number of Protons) minus (Number of Electrons) = $7 - 10 = -3$. Since the charge is negative, the ion is an anion. Referring to a periodic table, we find that an atom with 7 protons is a nitrogen atom. So an ion with 7 protons is derived from a nitrogen atom. The symbol for the ion is N^{3-} . In old textbooks, you may see this written as N^{-3} or $\text{N}^{- - -}$.

In the examples above, we are assuming that the ion being described is *monatomic*; that is, derived from just one atom. It is possible to have ions with more than one atom; these are called *polyatomic* ions.

3.12 Molecules

A molecule is an electrically-neutral group of two or more atoms that share electrons. We say that the atoms in a molecule are held together by *covalent bonding*.

A *formula* is used to describe the composition of a molecule. In a formula, we list the symbols of the elements that make up the molecule and use subscripts to indicate how many atoms of each element are in the molecule. Unwritten subscripts are implied to be 1. To eliminate possible confusion, symbols of elements must be written properly: the first letter must be capitalized; any succeeding letter must be in lower case.



► **Example**

About twenty percent of air molecules are O_2 molecules. How many atoms are in a molecule of O_2 ?

Answer: 2 atoms

The formula for the molecule (O_2) has a subscript of 2 for O. This means that there are two O atoms in one molecule of O_2 .

► **Example**

Which represents a molecule: Co or CO?

Answer: CO a molecule consisting of two atoms — one carbon atom (symbol: C) and one oxygen atom (symbol: O). Co is the symbol for the element cobalt; it represents one atom.

► **Example**

How many atoms are in a molecule of acetic acid, CH_3COOH ?

Answer: 8 atoms

The formula CH_3COOH implies that the molecule contains two C atoms, two O atoms, oxygen atoms, and four H atoms. Note that if there is no subscript indicated, the subscript is implied to be 1. In the formula above, The subscripts shown for H are 3 and 1, for a total of 4. The formula of this molecule could also be written as $C_2H_4O_2$. It is typically written as CH_3COOH to reflect the way the atoms are connected.

► **Example**

How many electrons and protons are in a molecule of ammonia (NH_3)?

Answer: 10 electrons, 10 protons

A molecule of NH_3 consists of one nitrogen atom and three hydrogen atoms. Referring to the periodic table, we find that each N atom has 7 protons; each H atom has 1 proton. Therefore, a molecule of NH_3 consists of 10 protons (7 in the N atom and 1 in each of the 3 H atoms). Since a molecule is electrically-neutral, it has an equal number of protons and electrons. Therefore, one molecule also has 10 electrons.

3.13 Polyatomic Ions

A polyatomic ion is an electrically-charged group of two or more atoms that share electrons. The atoms sharing electrons are said to be held together by covalent bonding. You can think of a polyatomic ion as a “charged molecule”, just as a monatomic ion is a “charged atom.”

The formula of a polyatomic ion lists the symbols of the elements that make up the ion. In the formula, we use subscripts to indicate how many atoms of each element are in one ion, and a superscript to indicate the charge.

► Example

The polyatomic ion called nitrate has a formula of NO_3^- . How many protons and electrons does a nitrate ion have?

Answer: 31 protons, 32 electrons

Referring to a periodic table, we find that each N atom has 7 protons and each O atom has 8 protons. Therefore, a nitrate ion (NO_3^-) has 31 protons, 7 in the N atom and 8 in each of the three O atoms: $7 + 3(8) = 31$.

Since the NO_3^- ion has a charge of -1 , it has one more electron compared to protons; therefore, the ion has $31+1$ (or 32) electrons.

► Example

The polyatomic ion called mercury(I) or mercurous has a formula of Hg_2^{2+} . How many protons and electrons does a mercurous ion have?

Answer: 160 protons, 158 electrons

Referring to a periodic table, we find that a mercury atom has 80 protons. Therefore, a mercurous ion (Hg_2^{2+}) has 2×80 , or 160 protons. The $+2$ charge means that the ion has two fewer electrons compared to protons. Therefore, the number of electrons is $160-2$, or 158. To check, recall that charge is equal to (Number of Protons) minus (Number of electrons): $160 - 158 = +2$.

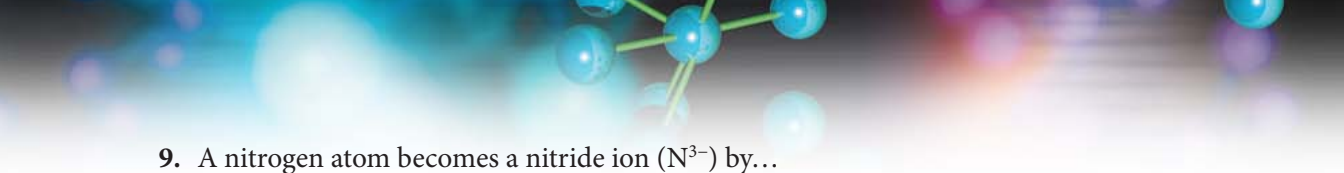


TEST YOURSELF

For answers and other study resources, see:

<http://i-assign.com/ebook/answers/chapter3.htm>.

- Which of the following subatomic particles are found in the nucleus of an atom?
A. protons and neutrons B. protons and electrons
C. neutrons and electrons D. protons, neutrons, and electrons
- The symbol ^{13}C or C-13 represents an atom with...
A. 13 protons B. 13 electrons C. 13 neutrons D. 13 nucleons
- Which of the following has the largest mass number?
A. ^{56}Mn B. ^{56}Fe
C. ^{56}Cr D. they all have the same mass number
- How many neutrons does an O-18 atom have?
A. 8 B. 10 C. 16 D. 18
- Which of the following has the largest total mass?
A. 2 protons + 4 electrons B. 2 neutrons + 2 protons
C. 6 electrons D. they all have the same mass
- The mass of one atom of Mg-26 is closest to:
A. 24.3 u B. 24.0 u C. 26.0 u D. 12.0 u
- Which of the following is false?
A. An atom's mass is concentrated in the nucleus
B. The atom's nucleus is positively charged
C. The number of electrons in an atom is equal to the number of protons
D. The number of protons in an atom is equal to the number of neutrons
- A magnesium atom becomes a magnesium ion (Mg^{2+}) by...
A. gaining two electrons B. losing two electrons
C. gaining two protons D. losing two protons

- 
9. A nitrogen atom becomes a nitride ion (N^{3-}) by...
- A. gaining 3 electrons B. losing 3 electrons
C. gaining 3 protons D. losing 3 protons
10. How many protons and electrons are in a nitride ion (N^{3-})?
- A. 7, 10 B. 7, 4 C. 10, 7 D. 4, 7
11. How many protons and electrons are in a magnesium ion (Mg^{2+})?
- A. 10, 12 B. 12, 10 C. 24, 22 D. 22, 24
12. Which of the following describes a cation?
- A. an aluminum ion (Al^{3+})
B. an oxygen atom that has gained 2 electrons
C. an ion with 17 protons and 18 electrons
D. an ion with more neutrons than protons
13. Which of the following describes an anion?
- A. a sodium ion (Na^+)
B. a calcium atom that has lost 2 electrons
C. an ion with 8 protons and 10 electrons
14. How many hydrogen atoms are in 5 molecules of acetic acid (CH_3COOH)?
- A. 3 B. 4 C. 15 D. 20
15. How many electrons are in a sulfur trioxide (SO_3) molecule and a sulfite ion (SO_3^{2-})?
- A. 40, 40 B. 40, 42 C. 38, 40 D. 78, 80
16. In a fictitious world, element X has only two isotopes: ^{77}X with a mass of 77.0 u and ^{78}X , with a mass of 78.0 u. The relative abundance of the heavier isotope is 30.0%. The average mass of the X atoms is...
- A. 77 u B. 77.3 u C. 77.5 u D. 78 u
17. In a fictitious world, element Z has only two isotopes: ^{35}Z with a mass of 35.00 u and ^{37}Z , with a mass of 37.00 u. What is the relative abundance of the lighter isotope if the average mass is 35.8 u?
- A. 40.0% B. 50.0% C. 60.0%

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Basic Physics Concepts

A good understanding of basic physics concepts is very useful for understanding Chemistry. In this chapter, we will review important concepts by examining one-dimensional motion. If the movement of an object is restricted to a straight line, we say that it is confined to move in one dimension. In general, to completely describe the motion of an object, we need to describe three dimensions; we need to describe how it is moving (1) “up and down”, (2) “left and right”, and (3) “front and back”. We will conclude this chapter by applying the concepts to describe the behavior of atoms.

4.1 The Position Vector

In order to locate anything, we need to first define a point of reference; we call this the *origin*. Then, to locate something, we simply specify two things:

1. how far it is from the origin, and
2. which direction we need to take in order to get there from the origin.

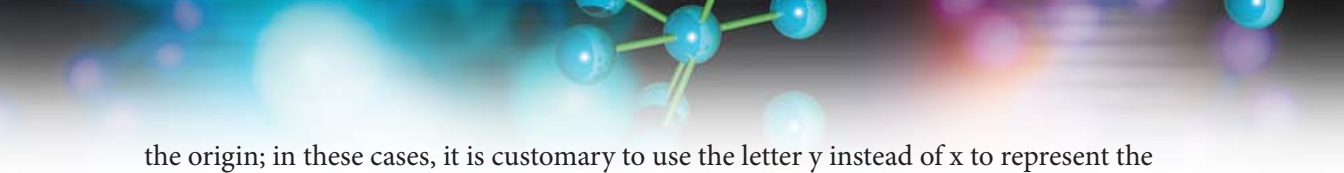
Location, or position, is an example of a *vector* — something that has magnitude and direction. Something that only has magnitude is called a *scalar*. If the movement of the object is restricted to a straight line, it is convenient to select a point on the line as the origin. At the origin, the location (x) is defined to be zero. The location is specified by using positive numbers if the object is on one side of the origin, and negative numbers are used if it is on the other side. The “magnitude” of the location is the distance from the origin and the algebraic sign (positive or negative) tells us the “direction.” It is customary to imagine that the line of motion is a horizontal line and to take locations that are to the right (or east) of the origin as positive, and locations that are to the left (or west) of the origin as negative. In other words,

$$x = +5.0 \text{ m}$$

means 5.0 meters to the right of the origin, and

$$x = -2.0 \text{ m}$$

means 2.0 meters to the left of the origin. We can also imagine the line of motion as a vertical line and to take location as positive north of the origin, and negative south of



the origin; in these cases, it is customary to use the letter y instead of x to represent the location.

4.2 The Displacement Vector

The difference in the location of an object at two instances is called its displacement. Suppose it is located at x_1 and x_2 at times t_1 and t_2 , respectively. The displacement is defined as:

$$\Delta x = x_2 - x_1$$

When the Greek letter delta (Δ) is written in front a symbol, it means “change in whatever the symbol stands for.” Thus, Δx means “change in x ”; it is calculated by subtracting the initial value (x_1 in this case) from the final value (which in this case is x_2).

► Example

An object moves 3.0 m to the left, what is the displacement?

Answer: -3.0 m, if we take locations right of the origin as positive and locations left of the origin as negative. Since the final location is to the left of the original location, we expect x_2 to be less than x_1 . Therefore, x_2 minus x_1 would be negative.

$$\Delta x = x_2 - x_1 = -3.0 \text{ m}$$

4.3 Distance

The distance that an object has traveled is equal to the absolute value of the displacement *if it does not change direction*.

$$d = |\Delta x|$$

If it changes direction, then we add up the distances traveled for each leg of the trip to get the total distance traveled. Distance is always a positive number.

► Example

An object moves 2.0 m to the right, then 3.0 m to the left. Calculate the displacements for each leg and the total distance traveled.

Answer: for the first leg, the displacement and distance traveled are:

$$\Delta x = +2.0 \text{ m}, d = 2.0 \text{ m}$$

and for the second leg, the displacement and distance traveled are:

$$\Delta x = -3.0 \text{ m}, d = 3.0 \text{ m}$$

The total displacement is:

$$\Delta x = (+2.0 \text{ m}) + (-3.0 \text{ m}) = -1.0 \text{ m}$$

but the total distance traveled is:

$$d = (2.0 \text{ m}) + (3.0 \text{ m}) = 5.0 \text{ m}$$

We can see that the object ends up being 1.0 m to the left of its original location; the displacement is -1.0 m . However, it has traveled a total distance of 5.0 m.

4.4 Speed

Speed refers to how fast an object is moving. The *average* speed of an object is calculated by dividing the distance traveled by the amount of time that has elapsed:

$$s = \frac{d}{\Delta t}$$

► Example

Suppose an object travels 10.0 km in 2.0 hr. Calculate its average speed?

Answer: 5.0 km/hr or 5.0 km hr⁻¹

We calculate the average speed by dividing the distance by the elapsed time.

$$s = \frac{d}{\Delta t} = \frac{10.0 \text{ km}}{2.0 \text{ hr}} = 5.0 \text{ km hr}^{-1}$$

We keep only two significant digits in the answer since the less precise term in the calculation, 2.0 hr, has only two significant digits.

In the preceding example, we say that the average speed is 5.0 km per hour. It does not necessarily mean that the object traveled 5.0 km every hour. It could have traveled 8.0 km during the first hour, then 2.0 km during the second hour. This would still amount to a total distance traveled of 10.0 km in 2.0 hours. Or it could have traveled 3.0 km during the first 30 minutes, then 7.0 km during the next 1-1/2 hour. In fact, there are an infinite number of possibilities. This is why what we have calculated is called the *average* speed. The actual speed at a specific point in time is called the *instantaneous* speed (or simply the *speed*). If you were traveling in a car, your instantaneous speed would be what your speedometer says at any given instant; it will most likely be changing throughout your entire trip.

4.5 Velocity

The *velocity*, v , is defined as the rate of change of location. For one-dimensional motion, the *average velocity* is:

$$v = \frac{\Delta x}{\Delta t}$$

It is equal to the speed if the object is moving towards more positive locations, and equal to the negative of the speed if the object is moving towards more negative locations. In other words, the velocity of an object refers to its speed **and** direction; the magnitude is the speed:

$$s = |v|$$

and the direction is specified by the algebraic sign.

► Example

An object is moving at velocity of -5.0 m/s. What is its speed?

Answer: $s = |-5.0 \text{ m/s}| = 5.0 \text{ m/s}$

Speed, by definition, is always a positive number.

► Example

A ball moves 20.0 m eastward for 4.00 s, then moves 20.0 m westward for 1.00 s. Calculate the average velocity and average speed.

Answer:

Let us take the eastward direction as the positive direction. For the first leg of the trip, the velocity is positive since the ball is moving eastward:


$$v_1 = \frac{\Delta x}{\Delta t} = \frac{20.0 \text{ m}}{4.00 \text{ s}} = 5.00 \text{ m s}^{-1}$$

For the second leg of the trip, the average velocity is:

$$v_2 = \frac{\Delta x}{\Delta t} = \frac{-20.0 \text{ m}}{1.00 \text{ s}} = -20.0 \text{ m s}^{-1}$$

The velocity is negative since the ball is moving westward. For the entire trip, the average velocity is:

$$v = \frac{\Delta x}{\Delta t} = \frac{0.00 \text{ m}}{5.00 \text{ s}} = 0.0 \text{ m s}^{-1}$$



The average velocity is zero because the overall displacement is zero; the ball returned to its original position. But the average of +5 and -20 is -12.5, not zero! Why the difference? The reason is that the ball spends four times longer moving eastward at 5.0 m s^{-1} . Essentially, what we have calculated is a weighted average.

For the overall trip, the total distance traveled is 40.0 m and the total elapsed time is 5.0 s. Therefore, the average speed is:

$$s = \frac{d}{\Delta t} = \frac{40.0 \text{ m}}{5.00 \text{ s}} = 8.00 \text{ m s}^{-1}$$

Again, this is not just the average of 5.0 and 20.0; this is also *not* the magnitude of the average velocity (which is zero). The average speed is the magnitude of the average velocity only if the direction of motion does not change.

4.6 Acceleration

An object is said to be accelerating if it changes velocity. The change in velocity may be due to change in speed or direction, or both. The acceleration vector is defined as the rate of change of velocity. Just like speed and velocity, acceleration can change during a finite time interval; the average acceleration is:

$$a = \frac{\Delta v}{\Delta t}$$

The SI unit for acceleration is meters per second per second (m/s/s) or meters per second-squared (m/s^2 or m s^{-2}).

► Example

True or False. An object moving at constant speed is not accelerating.

Answer: False. It could be accelerating if it is changing direction.

Based on the definition of acceleration, we can say that the acceleration and velocity vectors have the same algebraic sign if an object speeds up without changing direction. Acceleration and velocity have opposite signs if the object slows down or reverses direction.

► Example

An object moving on a straight line speeds up from 4.0 m s^{-1} to 8.0 m s^{-1} in 4.0 s . Calculate the average acceleration.

Answer: $+1.0 \text{ m s}^{-2}$

It is customary to take the original direction of motion as positive. Therefore, let us take the initial velocity as positive:

$$v_1 = +4.0 \text{ m s}^{-1}$$

Since the object is not changing direction, the final velocity is also positive:

$$v_2 = +8.0 \text{ m s}^{-1}$$

The average acceleration is:

$$a = \frac{\Delta v}{\Delta t} = \frac{v_2 - v_1}{\Delta t} = \frac{(8.0 \text{ m s}^{-1}) - (4.0 \text{ m s}^{-1})}{4.0 \text{ s}} = 1.0 \text{ m s}^{-2}$$

which turns out to be positive as well. This means that, on average, the object's speed increased by 1.0 m s^{-1} every second. In 4.0 seconds, the speed went up by 4.0 m s^{-1} (from 4.0 m s^{-1} to 8.0 m s^{-1}). The acceleration and velocity vectors are both positive; both vectors are pointing in the same direction when an object is speeding up. Had we taken the direction of motion as negative, we would have gotten an acceleration of -1.0 m s^{-2} .

► Example

An object moving in a straight line slows down from 4.0 m s^{-1} and comes to a complete stop in 2.0 s . Calculate the average acceleration.

Answer: -2.0 m s^{-2}

Let us take the initial velocity as positive:

$$v_1 = +4.0 \text{ m s}^{-1}$$

Since the object came to a stop, the final velocity is zero:

$$v_2 = 0.0 \text{ m s}^{-1}$$

The acceleration is:

$$a = \frac{\Delta v}{\Delta t} = \frac{v_2 - v_1}{\Delta t} = \frac{(0.0 \text{ m s}^{-1}) - (4.0 \text{ m s}^{-1})}{2.0 \text{ s}} = -2.0 \text{ m s}^{-2}$$

which is negative. This means that the acceleration vector is pointing in the opposite direction (compared to the original velocity). Any time an object slows down in a given direction, we should get opposite algebraic signs for acceleration and velocity. Had we taken the original direction as negative, we would have gotten a positive value for the acceleration.

► Example

True or False. A negative acceleration means that an object is slowing down.

Answer: False. It is true only if the original direction of motion is taken as positive. If the original direction of motion is taken as negative, then a negative acceleration means that the velocity is becoming even more negative and the object is speeding up in that direction.

► Example

A molecule, moving at a constant speed of 500.0 m s^{-1} towards a wall, collides with the wall, then moves in the opposite direction at a constant speed of 500.0 m s^{-1} during a time interval of 0.10 s . Calculate the average acceleration during this time interval?

Answer: $-1.0 \times 10^4 \text{ m s}^{-2}$

Let us take the initial velocity as positive:

$$v_1 = +500.0 \text{ m s}^{-1}$$

Since the final velocity is in the opposite direction, we assign it a negative value:

$$v_2 = -500.0 \text{ m s}^{-1}$$

Therefore, the average acceleration is:

$$a = \frac{\Delta v}{\Delta t} = \frac{v_2 - v_1}{\Delta t} = \frac{(-500.0 \text{ m s}^{-1}) - (500.0 \text{ m s}^{-1})}{0.10 \text{ s}} = -1.0 \times 10^4 \text{ m s}^{-2}$$


Here, we have an example of something moving at constant speed, but changing direction. The velocity is not constant and the acceleration is not zero.

4.7 Force

Force is defined as a push or a pull that objects experience when they interact with other objects. Force is a vector and the sum of all the forces acting on an object, the *net force* (F), is directly proportional to the observed acceleration of the object; the direct proportionality is the mass of the object (m). Mathematically, we say that:

$$F = m a$$

This equation means that, if an object is experiencing acceleration, there must be a *net* force acting on it. The greater the acceleration, the greater the net force. It also means that



a greater force is needed to cause the same acceleration for a larger mass. This equation is known as *Newton's second law of motion*. When we say *net* force, we mean the sum of all the forces acting on the object. The unit for force is Newton, N, which is equivalent to 1 kg m s^{-2} .

Since mass is always positive, *the force vector points in the same direction as the acceleration vector*. Force and acceleration have the same algebraic sign. If an object is speeding up as it is moving in a particular direction, then it must be experiencing a net pull or push in that direction. If it is slowing down, then it must be experiencing a net push or pull in the opposite direction. If it reverses direction, then it must be experiencing a net push or pull in the direction opposite the original direction.

► Example

An object heading east slows down. What is the direction of the net force vector?

Answer: West.

If it slows down as it is heading east, something must be pulling or pushing it westward.

► Example

The speed of a 10.0 kg object in “free fall” increases by 9.8 m/s every second. Calculate the net force on the object.

Answer: Let us assume that the downward direction is negative. Since the object is increasing speed as it moves downward, its acceleration is also negative. Therefore:


$$a = -9.8 \text{ m s}^{-2}$$

The acceleration must be due to a net force that is also negative (pointing downward):

$$F = m a = (10.0 \text{ kg})(-9.8 \text{ m s}^{-2}) = -98 \text{ N}$$

The value 9.8 m s^{-2} in the preceding example is observed for all falling objects near the surface of the earth, in the absence of any air around the object. It is called the *acceleration due to gravity*, and is represented by the letter *g*. Experience suggests that the force involved here (called gravitational force) exists between any pair of objects; any pair of objects will have an attraction for each other due to gravitational force. The magnitude of the gravitational force that the earth exerts on an object is called the object's *weight* (on earth):

$$W = m g$$



Newton's third law of motion says that for every action, there is an equal and opposite reaction. This means that the object also pulls on the earth with a force equal to mg directed towards the center of the object.

► Example

What is the weight of a 0.50 kg book? How much force does the book exert on the earth?

Answer: 4.9 N

Near the surface of the earth, the weight is:

$$W = m g = (0.50 \text{ kg})(9.8 \text{ m s}^{-2}) = 4.9 \text{ N.}$$

If we take the downward direction as negative, then we say that the force on the book due to gravity is -4.9 N . By Newton's third law, the book is also pulling on the earth with a force of $+4.9 \text{ N}$.

Consider a book, at rest, on a table. Since the book is not moving, its velocity is constant and equal to zero. Since velocity is constant, acceleration is also equal to zero (and also constant). Since acceleration is zero, the net force is also zero. We saw in the preceding example that the earth does exert a downward (gravitational) force on the book. There must be a force on the book equal in magnitude to its weight but directed upward in order for the net or total force to be equal to zero. Where does this upward force come from? It comes from the interactions of the atoms on the table's surface with the atoms of the book. Once these atoms get too close, they start to repel each other. It is customary to lump all of these forces together and call the net upward force as the *normal force*.

► Example

Suppose the speed of a 10.0 kg falling object increases by only 4.5 m s^{-1} , instead of 9.8 m s^{-1} , every second because of air resistance. Calculate the upward force due to air resistance.


Answer: +53 N

Let us assume that the downward direction is negative. Since the object is increasing speed as it moves downward, its acceleration is also negative. Therefore:

$$a = -4.5 \text{ m s}^{-2}$$

The acceleration must be due to a net force that is also negative (that is, pointing downward):

$$F = m a = (10.0 \text{ kg}) (-4.5 \text{ m s}^{-2}) = -45 \text{ N}$$



This net force is equal to the force due to gravity and the force due to air resistance:

$$F = F_{\text{gravity}} + F_{\text{air resistance}}$$

If we take the downward direction as negative, then the force due to gravity is:

$$F_{\text{gravity}} = (m)[-g] = (10.0 \text{ kg}) (-9.8 \text{ m s}^{-2}) = -98 \text{ N}$$

Therefore:

$$F_{\text{air resistance}} = F - F_{\text{gravity}} = (-45 \text{ N}) - (-98 \text{ N}) = +53 \text{ N}$$

which is positive; it is directed upward and opposes the effect of gravity. Thus, the object does not speed up as much.

Consider a book, at rest, on a table. Suppose we attempt to push it sideways by applying a force of, say, 10.0 N, but it does not move. Since the book is not moving, its velocity is constant and equal to zero. Since velocity is constant, acceleration is also equal to zero (and also constant). Since acceleration is zero, the net force is also zero! Since we are exerting a 10.0 N force on the book, there must be another force with a magnitude of 10.0 N acting on the book in the opposite direction. We call this force *friction*. It comes from the interactions of the atoms on the table's surface with the atoms of the book.

Any pair of particles in nature exerts a force on each other, called gravitational force, and numerous observations suggest that gravitational force depends on the masses of the particles and how far they are from each other.

$$F_{\text{grav}} = \frac{G m_1 m_2}{r^2}$$

where G is a constant ($6.67 \times 10^{-11} \text{ N m}^2 \text{ kg}^{-2}$), m_1 and m_2 are the masses of the particles and r is the (center-to-center) distance between them. Consider the earth (with mass $m_1 = 6.0 \times 10^{24} \text{ kg}$) and an object (with mass m_2) as two particles separated from each other by a distance equal to the radius of the earth ($r = 6.4 \times 10^6 \text{ m}$). We can calculate the gravitational force of attraction between the object and earth to be:

$$F = \frac{(6.67 \times 10^{-11} \text{ N m}^2 \text{ kg}^{-2})(6.0 \times 10^{24} \text{ kg})m_2}{(6.4 \times 10^6 \text{ m})^2} = (9.8 \text{ m s}^{-2})m_2$$

Since the radius of earth is very large, the acceleration due to gravity is essentially constant, 9.8 m s^{-2} , near the surface of the earth; the r^2 term in the denominator will hardly change the magnitude of the force. Gravitational force is attractive. An object of mass m is being pulled with a force equal to mg directed towards the center of the earth.

All objects are made up of very tiny particles called atoms. Each atom consists of an even smaller particle called the nucleus surrounded by even smaller particles called electrons. Each nucleus is made up of even smaller particles called protons and neutrons. Electrons

and protons are said to be “electrically charged” and numerous observations suggest that a force, called electrostatic or Coulombic, exists between any pair of charged particles and this force is stronger than the gravitational force between the particles. The Coulombic force depends on the charge of the particles (q_1 and q_2) and the distance between them (r):

$$F_{\text{coul}} = \frac{k q_1 q_2}{r^2}$$

In the preceding equation, which is known as Coulomb’s law (in honor of Charles Augustin de Coulomb), k is a constant equal to $9.00 \times 10^9 \text{ N m}^2 \text{ C}^{-2}$, the charge of an electron is $-1.602 \times 10^{-19} \text{ C}$, and the charge of the nucleus is a $(Z)(+1.602 \times 10^{-19} \text{ C})$, where Z is the number of protons in the nucleus. The unit of charge, C, stands for Coulomb. Coulombic force can be positive or negative; a positive value indicates repulsion (“like charges repel”) and a negative value indicates attraction (“unlike charges attract”). Electrons repel each other; a proton and an electron attract each other. The constant, k , is oftentimes written as:

$$\frac{1}{4 \pi \epsilon_0}$$

where π is 3.1415... and ϵ_0 (“epsilon naught”) is called the permittivity of vacuum, which has a value of $8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$.

► Example


The most probable distance of the electron from the nucleus of a hydrogen atom is 52.9 pm. Compare the gravitational and Coulombic forces at this distance. Given: mass of electron is $9.11 \times 10^{-31} \text{ kg}$, mass of proton is $1.67 \times 10^{-27} \text{ kg}$, $1 \text{ pm} = 10^{-12} \text{ m}$.

Answer: Plugging in the masses, charges and distance in the appropriate formulas, we find that the magnitude of the Coulombic force is about 10^{39} times larger.

$$F_{\text{grav}} = \frac{(6.67 \times 10^{-11} \text{ N m}^2 \text{ kg}^{-2}) (9.11 \times 10^{-31} \text{ kg}) (1.67 \times 10^{-27} \text{ kg})}{(52.9 \times 10^{-12} \text{ m})^2} = 3.63 \times 10^{-47} \text{ N}$$

$$F_{\text{coul}} = \frac{(9.00 \times 10^9 \text{ N m}^2 \text{ C}^{-2}) (-1.602 \times 10^{-19} \text{ C}) (1.602 \times 10^{-19} \text{ C})}{(52.9 \times 10^{-12} \text{ m})^2} = -8.25 \times 10^{-8} \text{ N}$$

All forces in nature can be classified into four fundamental types: electromagnetic, strong, weak, and gravitational. Strong and weak forces are significant only between particles at very, very, very short distances from each other (such as protons and neutrons in



a nucleus). In Chemistry, we are mostly concerned with electromagnetic forces when dealing with interactions of protons and electrons at typical atomic distances. Electromagnetic forces include electrostatic (Coulombic) and magnetic forces. We may consider gravitational forces when considering macroscopic (bulk) systems.

► Example

What type of fundamental forces is mainly responsible for friction?

Answer: electromagnetic

Friction is due to interactions among atoms. Forces among atoms are primarily electromagnetic in nature.

4.8 Kinetic Energy

If an object of mass m has a velocity v , then its kinetic energy is defined as:

$$K = \frac{1}{2} mv^2$$

The unit for kinetic energy is Joule (J), which is defined to be $\text{kg m}^2/\text{s}^2$ or $\text{kg m}^2 \text{s}^{-2}$.

► Example

Which has more kinetic energy?

A. 2.00 kg mass moving at 2.00 m s^{-1}

B. 2.00 kg mass moving at -2.00 m s^{-1}

Answer: Same.

A and B have the same mass but different velocities. But kinetic energy depends on the square of the magnitude of velocity, not the velocity itself. In other words, it depends only on speed, not direction. Kinetic energy is a scalar, not a vector. In this particular case, A and B have the same speed (2.00 m/s), even if they are moving in opposite directions.

► Example

What is the kinetic energy of a nitrogen molecule (mass = 4.65×10^{-26} kg) moving at a speed of 5.00×10^2 m s^{-1} ?

Answer: 5.81×10^{-21} J

$$\begin{aligned} K &= (1/2) m v^2 = (1/2) (4.65 \times 10^{-26} \text{ kg}) (5.00 \times 10^2 \text{ m s}^{-1})^2 \\ &= 5.81 \times 10^{-21} \text{ kg m}^2 \text{ s}^{-2}, \text{ or } 5.81 \times 10^{-21} \text{ J} \end{aligned}$$

4.9 Work and the Work-Energy Theorem

Work is defined as the application of a force over a distance. If a constant force, f , is applied on an object over a distance d , then the amount of work (w) done is:

$$w = f d$$

The unit for work is Joule (J), just like kinetic energy.

► Example

A force of 10.0 N is applied to an object while the object moves a distance of 0.50 m. Calculate the work.

Answer: $w = 5.0 \text{ J}$

$$w = f d = (10.0 \text{ N})(0.50 \text{ m}) = 5.0 \text{ J}$$

When work is done on an object, its kinetic energy increases if the force and velocity are pointing in the same direction; its kinetic energy decreases if the force and velocity are pointing in opposite directions. In other words, if something is moving to the right and it is pushed or pulled to the right, it will speed up. But if it is pushed or pulled to the left, then it will slow down and may eventually turn around. In fact, it can be shown that the work associated with the net force on the object is equal to the change in its kinetic energy; if the initial velocity is v_1 and the final velocity is v_2 , then:

$$w = \Delta K = K_2 - K_1 = \frac{1}{2} m v_2^2 - \frac{1}{2} m v_1^2$$

This is called the *work-energy theorem*.

Since ΔK is positive if the object speeds up and negative if the object slows down, it is convenient to use displacement instead of distance when calculating work:

$$w = f \Delta x$$


By doing this, we get a positive value for work if f and Δx have the same algebraic sign and a negative value if f and Δx have opposite signs.

► Example

What is the work due to gravity when a 1.00 kg object falls a distance of 0.50 m?

What is the speed at this point if the object starts from rest?

Answer: 4.9 J, 3.1 m s⁻¹



The force of gravity on the object is pointing downward. Let us take the downward direction as the negative direction. So, the acceleration is $-g$.

$$f = m a = (m)(-g) = (1.00 \text{ kg})(-9.8 \text{ m s}^{-2}) = -9.8 \text{ N}$$

The displacement is also negative since the object moved downward:

$$\Delta x = -0.50 \text{ m}$$

Therefore, work is: $w = f \Delta x = (-9.8 \text{ N})(-0.50 \text{ m}) = +4.9 \text{ J}$

Since we calculated a positive value, we say that the object gains 4.9 J of kinetic energy; it will be speeding up. If the object started from rest, then $v_1 = 0$ and

$$w = K_2 - K_1 = K_2 - 0 = (1/2) m v_2^2 - (1/2) m (0)^2$$

Solving for v_2 , we get:

$$v_2 = -\sqrt{\frac{2K_2}{m}} = -\sqrt{\frac{2w}{m}} = -\sqrt{\frac{2(4.9 \text{ kg m}^2 \text{ s}^{-2})}{1.00 \text{ kg}}} = -3.1 \text{ m s}^{-1}$$

Note that we took the negative square root since the object is moving downward and we have taken that as the negative direction. The speed is 3.1 m s^{-1} .

► Example

What is the net work done on a 0.50 kg object, initially at rest on the floor, if it is lifted, then held at a height (h) of 2.0 m?

Answer: Zero.

The initial and final velocities are both zero; the object is at rest initially and in the end. Therefore, the average acceleration is zero, the average net force is zero, and the net work done on the object is zero. The net work is equal to the change in kinetic energy, which is also zero.

Since the downward force due to gravity is $-mg$, the work due to gravity is $-mgh$. Therefore, the work due to the upward force must be $+mgh$, in order for the total work to be zero.

This means that the *average* upward force that needs to be exerted must be equal in magnitude to the force due to gravity. However, while the force due to gravity is constant ($-mg$), the upward force is not. It must first exceed mg in order to make the object move upward; eventually, it must be less than mg in order for the object to slow down and stop, and it must finally be equal to mg in order for the object to remain at rest.

4.10 Potential Energy

Any pair of particles is said to have a *potential energy* (V) due to the force they exert on each other, which depends only on the distance between them. Thus, potential energy is often defined as energy due to position. For any set of particles, the *total energy* (E) is defined as the sum of the kinetic energies of all the particles and the potential energies for every possible pair of particles.

► Example

Using K_i and V_{ij} to represent the kinetic energy of particle “ i ” and the potential energy due to the interaction of particles “ i ” and “ j ”, write the expression for the total energy of three particles (“1”, “2”, and “3”).

Answer: $E = K_1 + K_2 + K_3 + V_{12} + V_{13} + V_{23}$

The total energy is the sum of:


- K_1 , the kinetic energy of particle “1”
- K_2 , the kinetic energy of particle “2”
- K_3 , the kinetic energy of particle “3”
- V_{12} , the potential energy of interaction of particles “1” and “2”
- V_{13} , the potential energy of interaction of particles “1” and “3”, and
- V_{23} , the potential energy of interaction of particles “2” and “3”

Potential energy is defined such that, for any set of particles, the total energy is constant if there are no external forces affecting the particles. We could say that if we leave a set of particles alone, then its total energy is *conserved*; the potential and kinetic energies may change as the particles move, but the total energy remains the same. This means that a drop in potential energy implies an increase in the kinetic energy (faster movements) and vice versa.

► Example

Consider a ball and the earth as two particles; ignore the rest of the universe. As the ball is dropped from a certain height, what happens to the potential energy?

Answer: the potential energy decreases as the ball falls
We know that the ball will speed up as it falls. Therefore, its kinetic energy increases as it falls. Since the total energy must remain constant, the potential energy must decrease.



Whenever we are dealing with particles where one is much more massive than the other(s), as in the preceding example, it is customary to set the origin for describing the lighter particles at the location of the heavy particle. In this case, it is customary to consider potential energies as “belonging” to the lighter particles and, to a very good approximation, the sum of the potential and kinetic energies of the lighter particles can be taken as conserved. The nucleus of an atom is at least 1800 times more massive than an electron. Thus, when discussing energies of atoms, we typically only refer to potential and kinetic energies of the electrons.

► Example

Describe what happens to the potential energy of an electron as it moves away from a proton?

Answer: Since the electron and proton have opposite charges, they attract each other. The electron would be slowing down as it moves away from the proton. Its kinetic energy will be decreasing. Therefore, its potential energy will be increasing.

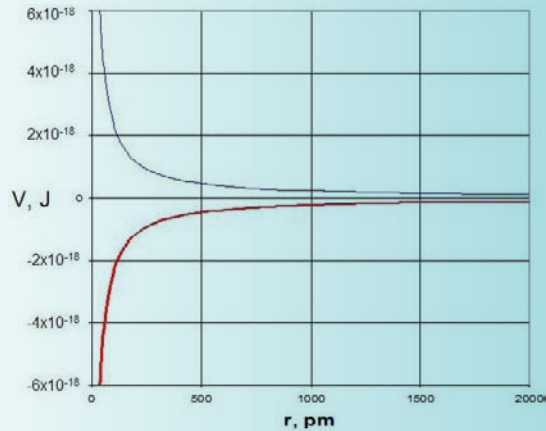
The value of potential energy does not really mean anything. What we are really interested in are *changes* in the value of the potential energy as particles move. The change in potential energy gives us information about the change in kinetic energy (whether a particle has sped up or slowed down). As a matter of convenience, we need to establish a “reference” so that we can have values for potential energy that we can use for calculations. For a pair of charged particles, a commonly used reference is the case where the particles are at infinite distance from each other; if we define the potential energy to be zero at this reference distance, then we can calculate the potential energy at any distance (r) using the following equation:

$$V = k \frac{q_1 q_2}{r}$$

where q_1 and q_2 are the charges and k is the same constant used in Coulomb’s law ($k=9.00 \times 10^9 \text{ N m}^2 \text{ C}^{-2}$). Examining the equation, we can see that as r approaches infinity (∞), the denominator becomes very large, making the potential energy (V) approach zero. As the two particles approach each other, the denominator (r) approaches zero and V rises towards $+\infty$ if the particles have like charges (q_1 and q_2 both positive or both negative); V drops towards $-\infty$ if the particles have unlike charges.

► Example

One of the two curves shown below corresponds to the potential energy between two electrons. Which one?

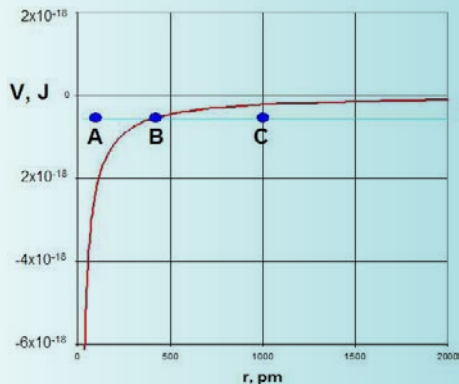



Answer: the blue curve

Two electrons would repel each other. As they move farther apart, they will be speeding up. This means they will be gaining kinetic energy. The potential energy will be dropping. The blue curve shows a potential energy that decreases and approaches zero as the distance (r) increases.

► Example

Shown below (red curve) is the potential energy for a proton and an electron (as in a hydrogen atom). If the green line represents the total energy, describe the two particles when they are separated at distances corresponding to points A, B, and C on the graph.





Answer: Based on Newton's 2nd law and Coulomb's law:

- Of the three points shown, point A corresponds to the case where the particles are closest to each other (about 100 pm apart). Note: 1 pm = 10^{-12} m.
 - If the particles happen to be approaching each other, the potential energy will be drastically dropping, which means that they will be speeding up their approach until they crash into each other. The kinetic energy, the vertical difference between the green curve (total energy) and red curve (potential energy), will be getting larger as r gets smaller.
 - If they happen to be moving away from each other, the potential energy will be increasing (red curve rising as r increases), and the particles will be slowing down (kinetic energy decreasing) until their separation corresponds to the distance at point B; this distance is around 420 pm.
- If the particles are separated by about 420 pm (which corresponds to point B), the potential and total energy would be equal (the red and green lines cross at point B). This means the kinetic energy is zero at this instant; the particles are motionless; all the energy is potential. However, there is an attractive force between the particles; so, they will start moving towards each other and speed up until they crash into each other.
- At distances larger than that at point B, as in point C (1000 pm), the kinetic energy is negative! Why? At these distances, the green curve is below the red curve; this means that the total energy is less than the potential. By definition, kinetic energy cannot be negative. $K = (1/2)mv^2$. Mass (m) is always positive and the square of the speed (v^2) is always positive. The part of the chart below the (red) potential energy curve is said to be a “forbidden region.” In other words, the particles can only separate as far as about 420 pm; from there, they move towards each other.

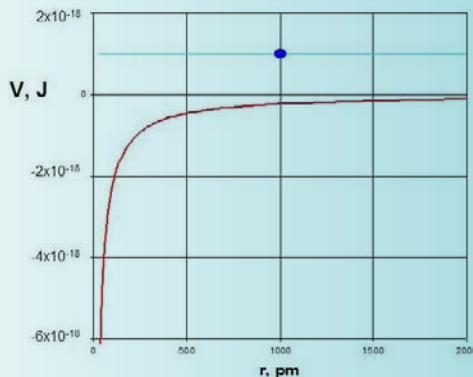
Note:

1. Since the proton is much more massive than the electron, we can take r as the location of the electron assuming the proton is fixed at the origin and take the energies mentioned in the discussion as just those of the electron.
2. The prediction we made for points A and B was troubling to scientists towards the end of the 19th century. It suggests that anytime an electron approaches a positive nucleus, it will eventually crash into it, which would mean that the atom as we now know it cannot possibly be stable long enough for any of us to exist. This, and other “anomalous” phenomena discovered around that time were eventually resolved with the develop-

ment of modern physics. The physics covered in this chapter, which was developed by Isaac Newton and others prior to the 20th century, is now referred to as *classical* physics. Among the strange predictions of modern physics is that there is a finite probability of the particles being in the forbidden region mentioned above. Thus, the said region is generally referred to as a “classically-forbidden” region.

► Example

Shown below (in red) is the potential energy for a proton and an electron (as in a hydrogen atom). If the green line (at 1×10^{-18} J) represents the total energy, describe what happens when the particles are separated by 1000 pm.

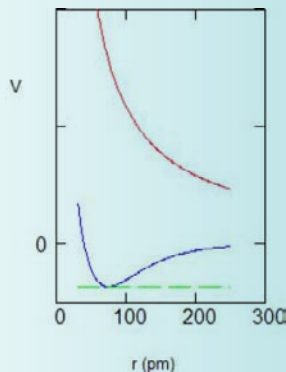


Answer: The blue point corresponds to the situation where the total energy is 1×10^{-18} J and the particles are separated by 1000 pm. According to classical physics:

- If they happen to be approaching each other, the distance (r) would be decreasing, the potential energy (red curve) would be decreasing, the kinetic energy would be increasing, the particles will be speeding up towards each other and eventually crash into each other.
- If they happen to be moving apart, the distance (r) would be increasing, the potential energy (red curve) would be increasing but eventually level off at zero, the kinetic energy would be decreasing and eventually level off at 1×10^{-18} J, the particles will be slowing down but eventually settle into a constant rate of separation and continue moving apart forever.

▶ Example

Consider the potential energy plots shown below. Which curve shows how the potential energy due to Coulombic interaction of two protons, V , depends on the distance between them?

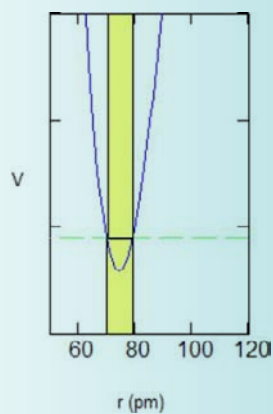


Answer: The red curve.

The potential energy approaches zero as r approaches infinity (∞) and rises to $+\infty$ as the protons approach each other. As two protons approach each other, the potential energy rises, which means that they will be slowing down (lose kinetic energy), which is what we expect since like charges repel each other. A curve that looks like this is often referred to as a (completely) repulsive potential.

Pairs of positively charged particles are hardly ever by themselves. For example, the two protons in an H_2 molecule are surrounded by two electrons, which have attractive interactions with the protons. In fact, the behavior of the two protons in H_2 is better described by the blue curve in the Figure above. V is zero at infinite distance. But as the nuclei approach each other, they actually gain kinetic energy as the potential energy dips below zero until they reach a distance of about 74 pm. As they get even closer, the potential energy starts to rise; this means that they start to slow down. The total energy of an average H_2 molecule at room temperature is shown on the graph by the green line. If we zoom in on this section (see below), we can conclude that the two protons in the average H_2 molecule are “stuck” together. With only as much total energy as indicated by the green line, they can only get as close as around 70 pm and cannot move farther than about 80 pm from each other. The nuclei will be oscillating between these two distances; the motion is called a *molecular vibration*. This “bonding” of two positive nuclei (that would otherwise repel each other) is made possible

by the sharing of electrons by the two atoms and is called *covalent bonding*. The distance where the minimum in V occurs is called the *bond length*.





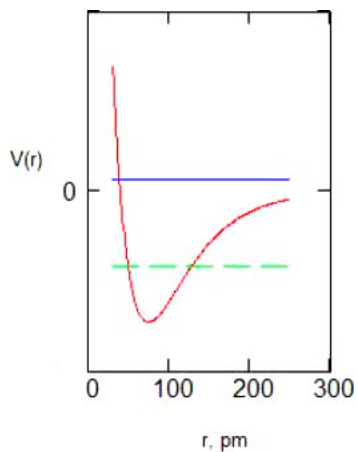
TEST YOURSELF

For answers and other study resources, see:

<http://i-assign.com/ebook/answers/chapter4.htm>.

1. An object is slowing down as it moves to the $+x$ direction. The acceleration of the object is...
A. positive B. negative C. zero
2. An object is speeding up as it moves in the $-x$ direction. The net force on the object is...
A. positive B. negative C. zero
3. When subjected to the same amount of force, which of these atoms would experience greater acceleration?
A. H B. He
4. When an atom moving in the $+x$ direction collides with a wall and reverses direction. Which of the following is true?
A. the acceleration of the atom is negative
B. the force on the atom is positive
C. the force on the wall is negative
5. At typical atomic distances, the predominant fundamental force between charged particles is...
A. strong B. weak C. electromagnetic D. gravitational
6. Which has greater kinetic energy?
A. A He atom moving at 300 m s^{-1}
B. A Ne atom moving at 300 m s^{-1}
C. neither; they have the same kinetic energy
7. As two protons approach each other, their potential energy...
A. increases B. decreases C. remains the same

8. Consider the potential energy curve shown in red below for H_2 . For which of the two energy levels indicated (by the blue and green lines) do we expect the two atoms to be able to move farther from each other?
- A. the level indicated by the blue line
 - B. the level indicated by the green line



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Classification of Matter

Matter can be classified according to its physical state, or according to its composition. In this chapter, we will examine the atomic interpretation of the differences among the categories.

5.1 Physical States of Matter

The *physical state* of a sample of matter can be described as *solid*, *liquid*, or *gaseous*. Intuitively, we know the distinctions between the three physical states. For example, we can easily tell that ice, wood and rock are solids, water, wine and gasoline are liquids, and that air, helium (in balloons) and neon (inside neon lamps) are gases.


We can formally define solid, liquid, and gas by describing two of their properties: shape and volume.

- Solids have definite shape and volume.
- Liquids have definite volume, but the shape follows the shape of the bottom of the container.
- Gases do not have definite volume or shape. They entirely fill up whatever container they are put into. They follow the entire shape and volume of the container.

Liquids and gases are also known as *fluids*; they have an indefinite shape because of their tendency to flow. When we say that solids and liquids have “definite volume,” we mean that it would require a great deal of effort to compress them (compared to gases) and that, unlike gases, they do not just spread out and fill up whatever container we put them in.

5.2 Phase Changes

A change in physical state is also called a *phase change*. When we heat a solid, it eventually turns into a liquid. This process is called *melting* or *fusion*. Further heating of the liquid eventually converts it to a gas. This process is called *evaporation* or *vaporization*. Sometimes, a solid can change directly into a gas; this process is called



sublimation. All of these processes are said to be *endothermic*; heat is absorbed from the surroundings when they occur. The opposite of these processes are *exothermic*; heat is released to the surroundings as they occur. The opposite of melting is *freezing*. The opposite of vaporization is *condensation* or *liquefaction*. The opposite of sublimation is *deposition*.

► **Example**

What terms are used to describe the following changes?

- A. a mothball “disappearing”
- B. ice turning into liquid water
- C. water droplets forming on the outside of a cold glass of water
- D. ice “shrinking” in a frost-free freezer
- E. sweat “disappearing” from your skin

Answers:

- A. sublimation
 - B. melting
 - C. condensation
 - D. sublimation
 - E. vaporization
-

► **Example**

Explain why you feel cold when you come in drenched from the rain?

Answer: Vaporization is an endothermic process. As the water vaporizes, water molecules draw heat from your body.

► **Example**

Explain why exposure to steam is more dangerous than exposure to boiling water?

Answer: As boiling water cools (when it comes in contact with your body), heat is transferred to your body. With steam, more heat is transferred to your body because the condensation of steam to boiling water is exothermic. In fact, it can be shown that the condensation alone generates nine times more heat.



5.3 Atomic Interpretation of Physical States and Phase Changes

All matter is made up of tiny particles called atoms, ions, and molecules. Differences in the characteristics of physical states can be explained with the notion that these particles:

- are always moving,
- move more or less independently of each other at very, very large distances,
- repel each other at very, very short distances (mainly due to repulsions of positively charged nuclei),
- attract each other at intermediate distances,
- gain kinetic energy (move faster) when heated, and
- are better able to move away from each other when they gain kinetic energy.

When we talk about distances between atoms being large or short, we are referring to distances compared to the size of the atoms. A distance of 0.1 to 1.0 nm would be considered “intermediate,” with the strongest attraction occurring at a distance of 0.2–0.5 nm between neighboring nuclei. At shorter distances (less than about 0.1 nm) repulsion between nuclei (the *internuclear repulsion*) rises very sharply. A distance of 3 nm would be considered “very large”; 1 nm is 10^{-9} m.

Explaining shape. Unlike liquids and gases, solids have definite shape because the particles that make up the solid do not have much freedom of movement. The amount of energy they have is just enough for them to vibrate about more or less fixed positions. As solids are heated, the particles gain energy. The increase in energy allows them to move faster and increase their range of motion as they are better able to overcome the attractive forces among them. The motion eventually becomes less restricted as the solid turns into a liquid, and eventually into a gas. The motion is least restricted among particles in the gas phase. They are able to spread out as far from one another as possible. Thus, a gas fills up whatever container you put it in.

Explaining compressibility. In solids and liquids, the particles are already as close to each other as possible (0.1–0.2 nm); pushing them even closer together will require a great amount of force to overcome the strong internuclear repulsions that would occur at the short distances. In the case of gases, the particles are very far apart. They can be pushed closer together without much resistance from the internuclear repulsions.



► Example

A 24.8 L sample of air at room temperature contains approximately 6.0×10^{23} molecules. Estimate the average distance between molecules.

Answer: 3.5 nm

To calculate the average distance, imagine spreading out the molecules so that they are evenly spaced. We do this by imagining a 24.8 L box and dividing it into 6.0×10^{23} cubic compartments, with one molecule in each compartment. Thus, the volume for each compartment is

$$V = \frac{24.8 \cdot 10^{-3} \text{ m}^3}{6.0 \cdot 10^{23}} = 4.13 \cdot 10^{-26} \text{ m}^3$$

Note that 24.8 L is equivalent to $24.8 \times 10^{-3} \text{ m}^3$. The volume of a cube is equal to a^3 , if a is the length of the side. So, to get the length of the side of each cubic compartment, we take the cube root of the volume.

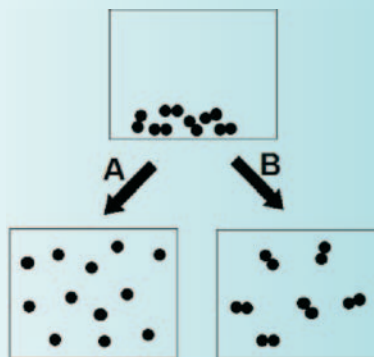
$$a = V^{\frac{1}{3}} = (4.13 \cdot 10^{-26} \text{ m}^3)^{\frac{1}{3}} = 3.5 \cdot 10^{-9} \text{ m}$$

or 3.5 nm. This is the center-to-center distance between adjacent cubes and our estimated average distance between the nuclei of neighboring air molecules. For comparison, if we imagine an N_2 molecule, which comprises about 80% of air molecules, as a sphere, it would have a radius of about 0.16 nm. This is about 20 times smaller than 3.5 nm.

When a substance is made up of molecules, heating will generally first lead to the spreading out of the molecules. A much higher temperature would be required to separate the molecules into atoms. Attractions between molecules and/or noble gas atoms are called *van der Waals* attractions and are weaker than attractions between neighboring atoms within a molecule, or neighboring ions with opposite charges. For example, the energy needed to separate an H atom from a CH_4 molecule is about 330 times larger than the energy needed to separate two CH_4 molecules from each other.

▶ Example

In the figure below, which process best represents the vaporization of liquid nitrogen (N_2)?



Answer: B.

The process illustrated in B occurs at 77K (or -196°C); at room temperature nitrogen exists as a gas and is made up of N_2 molecules. In order to break up the N_2 molecules into N atoms, we would need to heat our sample up to about 70000K.

5.4 Elements, Compounds and Mixtures

Samples of matter that we encounter in nature can generally be separated into two or more distinct components. We consider two components to be distinct if they have different sets of properties. However, once we start separating matter into its components, we reach a point where we have a sample that can no longer be separated into distinct components. We say that what we have at that point is an *element*. So far, a little over a hundred different elements have been identified; less than 100 are naturally-occurring.

If there are only a few elements, why is there so much variety in nature? The answer is that elements can combine in many, many different ways to form *compounds*. A compound is made up of two or more elements, but its properties do not resemble those of the elements that make it up. Each compound has a unique set of properties that differentiates it from other compounds. Collectively, we refer to elements and compounds as *substances*. Much of the matter we find in nature is a mixture of substances. A sample of matter containing only one substance is called *pure substance*. Pure substances are rarely found in nature; they are produced in the laboratory by separating mixtures.



► Example

Under ordinary conditions, hydrogen and oxygen are gases; a mixture of hydrogen and oxygen is also a gas. Water, on the other hand, is a compound of hydrogen and oxygen; under ordinary conditions, it is a liquid. Hydrogen peroxide is another compound of hydrogen and oxygen; its set of properties is different compared to water, hydrogen, or oxygen.

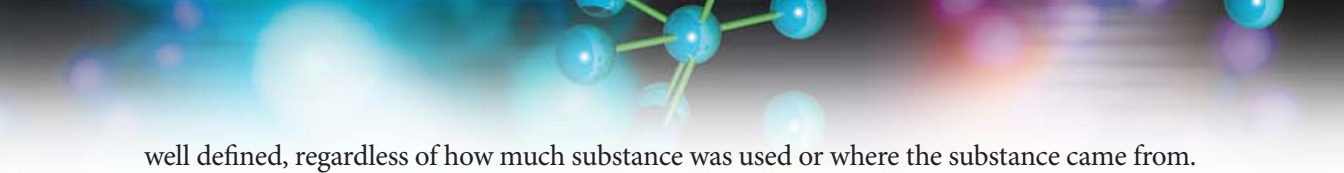
How can we tell if a sample is a mixture or a pure substance? A pure substance is usually *homogeneous*; by this, we mean that the properties are uniform throughout the entire sample. The only exceptions are at certain conditions where it is possible for more than one physical state of the substance to exist. At the melting point of a substance, for example, you will see both solid and liquid state; in this case, you have a *heterogeneous* sample of the pure substance.

Most heterogeneous samples are mixtures, but a mixture can also be homogeneous; such a mixture is called a *solution*. How can we tell if a homogeneous sample of matter is a mixture or a pure substance? The traditional method is to examine the behavior of the system when it is heated or cooled. While a pure substance is melting, its temperature remains constant; in practice we say it is constant if it does not change by more than 1–2°C. We say that a pure substance has a sharp melting point (or freezing point), while mixtures have a wide melting (or freezing) range. Similarly, a pure substance has a sharp boiling point, while mixtures have a wide boiling range.

Heterogeneous mixtures can be classified as coarse mixtures, suspensions, and colloids. Coarse mixtures are the most commonly encountered and are relatively easy to recognize; an example of a coarse mixture is a salad. In a *suspension*, very fine particles are evenly dispersed in a liquid or gas; examples: dust and air, orange juice with pulp. The dispersed particles in a suspension are visible to the naked eye and settle on standing. Colloids or colloidal dispersions are similar to suspensions; very fine particles are also evenly dispersed but they are too small for the unaided eye to actually discern; examples: fog, milk, lump-free gravy. The dispersed particles in a colloid are detectable by shining a bright light on the sample; the scattering of light by colloidal particles is called the *Tyndall effect*. Unlike in suspensions, the dispersed particles in a colloid do not settle on standing.

5.5 The Law of Definite Composition

The Law of Definite Composition, also known as the Law of Constant Composition or the Law of Definite Proportions, is a statement of the general observation that if a pure substance can be broken into two or more elements, the proportion of the elements obtained is



well defined, regardless of how much substance was used or where the substance came from. Similarly, if the process were reversed, the same proportion of elements would be used up to make the substance. A substance that can be broken into two or more elements is called a compound. Therefore, the law essentially says that a compound has a *definite composition*.

► Example

Example: the percentage of Cl by mass in 10.0 g of a compound is 25.0%. What is the percentage of Cl by mass in 20.0 g of this compound?

Answer: 25.0%

It does not matter how much of the compound we have. The percentage of any element in the sample is a constant.

► Example

A 16-g sample of a compound contains 12 g C and 4 g H. What is the mass of a sample of this compound that contains 24 g C? What is the mass of H in this sample?

Answer: 32 g, 8 g

The law of definite composition says that, since:

$$\frac{\text{mass}_C}{\text{mass}_{\text{total}}} = \frac{12 \text{ g}}{16 \text{ g}} = 0.75$$

for the 16 g sample, then the ratio is also 0.75 for any sample of this compound. In other words, for the other sample:

$$\frac{\text{mass}_C}{\text{mass}_{\text{total}}} = \frac{24 \text{ g}}{\text{mass}_{\text{total}}} = 0.75$$

Solving for $\text{mass}_{\text{total}}$, we get 32 g. Note that 12 is 75% of 16, and 24 is 75% of 32. The percentage of C in both samples is the same.

We can figure out the mass of H by subtracting the mass of C from the total mass:

$$32 \text{ g} - 24 \text{ g} = 8 \text{ g}.$$

Alternatively, we can use the fact that the mass-to-mass ratio of C to H is constant. For the 16 g sample, the ratio is:

$$\frac{\text{mass}_C}{\text{mass}_H} = \frac{12 \text{ g}}{4 \text{ g}} = 3$$

Therefore, for the sample that contains 24 g C, the ratio is also equal to 3.

$$\frac{\text{mass}_C}{\text{mass}_H} = \frac{24 \text{ g}}{\text{mass}_H} = 3$$

Solving for mass_H , we get 8 g.

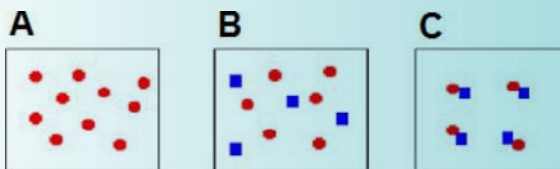
5.6 Atomic Interpretation of Elements, Compounds, and Mixtures

A pure sample of an element is made up of only one kind of atom. Separating it into two or more parts will give us parts that are made up of the same kind of atoms. Thus, the parts will have the same properties.

Compounds and mixtures are made up of at least two elements; therefore, they are made up of at least two kinds of atoms. Unlike a mixture, a compound has a definite composition because the atoms of the different elements in any sample of the compound are in a well-defined (fixed) ratio.

► Example

Which of the figures below best illustrate the atomic composition of a pure element, a pure compound, and a mixture?

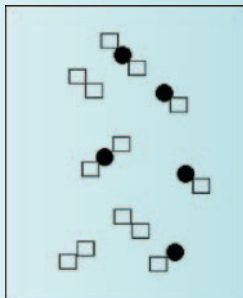


Answer: Figure A best represents a sample of a pure element; it shows only one kind of atom (red circles). Figure C best represents a sample of a pure compound; it shows two kinds of atoms, but the atoms are organized in a well-defined manner; it is made up of only one kind of molecule. Any “sample” you draw from Figure C will give you one blue square for every red circle. Figure B best represents a mixture of two elements. If you were to take a random “sample” of atoms from Figure B, you would not always get the same blue-to-red ratio.

▶ Example

Consider the pictorial representation of the molecular composition of a mixture. Assuming filled circles represent C atoms and unfilled squares represent O atoms, we can say that the figure represents a mixture of:

- A. an element and two compounds
- B. two elements and a compound
- C. three compounds
- D. two elements



Answer: A

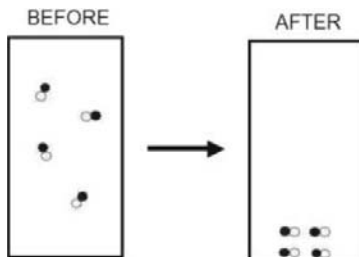
There are three substances in the mixture. One element (O_2) and two compounds (CO and CO_2).

TEST YOURSELF

For answers and other study resources, see:

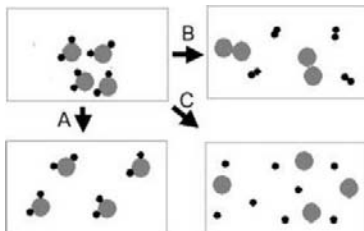
<http://i-assign.com/ebook/answers/chapter5.htm>.

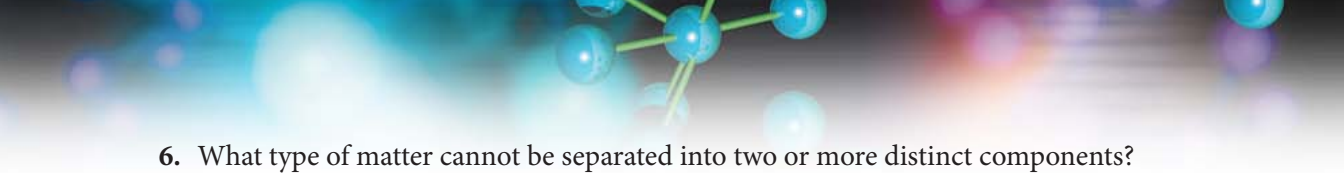
- For which of the following are the atoms, on average, farthest from one another?
A. air B. gasoline C. copper wire
- Water is made up of molecules. For which physical state is the motion of the water molecules most restricted?
A. solid (ice) B. liquid C. gas (steam)
- What physical state of matter is being described by the following phrase: “particles are as close to one another as possible and unable to move”
A. solid B. liquid C. gas D. none of these
- Consider the pictorial representation shown below for a change in physical state at the molecular level.



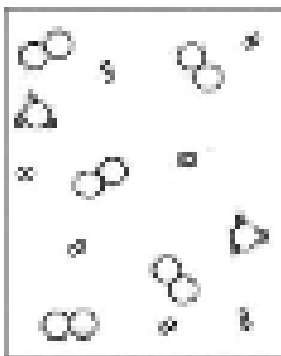
The picture best represents which of these changes:

- A. evaporation B. melting C. sublimation D. condensation
- Which of the pictorial representations best accounts for the conversion of water from liquid to steam?



- 
6. What type of matter cannot be separated into two or more distinct components?
A. element B. compound C. mixture D. pure substance
7. A naturally-occurring sample of matter most likely consists of...
A. a single element B. a single compound
C. a mixture D. pure substance
8. A sample of matter is heated and found to start melting at 75.0°C . While melting, the sample temperature continues to rise to about 85.0°C . This sample of matter is most likely...
A. an element B. a compound C. a mixture
9. Samples A, B, and C appear to be identical. Each sample is found to melt sharply at 122°C . However, a mixture of sample A and B is found to melt from $115\text{--}120^{\circ}\text{C}$, while a mixture of sample A and C is found to melt sharply at 122°C . Which of the following is true?
A. Samples A and B are composed of the same substance
B. Samples A and C are composed of the different substances
C. A mixture of B and C will have a sharp melting point
D. None of the above
10. If a medicine bottle has a “shake well before using” label, it most likely contains.....
A. a solution B. a colloid C. a suspension
11. Which of the following is a coarse mixture?
A. air B. 18K gold C. gasoline D. salad
12. A 25.0 gram sample of a compound is found to be 24% chlorine by mass. What is the percentage of chlorine in a 50.0 g sample of the compound?
A. 24% B. 48%
C. 12% D. It depends where the sample came from
13. A 25.0 gram sample of a compound is found to be 24% chlorine by mass. How much chlorine is in a 50.0 g sample of the compound?
A. 24 g B. 48 g C. 12 g

14. A 17.0 g sample of a compound contains 14.0 g nitrogen and 3.0 g hydrogen. How much hydrogen does a 34.0 g sample of the compound contain?
 A. 3.0 g B. 6.0 g C. 14.0 g D. 28.0 g
15. A 32.0 g sample of a compound contains 16.0 g oxygen, 12.0 g carbon, and 4.0 g hydrogen. How much oxygen is present in a sample of this compound that contains 36.0 g carbon?
 A. 12.0 g B. 5.33 g C. 48.0 g D. 36.0 g
16. A 7.0 g sample of a compound contains 3.0 g of element "X" and 4.0 g of element "Y". What is the mass ratio of element "X" to element "Y" in a 70.0 g sample of this compound?
 A. 0.75 B. 1.33 C. 7.5 D. 13.3
17. Consider the pictorial representation shown below for the molecular composition of a mixture. The figure represents a mixture of...



- A. an element and two compounds
 B. two elements and a compound
 C. three compounds

The Periodic Table

The periodic table is the most important resource for anyone studying Chemistry. The elements are arranged in the periodic table in a manner that facilitates understanding of the patterns in their properties.

6.1 Classifying the Elements

In a typical periodic table, elements are organized into 18 vertical columns with two additional (horizontal) rows below the 18 columns. Elements that belong to same vertical column are said to belong to the same *family* or *group*. Elements in the same horizontal row are said to belong to the same *period*.

▶ Example

Which of the following belongs to period 3: Na, Sc, or In?

Answer: Na

The term *Period* refers to a (horizontal) row. Period 3, the third horizontal row, is highlighted in green below. Na is the first element in period 3. Sc is in the fourth period. In is in the fifth period.

PERIODIC TABLE OF THE ELEMENTS

1 1A																	18 8A
1 H 1.008	2 He 4.003																
3 Li 6.941	4 Be 9.012																
11 Na 22.99	12 Mg 24.31	13 B 10.81	14 C 12.01	15 N 14.01	16 O 16.00	17 F 18.99	18 Ne 20.18										
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.64	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98.91	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.91	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po [209]	85 At [210]	86 Rn [222]
87 Fr [223]	88 Ra [226]	89 Ac [227]	104 Rf [261]	105 Db [262]	106 Sg [263]	107 Bh [264]	108 Hs [265]	109 Mt [266]	110 Ds [267]	111 Rg [268]	112 Cn [269]	113 Nh [270]	114 Fl [271]				
58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm [145]	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05	71 Lu 174.97				
90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np [237]	94 Pu [244]	95 Am [243]	96 Cm [247]	97 Bk [247]	98 Cf [251]	99 Es [252]	100 Fm [257]	101 Md [258]	102 No [259]	103 Lr [260]				

The representative elements. In the traditional American periodic table, columns 1, 2, and 13 through 18 are labeled using the numbers 1 through 8 (Arabic or Roman) followed by the letter A. In other words, column 1 is group IA or 1A, column 2 is group IIA or 2A, column 13 is group IIIA, column 14 is group IVA, etc.. Sometimes, column 18 or group VIIIA is labeled as group 0 (zero). These “A” groups are known as the *main* groups or *representative* groups, and they are indicated in Figure 1 by the red shading.

In the traditional American periodic table, columns 3 through 12 are labeled using IIIB (or 3B), IVB (or 4B), VB, VIB, VIIB, VIII (or VIIIB, or 8B; next 3 columns), IB, and IIB. The elements in these “B” groups are called the *transition* elements or *transition metals* and they are indicated in Figure 1 by the blue shading.

The two rows at the bottom are known as the *inner transition* elements (lanthanides and actinides); they are indicated in Figure 1 by the yellow shading. In the extended- or long-form of the periodic table, these rows are inserted between group IIA and group IIIB in rows 6 and 7. In other words, the lanthanides actually belong to period 6 (or row 6) and the actinides belong to period 7.

The representative elements Ga, In, Sn, Tl, Pb, and Bi are also known as the *post-transition metals*. These are shown in green in Figure 2.

Some groups have special names; see Figure 3. Elements in group IA, except hydrogen, are called the *alkali metals*. Elements in group IIB are called the *alkaline earth metals*. The transition elements are also known as the *transition metals*. Elements in group VIIIA (column 18) are called the *noble gases*. Elements in group VIIA (column 17) are known as the *halogens*. Elements in group VIA (column 16) are known as the *chalcogens*.

Figure 1. Representative, Transition and Inner Transition Elements

PERIODIC TABLE OF THE ELEMENTS

1 1A												13 3A						14 4A		15 5A		16 6A		17 7A		18 8A																					
1 H (1.0)	2 He (4.0)											3 B (10.8)	4 C (12.0)	5 N (14.0)	6 O (16.0)	7 F (19.0)	8 Ne (20.2)	9 Li (6.9)	10 Be (9.0)											11 Na (22.9)	12 Mg (24.3)											13 Al (26.9)	14 Si (28.1)	15 P (30.9)	16 S (32.1)	17 Cl (35.4)	18 Ar (39.9)
19 K (39.1)	20 Ca (40.1)	21 Sc (44.9)	22 Ti (47.9)	23 V (50.9)	24 Cr (52.0)	25 Mn (54.9)	26 Fe (55.8)	27 Co (58.9)	28 Ni (58.7)	29 Cu (63.5)	30 Zn (65.4)	31 Ga (69.7)	32 Ge (72.6)	33 As (74.9)	34 Se (78.9)	35 Br (79.9)	36 Kr (83.8)	37 Rb (85.5)	38 Sr (87.6)	39 Y (88.9)	40 Zr (91.2)	41 Nb (92.9)	42 Mo (95.9)	43 Tc (98.9)	44 Ru (101.1)	45 Rh (101.1)	46 Pd (106.4)	47 Ag (107.9)	48 Cd (112.4)	49 In (114.8)	50 Sn (118.7)	51 Sb (121.8)	52 Te (127.6)	53 I (126.9)	54 Xe (131.3)												
55 Cs (132.9)	56 Ba (137.3)	57 La (138.9)	72 Hf (178.5)	73 Ta (180.9)	74 W (183.8)	75 Re (186.2)	76 Os (190.2)	77 Ir (192.2)	78 Pt (195.1)	79 Au (197.0)	80 Hg (200.6)	81 Tl (204.4)	82 Pb (207.2)	83 Bi (208.9)	84 Po (209)	85 At (210)	86 Rn (222)	87 Fr (223)	88 Ra (226)	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (264)	108 Hs (265)	109 Mt (266)	110 Ds (267)	111 Rg (268)	112 Cn (269)	113 Nh (270)	114 Fl (271)	115 Mc (272)	116 Lv (273)	117 Ts (274)	118 Og (277)													
																		58 Ce (140.1)	59 Pr (140.9)	60 Nd (144.2)	61 Pm (144.9)	62 Sm (150.4)	63 Eu (151.9)	64 Gd (157.3)	65 Tb (158.9)	66 Dy (162.5)	67 Ho (164.9)	68 Er (167.3)	69 Tm (168.9)	70 Yb (173.0)	71 Lu (175.0)																
																		90 Th (232.0)	91 Pa (231.0)	92 U (238.0)	93 Np (237.0)	94 Pu (244.0)	95 Am (243.0)	96 Cm (247.0)	97 Bk (247.0)	98 Cf (251.0)	99 Es (252.0)	100 Fm (257.0)	101 Md (258.0)	102 No (259.0)	103 Lr (260.0)																

Figure 2. The Post-transition Metals

PERIODIC TABLE OF THE ELEMENTS

1 1A																	18 8A																												
1 H 1.008	2 2A												13 3A	14 4A	15 5A	16 6A	17 7A	18 8A																											
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18																												
11 Na 22.99	12 Mg 24.31	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95																												
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80																												
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3																												
55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)																												
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Db (261)	105 Dsb (262)	106 Ds (263)	107 Bh (264)	108 Hs (265)	109 Mt (266)	110 (269)	111 (272)	112 (277)	114 (277)																																	
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Figure 3. Groups with Special Names: **Alkali Metals** (1A), **Alkaline Earth Metals** (2A), **Chalcogens** (6A), **Halogens** (7A), and **Noble Gases** (8A)

PERIODIC TABLE OF THE ELEMENTS

1 1A																	18 8A																												
1 H 1.008	2 2A												13 3A	14 4A	15 5A	16 6A	17 7A	18 8A																											
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18																												
11 Na 22.99	12 Mg 24.31	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95																												
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80																												
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3																												
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87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Db (261)	105 Dsb (262)	106 Ds (263)	107 Bh (264)	108 Hs (265)	109 Mt (266)	110 (269)	111 (272)	112 (277)	114 (277)																																	
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58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0																																
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6.2 Properties of Elements

Patterns in properties of elements can be correlated with their location in the periodic table.

6.2.1 Metallic Character

Elements on the left side of the periodic table are observed to be metallic in pure form; see Figure 4. *Metals* are shiny, malleable, ductile, good electrical conductors, and good heat conductors. Something that is *malleable* can be hammered into thin sheets. Something that is *ductile* can be drawn out into a thin wire. Elements on the right side of the period are classified as nonmetals. Elements in between (B, Si, Ge, As, Sb, Te and Po) are known as the metalloids.

► Example

Which element is a good electrical conductor, Cu, Ge, Kr?

Answer: Cu

Cu is a metal. Ge is a metalloid. Kr is a nonmetal. Metals are the good electrical conductors.

Figure 4. Metals, Nonmetals and Metalloids

PERIODIC TABLE OF THE ELEMENTS

1 1A												13 3A		14 4A	15 5A	16 6A	17 7A	18 8A
1 H 1.008																		2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 18.99	10 Ne 20.18	
11 Na 22.99	12 Mg 24.31	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	8 8B	10 8B	11 1B	12 2B	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95	
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 51.99	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80	
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98.91	44 Ru 101.07	45 Rh 101.07	46 Pd 106.36	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.6	53 I 126.9	54 Xe 131.3	
55 Cs 132.9	56 Ba 137.3	57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm 144.9	62 Sm 150.4	63 Eu 151.9	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.1	71 Lu 175.0		
87 Fr 223	88 Ra 226	89 Ac 227	104 Rf 261	105 Db 262	106 Sg 266	107 Bh 264	108 Hs 277	109 Mt 268	110 Ds 271	111 Rg 272	112 Cn 285	114 Fl 289						
98 Ce 140.1	99 Pr 140.9	100 Nd 144.2	101 Pm 144.9	102 Sm 150.4	103 Eu 151.9	104 Gd 157.3	105 Tb 158.9	106 Dy 162.5	107 Ho 164.9	108 Er 167.3	109 Tm 168.9	110 Yb 173.1	111 Lu 175.0					
90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu 244.0	95 Am 243.0	96 Cm 247.0	97 Bk 247.0	98 Cf 251.0	99 Es 252.0	100 Fm 257.0	101 Md 258.0	102 No 259.0	103 Lr 260.0					

6.2.2 Physical States

Most naturally-occurring elements are solids under ordinary conditions. The exceptions (see Figure 5):

- Liquids: mercury and bromine. On a warm summer day, outside an air-conditioned laboratory, the following elements may also be found as

liquids: gallium (melts at 29.76°C or 85.57°F) and caesium (melts at 28.44°C or 83.19°F).

- Gases: hydrogen, nitrogen, oxygen, fluorine, chlorine, and the noble gases. Except for hydrogen, we find these elements on the rightmost side of the periodic table.

Figure 5. Physical States of Elements

1												2					
H																He	
3	4											5	6	7	8	9	10
Li	Be										B	C	N	O	F	Ne	
11	12											13	14	15	16	17	18
Na	Mg										Al	Si	P	S	Cl	Ar	
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
55	56		72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
87	88		104	105	106	107	108	109	110	111	112		114		116		
Fr	Ra		Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub		Uuq		Uuh		
57		58	59	60	61	62	63	64	65	66	67	68	69	70	71		
La		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
89		90	91	92	93	94	95	96	97	98	99	100	101	102	103		
Ac		Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

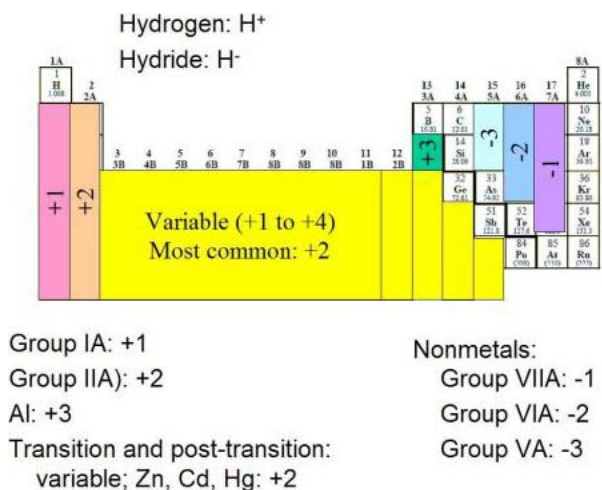
6.2.3 Tendency to Form Monatomic Ions

The charges of naturally-occurring monatomic ions can be correlated with the periodic table. The correlation is summarized in Figure 6. Ions derived from atoms of metallic elements tend to be positively charged. Ions derived from atoms of nonmetallic elements tend to be negatively charged.

Monatomic ions derived from elements belonging to group IA except H are always found in nature to have a charge of +1. Monatomic ions from Group IIA elements are always found in nature to have a charge of +2. The monatomic ion formed from aluminum is always found in nature to have a charge of +3. For transition and post transition metals, there are typically more than one type of cation found in nature. The most common charge of monatomic ions derived from transition metals is +2. Monatomic ions derived from atoms of zinc, cadmium, and mercury are always found in nature with a charge of +2.

Monatomic ions derived from nonmetallic elements in group VIIA (column 17, the halogens) are called halides and are always found to have a charge of -1 . Monatomic ions derived from elements of group VIA (column 16) are always found to have a charge of -2 . For group VA (column 15), the observed charge is always -3 .

Figure 6. Naturally-occurring Monatomic Ions



Monatomic ions derived from hydrogen are always observed to have a charge of either +1 or -1.

What about the other elements? The noble gases (group VIIIA), metalloids and nearby nonmetals tend not to form monatomic ions.

Monatomic cations share the same name as the atoms they are derived from. For example, K⁺, the ion derived from a potassium atom, is called potassium ion. However, names of monatomic cations derived transition and post-transition metals must specify the charge of the ion in Roman numeral, as in cobalt(III) for Co³⁺. Note that there is no space between the last letter in cobalt and the opening parenthesis. For monatomic anions, the name differs from that of the parent atom; the name of the anion ends in *ide*. For example, O, the neutral atom is oxygen, but the negatively charged O²⁻ is oxide.

► Example

Which of the following is called magnesium ion?

- A. Mg⁺ B. Mg⁻ C. Mg²⁺ D. Mg³⁺

Answer: C

All the choices are ions of magnesium, but the only one that we call magnesium ion is Mg²⁺ because it is the only one that we can find in nature. The other ions can be made in laboratory, but would be very short-lived.

► Example

What is the formula of lead(IV) ion?

Answer: Pb^{4+}

IV is the Roman numeral for 4. The symbol for lead is Pb.

► Example

What is the formula of nitride ion?

Answer: N^{3-}

The *ide* ending in name suggests that the ion is negatively charged. The **nitr** at the beginning of the name suggests that this ion is derived from a **nitrogen** atom (N). The only naturally-occurring monatomic ion derived from a nitrogen atom has a charge of -3 .

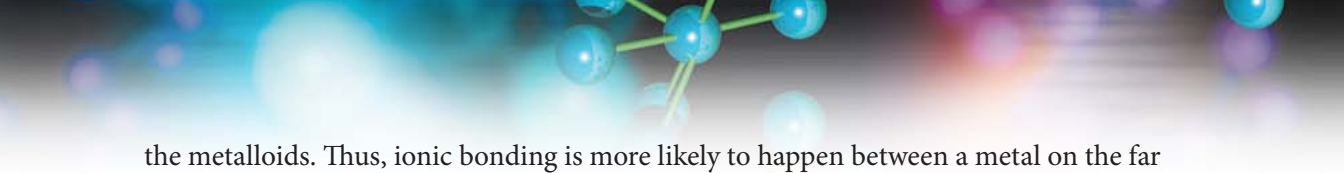
6.2.4 Covalent Bonding

When two atoms share electrons, they are said to be held together by a *covalent bond*. In contrast, ions with opposite charges are attracted to each other and are said to be held together by an *ionic bond*.

Since atoms of metallic elements tend to form cations and atoms of nonmetallic elements tend to form anions, we can say that ionic bonding is *likely* to occur between a metal and a nonmetal. Between two atoms of nonmetallic elements, electron sharing or covalent bonding is more likely to occur. Indeed, the pure forms of some nonmetallic elements are found in nature as collections of molecules. For example, oxygen can exist as a collection of O_2 molecules or O_3 molecules (ozone). O_2 is the form of oxygen that makes up about 20% of the air that we breathe. The elements that, in pure form, naturally occur as a collection of molecules under ordinary conditions are listed below:

- Diatomic: H_2 , N_2 , F_2 , Cl_2 , Br_2 , I_2
- Polyatomic: P_4 , S_8

When two atoms are sharing electrons, the sharing is generally unequal; this means that the electrons, on average, spend more time closer to one of the two atoms. We say that the electrons are *polarized* towards one of the atoms, that the bonding is *polar covalent*. Equal sharing, *pure covalent* bonding, happens only between atoms of the same element. Ionic bonding can be thought of as an extreme case of polar covalent bonding. It is best to say that the bond between a metal and nonmetal is *likely* (not *definitely*) ionic. In the periodic table, metallic and nonmetallic characteristics increase as you move away from



the metalloids. Thus, ionic bonding is more likely to happen between a metal on the far bottom left corner of the periodic table and a nonmetal on the far top right side (excluding the noble gases); the most ionic bond would occur between Fr and F. We tend to get into the “gray areas” when dealing with metal-nonmetal pairs closer to the metalloid line. In fact, a transition metal atom can form a covalent bond with a nonmetal or another transition metal atom; an entire subfield of chemistry (*coordination chemistry*) deals with this topic.

Three common polyatomic ions where a metal atom shares electrons with nonmetal atoms are permanganate (MnO_4^-), chromate (CrO_4^{2-}), and dichromate ($\text{Cr}_2\text{O}_7^{2-}$).

When mixed with water, transition and post-transition metal ions are, in fact, sharing electrons with water molecules. Copper(II) ions in water, for example, are more accurately represented by the formula $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ rather than Cu^{2+} . The Cu^{2+} ion is surrounded by four H_2O molecules such that electrons are shared between the O (of the H_2O molecules) and Cu. The sharing of electrons in this case is called *coordinate covalent bonding*. $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ is an example of what is called a *complex ion*.

6.2.5 Metallic Bonding

Between a pair of metal atoms, covalent bonding is more likely to occur. However, *among* a large number of metal atoms, electrons tend to be very loosely held and it is convenient to visualize the nuclei as being immersed in a “sea” of electrons; the bonding *among* the atoms in this case is called *metallic bonding*. This explains why metals are good electrical conductors.

6.2.6 Noble Gases

The noble gases are found in nature as collections of neutral atoms. Under *extreme* laboratory conditions, atoms of noble gases can be made to form molecules, but they have *no natural* tendency to form molecules or ions.

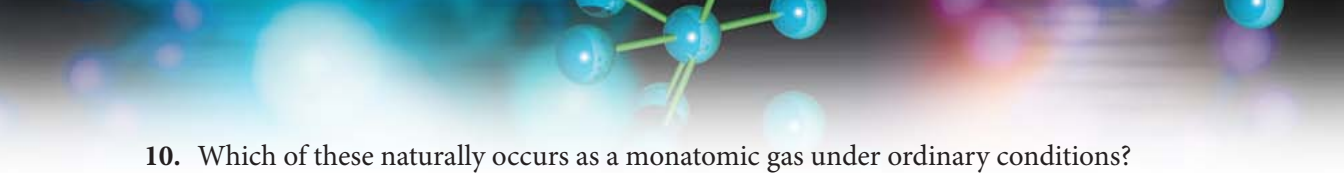


TEST YOURSELF

For answers and other study resources, see:

<http://i-assign.com/ebook/answers/chapter6.htm>.

- Which of the following elements is a transition metal?
A. silicon B. lead C. sodium D. chromium
- Which of the following elements is a post-transition metal?
A. silicon B. lead C. sodium D. chromium
- Which of the following elements is a metal that belongs to a main group or representative group?
A. magnesium B. zinc C. sulfur D. uranium
- All of the following are true, except...
A. Sodium is an alkali metal B. Neon is a noble gas
C. Calcium is an alkaline earth metal D. Oxygen is a halogen
- Which of the following is a metalloid?
A. potassium B. silicon C. iron D. helium
- Which of the following elements is the best electrical conductor?
A. carbon B. germanium C. manganese D. iodine
- Which of the following naturally-occurring ions is paired with its correct symbol?
A. potassium ion, K^{2+} B. sulfide, S^{3-}
C. barium ion, Ba^{2+} D. iodide, I^+
- Which of the following pairs of atoms is most likely to form an ionic bond?
A. C and H B. Ca and H C. Hg and Hg
- What type of bond is more likely between a carbon atom and an oxygen atom?
A. ionic B. covalent C. metallic

- 
10. Which of these naturally occurs as a monatomic gas under ordinary conditions?
A. helium B. sodium C. oxygen D. nitrogen
11. Which of these elements naturally occurs as a diatomic gas under ordinary conditions?
A. bromine B. iodine C. mercury D. chlorine
12. Which of these elements is not a gas under ordinary conditions?
A. bromine B. helium C. hydrogen D. oxygen
13. What type of bond holds the atoms together in the polyatomic ions chromate (CrO_4^{2-}) and nitrate (NO_3^-)?
A. ionic, ionic B. ionic, covalent
C. covalent, ionic D. covalent, covalent

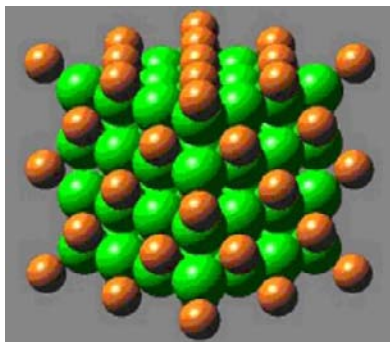
Compounds

7.1 Classifying Common Compounds

Compounds can be classified as either ionic or molecular. Ionic compounds are made up of ions held together by ionic bonds. Molecular compounds are made up of molecules. Within molecules, atoms sharing electrons are said to be covalently-bonded. Note that electron sharing (or covalent bonding) can also be present in ionic compounds if at least one of ions is polyatomic; in a polyatomic ion, the atoms are held together by covalent bonds. Ionic bond refers to the bond due to the attractive force between ions of opposite charges.

Shown in Figure 1 is a representation of how the ions are arranged in a regular pattern in barium chloride (BaCl_2); this regular arrangement is called a crystal lattice. The green spheres represent chloride ions (Cl^-) and the orange spheres represent barium ions (Ba^{2+}). This figure clearly illustrates why we say that there are no BaCl_2 “molecules”; we cannot tell which Cl^- ions go with which Ba^{2+} ion. All we know is that the count-to-count ratio

Figure 1. Crystal Lattice of BaCl_2

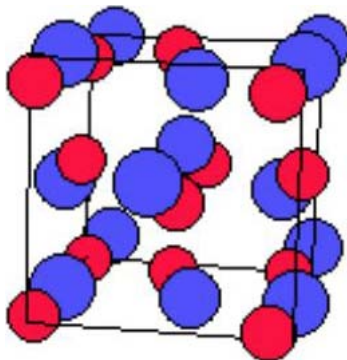


from <http://www.molsci.ucla.edu/pub/explorations.html#Crystalline Solids>.

of barium-to-chloride ions is 1-to-2. So, we refer to one barium and two chloride ions together as one formula unit; not one molecule.

Solid samples of molecular substances can also be crystalline, as illustrated in Figure 2 for carbon monoxide, but we can clearly distinguish which atoms “go together” as part of one molecule.

Figure 2. Crystal Lattice of CO



from <http://cst-www.nrl.navy.mil/lattice/struk/b21.html> (public domain)

7.1.1 Classifying Compounds Based on Name or Formula

Most compounds can be easily classified as ionic or molecular based on the name or the formula. Typically:

- names of ionic compounds either start with the name of a metallic element, or with *ammonium*.
- formulas of ionic compounds either start with the symbol of a metallic element, or with “NH₄” (which may be enclosed in parentheses); the cation in these cases is the polyatomic ion called ammonium, NH₄⁺.

► Example

Classify the following compounds as ionic or molecular:
sodium sulfide, carbon disulfide, ammonium sulfide

Answer: ionic, molecular, ionic

- Sodium is a metallic element. The cation in this compound is sodium ion (Na⁺).
- Carbon is a nonmetallic element.
- Ammonium sulfide is ionic; the cation is ammonium (NH₄⁺).

► Example

Classify the following as ionic or molecular: $\text{Mg}(\text{OH})_2$, CH_3OH , NH_4Cl

Answer: Mg is the symbol for magnesium, a metallic element. Therefore, $\text{Mg}(\text{OH})_2$ is an ionic compound; the cation is magnesium ion (Mg^{2+}). C is the symbol for carbon, a nonmetallic element. Therefore, CH_3OH is a molecular compound. N is a nonmetallic element but it is part of an “ NH_4 ” grouping in NH_4Cl ; this compound is an ionic compound; the cation is ammonium ion (NH_4^+).

7.1.2 Classifying Compounds Based on Properties

Ionic compounds typically have very high melting points. This means that most ionic compounds are solids at room temperature. If a compound is a liquid or gas at room temperature, it is most likely to be molecular. However, if it is a solid, it could be ionic or molecular. For molecular compounds, in general, the larger the molecules, the higher the melting point, and the higher the boiling point.

► Example

Which of these compounds is most likely to be gaseous at room temperature: NaCl , CH_4 , or C_8H_{18} ?

Answer: CH_4 ,

NaCl is an ionic compound; we expect it to have a very high melting point and it does. CH_4 and C_8H_{18} are molecular compounds. The smaller the molecules of a compound, the more likely we will find the substance as a gas at room temperature. CH_4 , methane, is the primary component of natural gas. It is a gas at room temperature. C_8H_{18} is octane, a component of gasoline; it is a liquid at room temperature. When something is a gas at room temperature, it means that its boiling point is much colder than room temperature.

Another way we can tell if a compound is ionic is if it conducts electricity when melted.



► **Example**

Which of these is not a good electrical conductor?

A. liquid NaCl, B. solid Cu, C. solid NaNO₃

Answer: solid NaNO₃

NaCl is an ionic compound; we expect ionic compounds to be good electrical conductors *if melted*. Cu is a metallic element; metals are good electrical conductors. NaNO₃ is an ionic compound; it would be a good electrical conductor if melted, but not in solid form.

Ionic compounds are *strong electrolytes*. Pure water is a very poor conductor of electricity, but dissolving an ionic compound in water produces a mixture that is a good electrical conductor.

Molecular compounds are, in general, *nonelectrolytes*. However, there are molecular compounds that once dissolved in water, can break up into ions, or react with water and produce ions in the process; this process is called *ionization*. Most of these compounds are *weak electrolytes* because the production of ions occurs only to a small extent. In fact, there are only six known molecular compounds that are completely ionized in water and are, therefore, strong electrolytes; these are the six strong acids: HCl (hydrochloric acid), HBr (hydrobromic acid), HI (hydriodic acid), HNO₃ (nitric acid), H₂SO₄ (sulfuric acid), and HClO₄ (perchloric acid). Acid molecules break up in water producing hydrogen ions (H⁺). We say that the acid is *ionized* or *dissociated* in water. Except for the six strong acids, acids are weak electrolytes.

► **Example**

What are the ions produced when hydrochloric acid (HCl) is dissolved in water?

Answer: H⁺ and Cl⁻. When a hydrogen ion (which has a +1 charge) breaks off from an HCl molecule (which is neutral), what is left behind must have a -1 charge.

► **Example**

Is hydrofluoric acid (HF) a strong or a weak electrolyte?

Answer: weak. HF is not one of the six known strong acids. Most of the HF molecules will remain intact when HF is dissolved in water; a very small fraction of the HF molecules will be dissociated into H⁺ and F⁻ ions.

7.2 Formula Units

The formula of a compound tells us the composition of one *formula unit* of the compound. For molecular compounds, the formula unit is the molecule. For ionic compounds the formula unit is the smallest collection of ions with a total charge of zero.

► Example

How many H atoms are in one formula unit of propanoic acid ($\text{CH}_3\text{CH}_2\text{COOH}$)?

Answer: 6

The subscripts of hydrogen in $\text{CH}_3\text{CH}_2\text{COOH}$ are 3, 2, and 1. Note that unwritten subscripts are implied to be 1. Adding up the subscripts, we get $3 + 2 + 1 = 6$. Therefore, there are 6 hydrogen atoms in one formula unit (or one molecule) of propanoic acid.

► Example

Explain why the formula of a compound made up of calcium ions (Ca^{2+}) and nitride ions (N^{3-}) is written as Ca_3N_2 ?

Answer: One formula unit of an ionic compound must have a total charge of zero. The simplest set of calcium (Ca^{2+}) and nitride (N^{3-}) ions with a total charge of zero is: **three** calcium ions and **two** nitride ions:

Charge of three calcium ions: $(3)(+2) = +6$

Charge of two nitride ions: $(2)(-3) = -6$

Total charge = 0

Therefore, the formula of calcium nitride is Ca_3N_2 . *Note that charges of the ions are not indicated when writing the formula of an ionic compound.*

7.3 Names and Formulas of Common Ions

The first step in reading or writing formulas of common compounds is to classify the compound as either ionic or molecular. Once we recognize the formula to be that of an ionic compound, reading it is just a matter of naming the cation, then the anion. It is, therefore, important to be familiar with the names and formulas of common ions.

7.3.1 Monatomic Ions

Names and formulas of naturally-occurring monatomic ions are discussed in section 6.2.3.

7.3.2 Polyatomic Ions

Names of polyatomic ions are trivial. By trivial, we mean that we just have to know them; there is nothing to figure out. It is like saying that a person's name is, say, John. Table 1 lists the polyatomic ions that are commonly encountered in compounds.

Table 1. Common Polyatomic Ions

Polyatomic cations:

- mercury(I) or mercurous: Hg_2^{2+}
- ammonium: NH_4^+

Polyatomic anions with names ending in *ate*:

borate: BO_3^{3-}	perchlorate: ClO_4^-
carbonate: CO_3^{2-}	perbromate: BrO_4^-
bicarbonate or hydrogen carbonate: HCO_3^-	periodate: IO_4^-
nitrate: NO_3^-	permanganate: MnO_4^-
chlorate: ClO_3^-	chromate: CrO_4^{2-}
bromate: BrO_3^-	dichromate: $\text{Cr}_2\text{O}_7^{2-}$
iodate: IO_3^-	molybdate: MoO_4^{2-}
phosphate: PO_4^{3-}	acetate: $\text{C}_2\text{H}_3\text{O}_2^-$ or CH_3COO^-
hydrogen phosphate: HPO_4^{2-}	persulfate (or peroxydisulfate): $\text{S}_2\text{O}_8^{2-}$
dihydrogen phosphate: H_2PO_4^-	thiosulfate: $\text{S}_2\text{O}_3^{2-}$
arsenate: AsO_4^{3-}	dithionate: $\text{S}_2\text{O}_6^{2-}$
selenate: SeO_4^{2-}	cyanate: OCN^-
sulfate: SO_4^{2-}	thiocyanate: SCN^-
bisulfate or hydrogen sulfate: HSO_4^-	

Polyatomic anions with names ending in *ite* have one less oxygen than those ending in *ate*, and have the same charge.

Example: nitrate is NO_3^- , nitrite is NO_2^-

Exception: dithionate is $\text{S}_2\text{O}_6^{2-}$, dithionite is $\text{S}_2\text{O}_4^{2-}$

Polyatomic ions with names ending in *ite* but beginning with *hypo* have one less O and the same charge compared to those without the *hypo* prefix. Example: chlorite is ClO_2^- and hypochlorite is ClO^- .

Polyatomic anions with names ending in *ide*.

hydroxide: OH^-

cyanide: CN^-

peroxide: O_2^{2-}

superoxide: O_2^-

carbide: C_2^{2-}

persulfide: S_2^{2-}

azide: N_3^- (note: this is different from nitride, N^{3-} , which is monatomic)

7.4 Names and Formulas of Binary Compounds

Binary compounds are compounds made up of only two elements.

► Example

Which of the following is a binary compound? CH_3OH , O_2 , HCl

Answer: Among the substances listed, only HCl is made up of two elements: hydrogen and chlorine. CH_3OH is a ternary compound; it's made up of three elements (C, H, and O). O_2 is not even a compound.

It is easy to recognize names of binary compounds. It consists of two words. We should see the **name of an element in the first word**, and the **stem of the name of an element in the second word**. The second word should end in **ide**.

► Example

Which of the following are binary compounds? ethyl acetate, ammonium chloride, sodium phosphate, magnesium chloride, carbon tetrachloride, disulfur difluoride

Answer: Among the compounds listed, only the last three (**magnesium chloride**, **carbon tetrachloride**, and **disulfur difluoride**) are binary. Note that there may be a **prefix** (such as **di** and **tetra**) preceding the name of the element.

7.4.1 Reading Formulas of Binary Compounds

Given the formula of a binary compound, how do we determine its name? First, we need to classify the compound as ionic or molecular. We can tell it is ionic if the first element is metallic. Next, we apply the following rules:

For binary, ionic compounds, the name consists of two words. **No prefixes** are used regardless of the subscripts.

- First word: name of the cation, which is just the name of the metallic element. If the metallic element is a transition or post-transition metal, specify its charge in Roman numerals inside parentheses.

- Second word: name of the anion, which is just the stem of the name of the nonmetallic element, followed by *ide*.

Exceptions:

- If the second element is N and its subscript is 3, the anion is azide (N_3^-), which is a polyatomic ion with a charge of -1 instead of nitride (N^{3-}), which is monatomic with a charge of -3 .
- If the second element is O and its subscript is 2, the anion could be two oxide ions (O^{2-}), or one peroxide ion (O_2^{2-}), or one superoxide ion (O_2^-). Figure out which one using the rule that the formula unit must be neutral.
- If the second element is S and its subscript is 2, the anion could be two sulfide ions (S^{2-}), or one persulfide ion (O_2^{2-}). Figure out which one using the rule that the formula unit must be neutral.

► Example

What are the cation and anion in FeS ? What is the name of the compound?

Answer: Fe^{2+} is the cation, S^{2-} is the anion. The name is iron(II) sulfide.

We know the compound is ionic because Fe is a metal. We know the cation is monatomic and derived from Fe. Since Fe is a transition metal, we have to figure out its charge based on the charge and subscript of the anion.

S is sulfur and the only naturally-occurring monatomic ion from sulfur has a charge of -2 and is called sulfide; the anion is S^{2-} .


We figure out that the charge of iron here is $+2$, because the total charge of the ions must add up to zero. So the name of the cation is iron(II).

► Example

What are the cation and anion in Na_2O_2 ? What is the name of the compound?

Answer: Na^+ is the cation, O_2^{2-} is the anion. The name is sodium peroxide.

We know the compound is ionic because Na is a metal. The only monatomic ion derived from Na, which belongs to group IA, has a charge of $+1$. Therefore, the cation is Na^+ , and there are **two** of this in Na_2O_2 . The total positive charge is **2(+1)**, or $+2$.



We need to figure out if the “O₂” part of Na₂O₂ represents one polyatomic ion or two monatomic ions. Based on Table 1, the possible polyatomic ions are:

peroxide (O₂²⁻) and superoxide (O₂⁻)

The only possible monatomic ion is oxide, the only known naturally-occurring monatomic ion from oxygen is O²⁻ (oxide). One peroxide has total charge of -2. One superoxide has a total charge of -1. Two oxides have a total charge of 2(-2), or -4.

Since the total positive charge is +2, the total negative charge must be -2. Therefore, the anion must be peroxide.

One formula unit of this compound consists of two Na⁺ ions and one O₂²⁻ ion.

For binary, molecular compounds, the name consists of two words.

- First word consists of: prefix corresponding to the subscript of the first element, then the name of the first element.
- Second word consists of: prefix corresponding to the subscript of the second element, then the stem of the name of the second element, then *ide*.

Prefixes: 2=di, 3=tri, 4=tetra, 5=penta, 6=hexa, 7=hepta, 8=octa, 9=nona, 10=deca. A subscript of one is not written in formulas; no prefix is used when the subscript is one.

► Example

P₄O₁₀ is a binary molecular compound. What is its name?

Answer: tetraphosphorus decoxide. Note: the “a” is dropped from a prefix ending in “a” if it is followed by “o”. Here, we used “dec” instead of “dec~~a~~.”

7.4.2 Writing Formulas of Binary Compounds

Given the name of a binary compound, how do we determine its formula? First, we need to determine if it is ionic or molecular. Then, we apply the following rules:

For a Binary Molecular Compound:

- write the symbols of the elements mentioned in the name, then
- write subscripts corresponding to their prefix.

► Example

Carbon tetrachloride is a binary molecular compound. What is its formula?

Answer: CCl_4 .

The subscript for carbon is implied to be 1 (no prefix). The subscript for chlorine is 4 since tetra means 4.

For a Binary Ionic Compound:

- based on the charges of the cation and anion, figure out the smallest possible subscripts so that
(cation subscript)(cation charge) + (anion subscript)(anion charge) = 0,
then
- write the symbol for each element and indicate the appropriate subscript.

► Example

Iron(III) sulfide is an ionic compound. What is its formula?

Answer: iron(III) is Fe^{3+} . Sulfide is S^{2-} . So, one formula unit of this compound must have 2 cations and 3 anions. $2(+3) + 3(-2) = 0$.

The formula is: Fe_2S_3 .

7.4.3 Binary Compounds with Trivial Names

Some compounds are more commonly referred to by their trivial names. You should be familiar with these:

- H_2O , water
- H_2O_2 , hydrogen peroxide
- CO , carbon monoxide
- CH_4 , methane
- SiH_4 , silane
- GeH_4 , germane
- NH_3 , ammonia
- PH_3 , phosphine
- AsH_3 , arsine
- NO , nitric oxide
- N_2O , nitrous oxide
- N_2H_4 , hydrazine

7.5 Names and Formulas of Compounds Containing Polyatomic Ions

Given the formula of a compound containing one or two polyatomic ions, how do we determine its name? For any ionic compound, we simply name the cation, then the anion.

► Example

What is the name of $\text{Fe}(\text{NO}_3)_3$?

Answer: Iron(III) nitrate.

The cation is Fe^{x+} ; we need to figure out what x is since Fe is a transition metal.

The anion must be NO_3^- , which is called nitrate (see Table 1) and has a charge of -1 . Since there are **three** anions in $\text{Fe}(\text{NO}_3)_3$, each with a -1 charge, the total negative charge is $3(-1)$, or -3 . Therefore, the total positive charge must be $+3$; $x=3$. The iron in this compound must have a $+3$ charge. So the cation is iron(III).

Given the name of a compound containing one or more polyatomic ions, how do we determine its formula?

- Write the formulas of the ions in the order they are mentioned; omit the charges, and write subscripts, so that
(cation subscript)(cation charge) + (anion subscript)(anion charge) = 0.
- If the subscript of a polyatomic ion is larger than 1, enclose the entire formula for the ion in parentheses, then write the subscript after the closing parenthesis.

► Example

What is the formula of ammonium sulfate?

Answer: $(\text{NH}_4)_2\text{SO}_4$

Ammonium is NH_4^+ , sulfate is SO_4^{2-} . So one formula unit of this compound should have two cations and one anion.
 $2(+1) + 1(-2) = 0$. The simplest combination of ions with a total charge of zero is two ammonium ions and one sulfate ion. Write a subscript of 2 for ammonium, and no subscript for sulfate.
The formula is $(\text{NH}_4)_2\text{SO}_4$.

7.6 Names and Formulas of Acids

Some molecular compounds produce H^+ ions when dissolved in water. These compounds are called *acids* and they are often named as though they are ionic; the cation, in this case, is hydrogen (H^+). When writing formulas for these compounds, H is usually written first, with a subscript corresponding to the number of H^+ ions produced when one molecule of the compound goes into water. The rest of the formula corresponds to the formula of the anion formed when the molecule dissociates (breaks up) in water; the magnitude of the charge of the anion corresponds to the number of H^+ ions formed.

► Example

Give two possible names for H_2S .

Answer: dihydrogen sulfide, hydrogen sulfide

Based on the rule for naming binary molecular compound, it is called dihydrogen sulfide. However, because it is an acid, we can also name it as if it is ionic, and simply refer to it as hydrogen sulfide. The name of the cation is hydrogen (H^+) and the name of the anion formed when two H^+ ions break off from H_2S is S^{2-} ; the anion is called sulfide.

Another way acids are named is based on the name of the anion produced when the H^+ ions break off from the acid molecule. Anions have names ending in *ide*, *ite*, or *ate*.

If the name of anion ends in **ide**, the acid name starts with **hydro** followed by the stem of the name of the anion, followed by **ic acid**.

► Example

Give two possible names for HCl .

Answer: hydrogen chloride, hydrochloric acid

HCl is a binary molecular compound called hydrogen chloride. The ion produced with H^+ breaks off from HCl is **chloride** (Cl^-). Therefore, the name is **hydrochloric acid**.

► Example

Hydrogen cyanide (HCN) is also known as _____ acid.

Answer: hydrocyanic

The anion formed when H^+ breaks off from the molecule is cyanide (CN^-). The other name for hydrogen cyanide is hydrocyanic acid.

If the name of the anion ends in **ate**, the acid name starts with the stem of the name of the anion, followed by **ic acid**.

► Example

Give two possible names for HNO_3 .

Answer: hydrogen nitrate, nitric acid

The anion formed when H^+ breaks off from HNO_3 is nitrate (NO_3^-). Therefore, the name is hydrogen nitrate or nitric acid.

If the name of the anion ends in **ite**, the acid name starts with the stem of the name of the anion, followed by **ous acid**.

► Example

Give two possible names for HNO_2 .

Answer: hydrogen nitrite, nitrous acid

The anion formed when H^+ breaks off from HNO_2 is nitrite (NO_2^-). Therefore, the name is hydrogen nitrite or nitrous acid.

7.7 Salts and Hydrates

If the anion of an ionic compound is not oxide or hydroxide, it is called a *salt*.


► Example

Which of the following are salts? NaCl , CaCO_3 , NaOH , CaO , HCl , CH_4

Answer: NaCl and CaCO_3

HCl and CH_4 are not ionic compounds.

NaOH and CaO are ionic, but their anions are hydroxide (OH^-) and oxide (O^{2-}).



Salt hydrates are compounds that produce water (H_2O) and salt when heated; the salt produced is called the anhydrous salt. The formula of the hydrate is written as follows:

- write the formula of the salt.
- write a large dot.
- write the ratio of number of water molecules produced to the number of formula units of salt produced.
- write H_2O .

► Example

When Epsom salt (a hydrate) is heated, 14 water molecules are produced for every 2 formula units of anhydrous MgSO_4 produced. What is the formula of the hydrate?

Answer: $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

The ratio of water molecules to anhydrous formula units is 14-to-2; $14/2 = 7$.

To name a hydrate, simply name the salt, then specify the extent of hydration using the following prefixes:

1 = mono, 2 = di, 3 = tri, 4 = tetra, 5 = penta, 6 = hexa,
7 = hepta, 8 = octa, 9 = nona, 10 = deca, 1/2 = hemi, 3/2 = sesqui

► Example

Name this compound: $\text{CaSO}_4 \cdot (1/2) \text{H}_2\text{O}$.

Answer: calcium sulfate hemihydrate

► Example

Write the formula for sodium carbonate decahydrate.

Answer: $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$



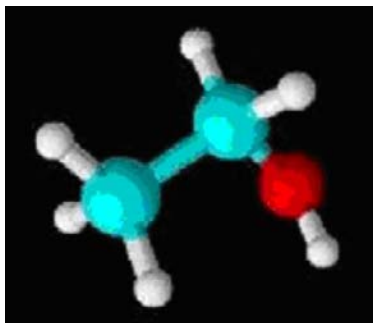
TEST YOURSELF

For answers and other study resources, see:


<http://i-assign.com/ebook/answers/chapter7.htm>.


- Which of the following is an ionic compound?
A. ethyl acetate B. sulfuric acid
C. sodium hydrogen carbonate D. hydrazine
- Which of the following is a molecular compound?
A. phosphorus trichloride B. ammonium chloride
C. lithium aluminum hydride D. sodium dihydrogen phosphate
- Which of the following is a molecular compound?
A. Na_2S B. NH_3 C. $(\text{NH}_4)_2\text{SO}_4$ D. N_2
- Which of the following is a solid with a very high melting point and conducts electricity when melted?
A. CaCl_2 B. CCl_4 C. H_2O
- Which of the following is a strong acid?
A. H_2SO_4 B. $\text{HC}_2\text{H}_3\text{O}_2$ C. HCOOH D. HNO_2
- Which of the following is a strong electrolyte?
A. CH_3OH B. KOH C. HF D. NH_3
- Which of the following is a strong electrolyte?
A. HCl B. $\text{C}_6\text{H}_{12}\text{O}_6$ C. H_2S D. NH_3
- A molecule of fructose consists of six carbon atoms, twelve hydrogen atoms, and six oxygen atoms. The formula of fructose is...
A. $\text{C}_6\text{H}_{12}\text{O}_6$ B. CHO C. CH_2O
- A molecule of acetic acid consists of four hydrogen atoms, two carbon atoms, and two oxygen atoms. Which of these cannot possibly be the formula of acetic acid?
A. $\text{H}_4\text{C}_2\text{O}_2$ B. H_2CO C. $\text{HC}_2\text{H}_3\text{O}_2$ D. CH_3COOH

10. Which of these is not the formula of the compound represented by the figure below, if blue spheres represent carbon atoms, white spheres represent hydrogen atoms and red sphere represents an oxygen atom?



- A. CHO B. C₂H₆O C. C₂H₅OH D. CH₃CH₂OH
11. What is the formula of an ionic compound consisting of Ca²⁺ and Cl⁻ ions?
A. CaCl B. Ca₂Cl C. CaCl₂ D. Ca₂Cl₂
12. What is the formula of an ionic compound consisting of Na⁺ and CO₃²⁻ ions?
A. NaCO₃ B. Na₂(CO₃)₂ C. NaCO D. Na₂CO₃
13. What is the formula of an ionic compound consisting of Ca²⁺ and CO₃²⁻ ions?
A. CaCO₃ B. Ca₂(CO₃)₂ C. CaCO D. Ca₂CO₃
14. What is the formula of an ionic compound consisting of Mg²⁺ and PO₄³⁻ ions?
A. Mg₂PO₃ B. Mg₃(PO₄)₂ C. Mg₃PO₂ D. MgPO₄
15. Which of the following is the correct name for PCl₅?
A. phosphorus chloride B. phosphorus chlorine
C. phosphorus pentachlorine D. phosphorus pentachloride
16. Which of the following is the correct name for MgCl₂?
A. magnesium chloride B. magnesium dichloride
C. magnesium chlorine D. magnesium dichlorine

- 
17. Which of the following is the correct name for Na_2S ?
- A. sodium sulfide B. disodium sulfide
C. sodium sulfite D. sodium sulfate
18. Which of the following is correct name for CuCl_2 ?
- A. copper(II) chloride B. copper(I) chloride
C. copper chloride(II) D. copper(I) dichloride
19. Which of the following is the correct formula for dinitrogen tetroxide?
- A. NO B. N_2O_3 C. N_2O_4 D. NO_2
20. Which of the following is the formula for iron(III) sulfide?
- A. FeS B. Fe_3S C. Fe_2S_3 D. Fe_3S_2
21. Which of the following is the formula for cobalt(II) chloride?
- A. CoCl B. CoCl_2 C. Co_2Cl D. Co_2Cl_2
22. Which of the following is the correct formula for sodium phosphate?
- A. NaP B. NaPO_3 C. Na_3PO_4 D. $\text{Na}_3(\text{PO}_4)_2$
23. Which of the following is the correct formula for ammonium sulfide?
- A. $(\text{NH}_4)_2\text{S}$ B. NH_4SO_3 C. $(\text{NH}_3)_2\text{SO}_4$
24. Which of the following is the correct formula for iron(III) sulfate?
- A. Fe_3S B. FeSO_4 C. $\text{Fe}_2(\text{SO}_3)_3$ D. $\text{Fe}_2(\text{SO}_4)_3$
25. Which of the following is the correct formula for potassium hydrogen phosphate?
- A. KHPO_4 B. K_2HPO_4 C. KH_2PO_4
26. Which of the following is the correct name for K_2CO_3 ?
- A. dipotassium carbon trioxide B. potassium carbide
C. dipotassium carbonate D. potassium carbonate
27. Which of the following is the correct name for FeSO_4 ?
- A. iron(I) sulfate B. iron(II) sulfate C. iron(III) sulfite D. iron sulfite

- 
28. Which of the following is the correct name for BaO_2 ?
- A. barium oxide B. barium peroxide
C. barium dioxide D. barium(IV) oxide
29. Which of the following is sulfurous acid?
- A. H_2SO_4 B. H_2SO_3 C. H_2S
30. Which of the following is another name for hydrogen cyanide (HCN)?
- A. hydrocyanic acid B. cyanic acid C. cyanous acid

Chemical Changes

The term *chemical change*, or chemical reaction, refers to the transformation of one or more substances into others. We say that a chemical change has occurred if there is a *change in composition*. If a change does not involve a change in composition, then it is called a *physical change*.

8.1 Reactants and Products

We refer to the substances involved in a chemical change as *reactants* and *products*. Reactants are transformed into products. Therefore, as a chemical change occurs, the amount of reactants will be decreasing and the amount of products will be increasing.

► Example

Suppose a drop of water added to a white solid results in the formation of a blue solid. Identify the reactants and products.

Answer: the white solid and water are reactants; the blue solid is a product.

This reaction is something that we would actually observe if we were to add a drop of water to copper sulfate (CuSO_4), which is a white solid. The reaction produces a compound called copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), which is a blue solid.

► Example

During a chemical change, the amount of substance X increases from 5.0 g to 6.0 g. Is X a reactant or a product?

Answer: product

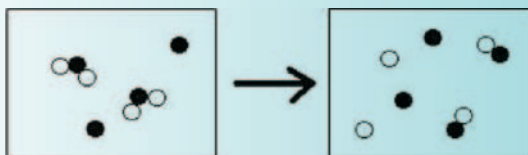
Since the amount of X increased, we call it a product of the reaction.

8.2 Atomic Interpretation of Chemical Change

At the atomic level, a chemical change involves a reorganization of atoms into different formula units. For physical changes, the formula units remain intact; they simply move apart (as in vaporization of a liquid or breaking of a rock) or move closer together (as in condensation of a gas into a liquid).

► Example

Consider the following pictorial representation for a change at the atomic level.



Is the change chemical or physical?

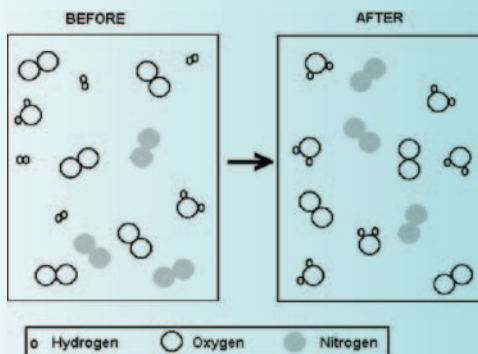
Answer: chemical


One of the atoms represented by unfilled circles appears to have broken off from each of the two molecules shown on the left.

► Example

Consider the following pictorial representation for a chemical change at the atomic level.

What are the reactants? Products? Which molecules are not involved in the reaction?





Answer: H_2 is a reactant; we have less of it after the reaction. O_2 is also reactant. H_2O is a product; we have more of it after the reaction. N_2 is neither a reactant nor a product. We have the same amount before and after.

8.3 Chemical Equations

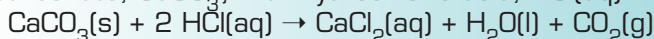
A chemical equation is a symbolic representation for what happens in a chemical change. In a chemical equation:

- the formulas of the reactants (separated by + signs) are written first,
- an arrow pointing to the right is then drawn,
- the formulas of the products (separated by + signs) are written next, and
- numbers, called coefficients, are written in front of the formulas of reactants and products; unwritten coefficients are implied to be 1.

It is preferable, but not required, to indicate the physical states of the reactants and products by using the following labels: (s) for solid, (l) for liquid, (g) for gaseous, and (aq) for *aqueous solution*; something is said to be in aqueous solution if it is dissolved in water.

► Example

Consider the chemical equation for the reaction of calcium carbonate, CaCO_3 , with hydrochloric acid, $\text{HCl}(\text{aq})$.



Identify the reactants and products, as well as their physical states. What are the coefficients?

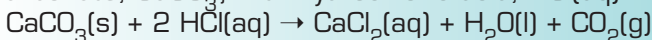
Answers:

- The reactants are solid CaCO_3 and HCl in aqueous solution; they are written first.
- The products are CaCl_2 in aqueous solution, liquid H_2O , and gaseous CO_2 ; they are written to the right of the arrow.
- The coefficient of HCl is 2. The coefficients of CaCO_3 , CaCl_2 , H_2O , and CO_2 are all 1.

The purpose of coefficients is to *balance* the chemical equation. Balancing a chemical equation means adjusting the coefficients so that the number of atoms of each element is the same on both sides of the arrow. This is done because no atoms should be created or destroyed during a chemical change. To count the number of atoms, we simply *multiply the coefficient by the subscript*.

► Example

Consider the chemical equation for the reaction of calcium carbonate, CaCO_3 , with hydrochloric acid, $\text{HCl}(\text{aq})$.



How many atoms of Cl atoms are shown on either side of the arrow?

Answer: 2

The Cl atoms are found in HCl on the left and CaCl_2 on the right:



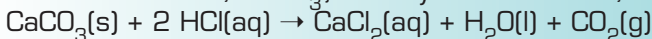
The coefficient of HCl is 2; the subscript of Cl in HCl is implied to be 1: $2 \times 1 = 2$

The coefficient of CaCl_2 is implied to be 1; the subscript of Cl in CaCl_2 is 2: $1 \times 2 = 2$

There are an infinite number of sets of coefficients that we can use to balance a chemical equation. We can multiply all of the numbers in a valid set of coefficients by the same factor and come up with another set of coefficients that will also give us a balanced equation.

► Example

Consider the balanced chemical equation for the reaction of calcium carbonate, CaCO_3 , with hydrochloric acid, $\text{HCl}(\text{aq})$:



If the coefficient of HCl were changed to 6, what other coefficients would be needed to keep the equation balanced?

Answer: The other coefficients need to be changed to 3, 3, 3, and 3. The coefficients shown are (1, 2, 1, 1, and 1). Changing the coefficient of HCl to 6 means multiplying what it is right now by 3: $2 \times 3 = 6$. To keep the equation balanced, all other coefficients must be multiplied by 3.

It is customary, *but not necessary*, to use the smallest set of whole number coefficients. How can we tell if we have the smallest set of whole number coefficients?

- Find the greatest common factor (GCF) of all the coefficients. If the GCF is 1, then we have the smallest set of whole number coefficients.

How can we tell that the GCF is 1?

- Divide all the coefficients by the smallest. If one of the resulting numbers is not a whole number, then the GCF is already 1.

► Example

Which of the following sets of coefficients can be reduced to a simpler set of whole numbers?

- A. 1, 3, 3, 2 B. 5, 2, 3, 4 C. 3, 6, 6

Answer: C

- For set A, (1, 3, 3, 2), the smallest whole number is 1. The greatest common factor is 1.
- For set B, (5, 2, 3, 4), the smallest whole number is 2. Dividing all the numbers by this gives us a set (2.5, 1, 1.5, 2) that includes non-integers. This means that the greatest common factor for set B is already 1.
- For set C, (3, 6, 6), the smallest whole number is 3. Dividing all the numbers by this gives us a simpler set of whole numbers, (1, 2, 2).

Coefficients in chemical equations can be fractional, as in:

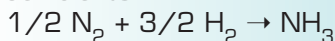


How could we have half of a molecule? We cannot. However, coefficients do not necessarily mean individual counts; in practice, they are often taken as group counts. Because atoms and molecules are so small, it is convenient to count them in groups called moles. A *mole* of molecules is about 602 billion trillion molecules. In the example above, $1/2 \text{CO}_2$ would be interpreted not as half of a CO_2 molecule, but as half a mole of CO_2 molecules (or 301 billion trillion CO_2 molecules).

If, in balancing an equation, we end up using fractional coefficients and later decide to change the coefficients to whole numbers, all we have to do is multiply each of the fractional coefficients by the least common multiple (LCM) of the denominators.

► Example

Rewrite the following chemical equation using whole number coefficients:



Answer: $\text{N}_2 + 3 \text{H}_2 \rightarrow 2 \text{NH}_3$

The coefficients are (1/2, 3/2, and 1) or (1/2, 3/2, and 1/1). The denominators are 2, 2, and 1. The least common multiple of these numbers is 2. Multiplying all the coefficients by 2 gives us (2 × 1/2, 2 × 3/2, and 2 × 1) or (1, 3, and 2).

8.4 Strategies for Balancing Chemical Equations

Balancing chemical equations means adjusting the coefficients *after* correct formulas of reactants and products have been written. In other words, subscripts should never be changed when balancing a chemical equation. When balancing an equation, it is helpful to:

- first try to balance elements that appear only once on either side.
- balance by adjusting coefficients (in the deficient side) upward.
- recheck previously balanced elements after every adjustment.

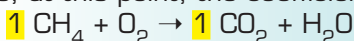
► Example

Balance: $\text{CH}_4 + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$,

Answer: $\text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O}$

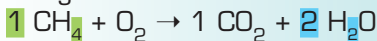
It is better to try to balance C and H before O since O appears twice on the right side.

Balance C. We can see that the coefficients of CH_4 and CO_2 must be equal since these are the only formulas containing C and the subscript of C in both cases is the same. C is already balanced as is; at this point, the coefficients of CH_4 and CO_2 are both 1.



Balance H. There are 4 H atoms in CH_4 , but only 2 in H_2O . The coefficients of CH_4 and H_2O must be in a 1-to-2 ratio. There should be twice as many H_2O molecules compared to CH_4 in order to have the same number of H atoms on both sides.

Balance H by adding another H_2O to the right side (increasing the coefficient of H_2O up to 2) since there are fewer H atoms on the right.



Since $1 \times 4 = 2 \times 2$, H is now balanced.

Recheck C. C is still balanced.

Balance O.

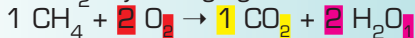
- Left side: O atoms are found in O_2 , which has an implied coefficient of 1. $1 \times 2 = 2$



- Right side: O atoms are found in CO_2 and H_2O . $(1 \times 2) + (2 \times 1) = 4$



- We need 2 more O atoms on the left side. We do this by adding another O₂, by changing the coefficient of O₂ from 1 to 2.



Now, O is balanced: $2 \times 2 = (1 \times 2) + (2 \times 1)$

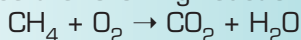
Recheck C and H. Both are still balanced.

Balancing an equation can be facilitated with simple algebra:

- Assign variables names to the coefficients.
- Set up algebraic equations that must be satisfied to balance each element.
- Assign a number to one of the variables, then solve for the others.

► Example

Use algebra to balance the following reaction:



Solution:

Let the coefficients be w , x , y , and z :



- Eq. 1, To balance C: $(w)(1) = (y)(1)$
- Eq. 2, To balance H: $(w)(4) = (z)(2)$
- Eq. 3, To balance O: $(x)(2) = (y)(2) + (z)(1)$

In Eq. 3, $(x)(2)$ is the number of O atoms on the left, $(y)(2) + (z)(1)$ is the number on the right. On the left, O is found in O₂, which has a coefficient of x . On the right, O is found in CO₂, which has a coefficient of y and H₂O, which has a coefficient of z .

We can assign *any* number to one of these variables and solve for the others. Let $w = 1$. Then:

- Substituting $w = 1$ into Eq. 1 gives us: $(1)(1) = (y)(1)$, or $y = 1$
- Substituting $w = 1$ into Eq. 2 gives us: $(1)(4) = (z)(2)$; solving for z , we get $z = 2$
- Substituting $y = 1$ and $z = 2$ into Eq. 3 gives us: $(x)(2) = (1)(2) + (2)(1)$; solving for x , we get $x = 2$

Thus: $w = 1$, $x = 2$, $y = 1$, and $z = 2$.

If we started with $w = 2$, we would have gotten $x = 4$, $y = 2$, and $z = 4$.

We could have assigned a value to y or z first; we would still be able to figure out all the other coefficients. However, starting with a value for x , which is essentially trying to balance O first, will give us three equations in three unknowns (w , y , and z), which will be more complicated to solve.



8.5 Signs of a Chemical Change


Each substance has a unique set of properties that makes it different from other substances. If there is a change in the properties as a result of putting two or more substances in contact, or subjecting a sample of matter to heat, light or electricity, then it is very likely that a chemical change has occurred. If we cannot explain a change in terms of *unchanged* molecules or ions simply moving around, then it is very likely that we are dealing with a chemical change.

Some signs that a chemical change has most likely occurred are unusual changes in color, odor, taste or burning (a flame is a hot glowing gaseous product of a combustion reaction). Some signs that a chemical change *may* have occurred include: production of heat, absorption of heat, production of gas bubbles in a liquid, and formation of a solid when two liquids are mixed (precipitation).

A lack of visible change does not imply that a chemical change has not occurred. For example, sodium hydroxide dissolved in water, $\text{NaOH}(\text{aq})$, is a colorless liquid. Acetic acid in water, $\text{CH}_3\text{COOH}(\text{aq})$, is also a colorless liquid. If we mix the two liquids, we still get a colorless liquid; we will not be able to observe a visible change. But there is, in fact, a chemical change. $\text{NaOH}(\text{aq})$ is bitter, $\text{CH}_3\text{COOH}(\text{aq})$ is sour, but the resulting mixture is salty. $\text{CH}_3\text{COOH}(\text{aq})$ smells like vinegar while $\text{NaOH}(\text{aq})$ is odorless. The resulting mixture could be odorless or could still smell a little bit like vinegar (if there are acetic acid molecules left unreacted). If we were to measure the temperature of the liquids before and after mixing, we would also find that the temperature of the resulting mixture is higher; this reaction generates heat; we say it is an *exothermic* reaction.

Production of heat generally accompanies most physical and chemical changes. Therefore, *generation of heat alone does not imply that a chemical change has occurred.* Example: steam condensing into a liquid generates a lot of heat, but it is just a physical change. Production of heat and light together, as in the burning of paper, involves a chemical change; these are called *combustion* reactions. However, the production of heat and light by an incandescent light bulb does not involve a chemical change.

Production of gas bubbles in a liquid could occur by stirring, shaking, or heating the liquid. It can also occur by pulling a vacuum above the liquid. In these cases, the change involved is just a physical change. However, if bubble formation results simply by mixing a liquid with something else (no stirring, heating, shaking or vacuuming involved), then the gas bubbles are very likely to be the product of a chemical change. If a chemical reaction produces a gas that is not very soluble in the liquid, the gas will be observed leaving the water as bubbles (“fizz”). A familiar example is carbon dioxide, CO_2 , which fizzes out when baking soda is mixed with vinegar. The fizz observed when opening a can of carbonated drink does not involve a chemical change; the can is pressurized; opening it lowers the pressure and lowers the solubility of carbon dioxide.



Precipitation usually indicates a chemical change. However, it can happen if you mix different liquids such that a substance dissolved in one of the liquids suddenly becomes insoluble; in this case, the precipitation is not considered a chemical change.

A change in color, odor or taste does not necessarily imply that a chemical change has occurred. For example, our eyes perceive a mixing of yellow and blue as green. So, mixing a yellow liquid with a blue liquid to produce a green liquid does not necessarily mean that a chemical change has occurred. But if mixing a yellow liquid with a blue liquid produces a red liquid, then we can be confident that a chemical change has occurred. If you mix something sweet and something sour and your taste buds senses a “sweet and sour” taste, it does not necessarily mean that a chemical change has occurred as a result of the mixing. But if you sense a bitter taste instead, then a chemical change has occurred as a result of the mixing.

► Example

Which of these most likely describes a chemical change?

- A. Food rotting,
- B. Gasoline burning,
- C. Stain fading when treated with bleach
- D. Water boiling,
- E. Ice melting,
- F. A chalk cut into two pieces,
- G. Green leaves turning brown in autumn,
- H. Sugar dissolved in water

Answers: A, B, C, G

8.6 Simple Types of Reactions

The simplest types of reactions can be classified as combination, decomposition, displacement, metathesis, and combustion.

8.6.1 Combination Reactions

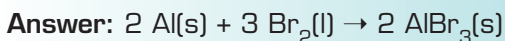
Combination reactions, also known as composition or synthesis reactions, involve two or more reactants and *only one product*. Commonly observed combination reactions include the following:

- combination of two elements to form a compound.
- combination of ammonia (NH_3) with an acid to form an ammonium salt.
- combination of a metal oxide with water to form a metal hydroxide.
- combination of a nonmetal oxide with water to form an acid.
- combination of a metal hydroxide with carbon dioxide to form a metal bicarbonate.



► **Example**

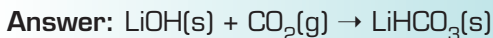
Write the chemical equation for the reaction of aluminum metal with liquid bromine.



Aluminum metal is $\text{Al}(s)$. Bromine is made up of diatomic molecules (Br_2) under ordinary conditions. The expected product of a metal and nonmetal is an ionic compound. The metallic element is expected to form a cation; the only naturally-occurring monatomic ion from Al has a charge of +3; the only naturally-occurring monatomic ion from Br has a charge of -1. Thus, the product is AlBr_3 . Since ionic compounds generally have high melting points, we expect AlBr_3 to be a solid under ordinary conditions.

► **Example**

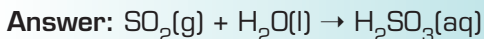
Write the chemical equation for reaction of LiOH with CO_2 gas.



Metal hydroxides are known to react with CO_2 to form metal bicarbonate. Thus, we predict the product of lithium hydroxide and CO_2 to be lithium bicarbonate (LiHCO_3). LiOH and LiHCO_3 are both ionic compounds and are expected to be solids under ordinary conditions. This is the reaction used in the space shuttle to prevent the build up of CO_2 in the air that astronauts breathe; we exhale CO_2 .

► **Example**

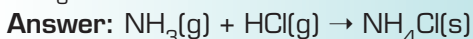
Write the chemical equation for the reaction of $\text{SO}_2(g)$ (from a volcano) with rain.




SO_2 is a nonmetal oxide. Nonmetal oxides react with water to form acids. H_2SO_3 is sulfurous acid.

► **Example**

Write the chemical equation for the reaction of ammonia gas (NH_3) with hydrogen chloride gas (HCl).

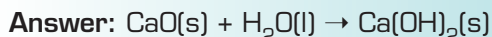




The product is an ammonium salt, ammonium chloride. Since ammonium chloride is an ionic compound, we expect it to be a solid under ordinary conditions.

► Example

Write the chemical equation for the reaction of calcium oxide with water.



The product of a metal oxide and water is a metal hydroxide. This reaction is highly exothermic and is used for on-the-spot food warming in self-heating cans.

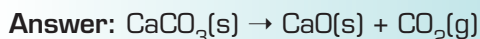
8.6.2 Decomposition Reactions

A *decomposition* is the opposite of a combination reaction. It involves *only one reactant*, and two or more products. Commonly observed decomposition reactions occur when the following compounds are heated (*thermal decomposition*):

- metal carbonates; the products are metal oxide and $\text{CO}_2(g)$.
- metal bicarbonates; the products are metal hydroxide and $\text{CO}_2(g)$.
- metal hydroxides; the products are metal oxide and $\text{H}_2\text{O}(g)$.
- acids; the products are nonmetal oxide and $\text{H}_2\text{O}(g)$.
- metal chlorates; the products are metal chloride and $\text{O}_2(g)$.
- peroxides; the products are oxide and $\text{O}_2(g)$.
- binary compounds; the products are the elements.

► Example

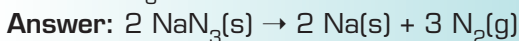
Write the chemical equation for the decomposition of calcium carbonate.



This is the reaction that occurs when limestone is heated in a furnace in a process called calcination. The product, calcium oxide (CaO), is called quicklime and is used to make cement.

► Example

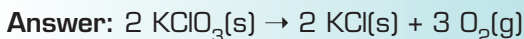
Write the chemical equation for the decomposition of sodium azide (NaN_3).



This is the reaction that occurs in a car's airbag. The N_2 gas produced by the reaction causes the airbag to inflate.

► Example

Write the chemical equation for the thermal decomposition of KClO_3 .

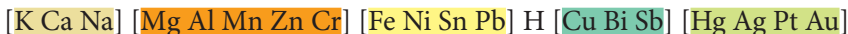


This is a commonly used procedure for generating O_2 in introductory chemistry laboratory courses.

8.6.3 Displacement Reactions

A *displacement* reaction, also known as *single replacement*, involves the replacement of an element in a compound by another element. A metallic element may displace another metallic element from an ionic compound, or hydrogen from acid, depending on the conditions. Most of these reactions involve compounds in aqueous solution.

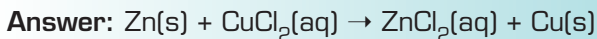
The term *activity series* refers to a list that we can use to predict which metallic element is more likely to displace another. A subset of this series that includes the most common metallic elements is:




The metal listed first can displace one that is listed later. The elements in the first group (K, Ca, and Na) are so reactive that they can readily displace H_2 from cold water; the other product is an aqueous solution of the metal hydroxide. The second group readily displaces H_2 from steam; they react slowly with room temperature water. The first, second, and third groups are able to displace H_2 from acids.

► Example

Write the chemical equation for the reaction of zinc metal with copper(II) chloride.



The expected products are zinc chloride and copper metal. Naturally occurring zinc ion is always observed to have a



+2 charge and naturally occurring chloride ion is always observed with a -1 charge. Therefore, the formula of the zinc chloride product is ZnCl_2 .

► Example

Write the chemical equation for the reaction that occurs when potassium (K) is mixed with an aqueous solution of NaCl.

Answer: $2 \text{K(s)} + 2 \text{H}_2\text{O(l)} \rightarrow 2 \text{KOH(aq)} + \text{H}_2\text{(g)}$

The H_2O comes from the aqueous solution. Even if K were to displace Na from NaCl, the Na produced will immediately react with H_2O since Na is a very reactive metal. In fact, formation of Na is not observed when this reaction is carried out. What is observed is the formation of bubbles, which indicates the formation of a gaseous product that is insoluble in water. We can test the gas and verify that it is, in fact, H_2 .

A *displacement* reaction can also involve displacement of a nonmetal by another nonmetal. The commonly observed reactions involve halogens; among the halogens, F is found to be the most active, followed by Cl, Br, and I.

► Example

Write the chemical equation for the reaction of chlorine gas with an aqueous solution of potassium bromide.

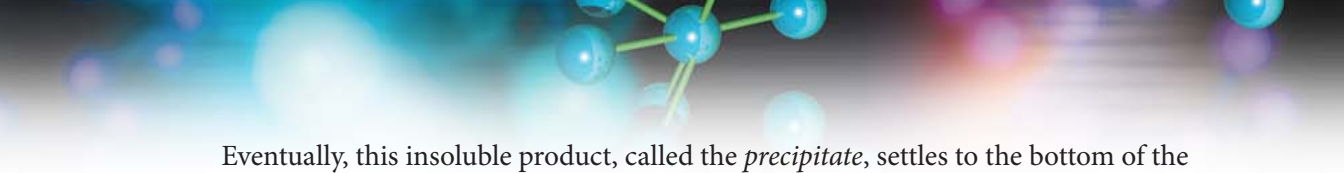
Answer: $\text{Cl}_2\text{(g)} + 2 \text{KBr(aq)} \rightarrow 2 \text{KCl(aq)} + \text{Br}_2\text{(l)}$

Remember that the elemental form of the halogens is diatomic.

8.6.4 Metathesis Reactions

Metathesis reactions are also known as *double decomposition* or *double replacement*. A *metathesis* reaction usually involves two compounds that produce ions in water. The reaction can be thought of as an exchanging of partners. The positive ion from one compound combines with the negative ion from the other compound. Commonly observed metathesis reactions include:

- *precipitation* reactions. In a precipitation reaction, the mixing of two aqueous solutions leads to the formation of a product that is insoluble in water. As a result, the insoluble product comes out of solution and makes the mixture appear cloudy.

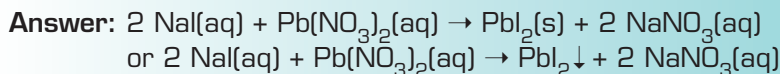


Eventually, this insoluble product, called the *precipitate*, settles to the bottom of the container. In the chemical equation the physical state of the precipitate is indicated by (s); alternatively, a downward pointing arrow (\downarrow) is drawn next to the formula.

- *acid-base neutralization* reactions. This type of reaction occurs when an acid reacts with a metal hydroxide or metal oxide. The products are water (H_2O) and a salt. Precipitation may occur at the same time if the salt happens to be insoluble in water.

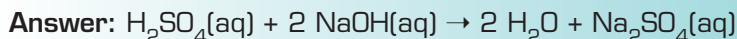
► Example

Write the chemical equation for the precipitation of lead(II) iodide when aqueous solutions of sodium iodide and lead(II) nitrate are mixed.



► Example

Write the chemical equation for the neutralization of sulfuric acid by sodium hydroxide in aqueous solution.




Bubble formation is generally observed for metathesis reactions that lead to the formation of H_2CO_3 or H_2SO_3 . The reason for this is that these compounds tend to decompose to H_2O and CO_2 or SO_2 . CO_2 and SO_2 are gaseous in pure form and are not very soluble in water. Bubble formation and a sharp odor are also observed for metathesis reactions that lead to the formation of H_2S . H_2S is gaseous in pure form and is not very soluble in water.

► Example

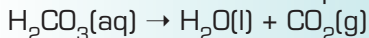
Write the chemical equations to explain the bubbles observed when baking soda, $\text{NaHCO}_3(\text{s})$, reacts with vinegar, $\text{HC}_2\text{H}_3\text{O}_2(\text{aq})$.

Answer: The reaction of baking soda (or sodium bicarbonate) with acetic acid (in vinegar) is a metathesis reaction that leads to the formation of carbonic acid (H_2CO_3):





Carbonic acid then decomposes to H₂O and CO₂.



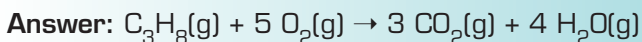
CO₂ is not very soluble in water and it comes out of solution as gas bubbles.

8.6.5 Combustion

Combustion, or burning, involves a reaction of a material with oxygen (O₂), accompanied by the production of heat and light. The products of combustion are the oxides of the elements present in the material.

► Example

Write the chemical equation for the combustion of propane gas (C₃H₈).



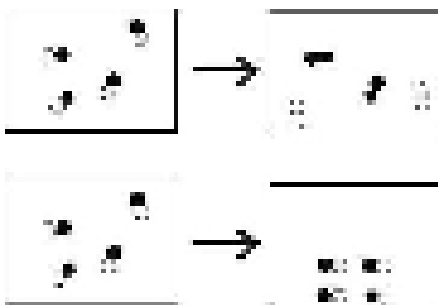
Note that the products are the oxide of carbon (carbon dioxide, CO₂) and the oxide of hydrogen (water, H₂O). If there is insufficient O₂ available, carbon monoxide (CO) may also be formed. If the compound contains nitrogen, N₂ is formed unless a very large excess of oxygen is used (in which case, oxides of nitrogen are formed such as NO and NO₂). If the compound contains sulfur, SO₂ and SO₃ are also produced.

TEST YOURSELF

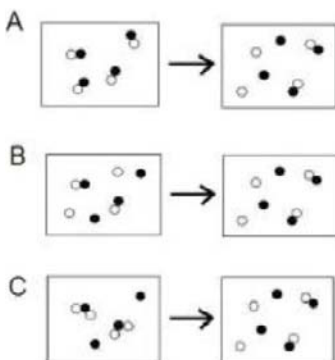
For answers and other study resources, see:

<http://i-assign.com/ebook/answers/chapter8.htm>.

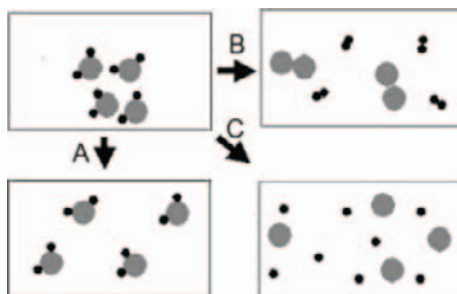
- A mixture contains 25.0 g of substance X and 10.0 g of substance Y. A few minutes later, due to a chemical change, it is found that the mixture now contains 30.0 g of substance X and 5.0 g of substance Y. For the reaction described here...
 - X is the reactant and Y is the product
 - Y is the reactant and X is the product
 - Both X and Y are reactants
 - Both X and Y are products
- Consider the pictorial representation shown below for a process at the atomic/molecular level. Which process involves a chemical change?
 - 1 only
 - 2 only
 - both
 - neither



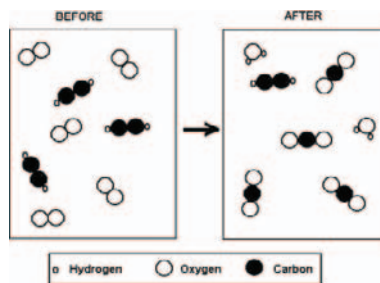
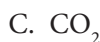
- Consider the pictorial representation shown below for a process at the atomic/molecular level. Which process does not involve a chemical change?



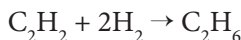
4. Which pictorial representation best accounts for the conversion of water from liquid to steam?



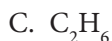
5. Consider the pictorial representation of a chemical change shown below. Which of the following is not a product of the reaction?



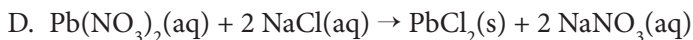
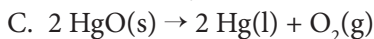
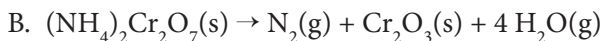
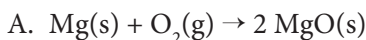
6. Consider the chemical equation for the hydrogenation of acetylene:



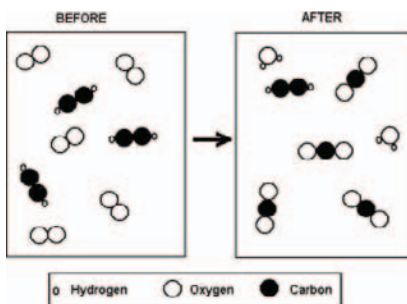
Which of these is the formula of a reactant in this reaction?



7. Consider the following observations of a chemical change: A small amount of orange-red solid is heated in a test tube. A little explosion occurred and a green powder was obtained. The mass of the green solid was found to be less than that of the original orange-red solid. Which of the following chemical equations is consistent with the observations above?



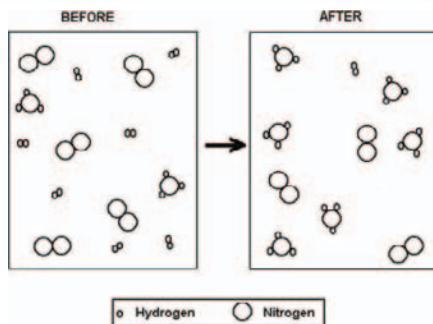
8. Which of the following is not a balanced chemical equation?
- A. $2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O}$ B. $4 \text{H}_2 + 2 \text{O}_2 \rightarrow 4 \text{H}_2\text{O}$
 C. Both A and B D. None of the above
9. Which of the following is the balanced chemical equation for the following reaction?
- $\text{Mg} + \text{O}_2 \rightarrow \text{MgO}$
- A. $\text{Mg} + \text{O} \rightarrow \text{MgO}$ B. $\text{Mg} + \text{O}_2 \rightarrow \text{MgO} + \text{O}$
 C. $\text{Mg}_2 + \text{O}_2 \rightarrow 2 \text{MgO}$ D. $2 \text{Mg} + \text{O}_2 \rightarrow 2 \text{MgO}$
10. Consider the following chemical equation where coefficients are represented by the letters w, x, y, and z: $w \text{Al}_2\text{O}_3 + x \text{H}_2\text{SO}_4 \rightarrow y \text{Al}_2(\text{SO}_4)_3 + z \text{H}_2\text{O}$
 If $w = 1$, then which of these is true?
- A. $y = 2$ B. $z = 3$ C. $x = 6$
11. Consider the combustion of propane: $\text{C}_3\text{H}_8 + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$ (unbalanced)
 Using the smallest set of whole numbers, the sum of the coefficients in the balanced chemical equation is:
- A. 7 B. 9 C. 12 D. 13
12. Consider the pictorial representation of a chemical change shown below:



Using the smallest set of whole numbers, the coefficient of C_2H_2 in the balanced chemical equation for this reaction is...

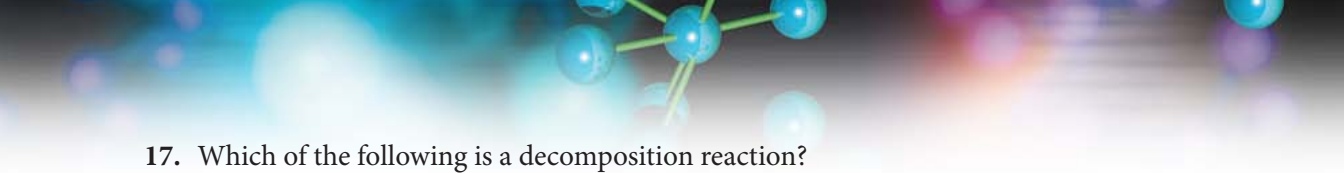
- A. 1 B. 2 C. 3 D. 4

13. Consider the pictorial representation of a chemical change shown below:



Using the smallest set of whole numbers, the coefficient of NH_3 in the balanced chemical equation for this reaction is...

- A. 2 B. 3 C. 4 D. 6
14. Which of the following observations is a definite sign that a chemical change has occurred?
- A. Mixing a blue-colored liquid with a yellow-colored liquid, yields a green-colored mixture
- B. Mixing a blue-colored liquid with a colorless liquid yields a yellow-colored liquid
- C. Neither
- D. Both
15. Which of the following observations implies that a chemical change has definitely not occurred?
- A. Mixing two colorless liquids yields a colorless liquid
- B. A piece of paper, held next to a flame, catches fire and leaves a black residue
- C. Both
- D. Neither
16. Which of the following is a correct chemical equation for a combination reaction between a metallic element and nonmetallic element?
- A. $\text{Mg(s)} + \text{N}_2(\text{g}) \rightarrow \text{MgN}_2(\text{s})$
- B. $\text{Mg(s)} + \text{O}_2(\text{g}) \rightarrow \text{MgO}_2(\text{s})$
- C. $\text{Mg(s)} + \text{N(g)} \rightarrow \text{MgN}$
- D. None of these

- 
17. Which of the following is a decomposition reaction?
- A. $2 \text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{CO}_2(\text{g})$
 - B. $\text{Mg}(\text{s}) + 2 \text{HCl}(\text{aq}) \rightarrow \text{MgCl}_2(\text{aq}) + \text{H}_2(\text{g})$
 - C. $\text{Ba}(\text{OH})_2(\text{aq}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow 2 \text{H}_2\text{O}(\text{l}) + \text{BaSO}_4(\text{s})$
 - D. $2 \text{H}_2\text{O}_2(\text{aq}) \rightarrow 2 \text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$
18. What is the salt produced by the neutralization reaction of magnesium hydroxide, $\text{Mg}(\text{OH})_2$, and hydrochloric acid, HCl ?
- A. MgCl
 - B. MgCl_2
 - C. HOH
 - D. none of these
19. What is chemical equation for the neutralization of stomach acid, HCl , by milk of magnesia, $\text{Mg}(\text{OH})_2$?
- A. $\text{HCl} + \text{Mg}(\text{OH})_2 \rightarrow \text{HMg} + \text{Cl}(\text{OH})_2$
 - B. $2 \text{HCl} + \text{Mg}(\text{OH})_2 \rightarrow 2 \text{HOH} + \text{MgCl}_2$
 - C. $\text{HCl} + \text{Mg}(\text{OH})_2 \rightarrow \text{H}_2\text{O} + \text{MgCl}$
 - D. $\text{HCl} + \text{Mg}(\text{OH})_2 \rightarrow \text{H}_2\text{O} + \text{MgHCl}$
20. What is the chemical equation for the neutralization of nitric acid, HNO_3 , by calcium oxide (CaO)?
- A. $\text{HNO}_3 + \text{CaO} \rightarrow \text{HO} + \text{CaNO}_3$
 - B. $2 \text{HNO}_3 + \text{CaO} \rightarrow \text{H}_2\text{O} + \text{Ca}(\text{NO}_3)_2$
 - C. $\text{HNO}_3 + \text{CaO} \rightarrow \text{NO}_4 + \text{CaH}$
 - D. $2 \text{HNO}_3 + \text{CaO} \rightarrow \text{H}_2\text{O} + \text{CaNO}_3$

History of Atomic Theory

In this chapter, we examine how our notion about atoms has developed over time.

9.1 Atomism


The word atom literally means uncut (a = not, tomos = cut). The philosophy of *atomism*, espoused by the Greek philosopher Democritus (460 BC-370 BC), asserts that the world is made up of two things: atoms and the void. In other words, matter is made up of tiny, indestructible particles called atoms and in between atoms, there is nothing. However, atomism did not flourish, as it was contrary to the ideas supported by more influential people of that time (Plato, Aristotle). Furthermore, the Greek philosophers were thinkers, not workers. They did not have any experimental support for their ideas.

The scientific method as we know it, the use of empirical (experimental) data to support ideas, was not developed until centuries later. Publications regarding the “proper way” to do science date as far back as the early 1600s. Before that, alchemists (early chemists) developed laboratory techniques that were eventually used for scientific work. The alchemists’ goals were to turn lead into gold, cure diseases with herbs, develop the elixir of life (panacea) and develop a universal solvent that can dissolve anything (“alkahest”). Alchemists were considered scientists but, these days, their approach to achieving their goals is not what we would consider as “scientific”. Although alchemists did not advance our knowledge about atoms, they promoted observation and experimentation and served as bridge between Greek philosophers’ “pure thought” and modern scientific method.

9.2 Dalton’s Atomic Theory

John Dalton elevated the idea of atomism to a scientific theory in 1803. In Dalton’s atomic theory, the following assumptions (postulates) are made:

- matter consists of small indivisible particles called atoms.
- an element consists of identical atoms (same mass).

- 
- atoms of different elements have different masses.
 - atoms of two or more elements combine in small whole-number ratios to form compounds.
 - a chemical change involves the rearrangement of atoms.

Extensive work by several scientists provided the empirical support for Dalton's ideas. Among the most notable are the works of Antoine Lavoisier (the "father" of Modern Chemistry) and Joseph Proust.

9.2.1 Law of Conservation of Mass

Lavoisier's work led to the formulation of the *Law of Conservation of Mass*, which says that the amount of matter is constant even during a chemical change. Dalton's assumption that atoms are indestructible and merely rearrange during chemical changes explains this general observation.

9.2.2 Law of Definite Proportions

Proust's work led to the formulation of the *Law of Definite Proportions*, or *Law of Definite Composition*, which says that compounds (substances made up of more than one element) have a well-defined composition. By this, we mean that the mass-to-mass ratio of any two elements in the compound is the same for any sample of the compound. It also means that the percentage of any element in any sample of the compound is well-defined (constant).

The Law of Definite Proportions is explained by Dalton's assumptions that all atoms of an element have the same mass and that the count-to-count ratios of atoms from different elements in a compound are well-defined small whole number ratios.

► Example

Suppose a compound is made up of elements X and Y, such that the count-to-count ratio of X to Y is 1:2. Also suppose that each X atom has a mass of x units, and each Y atom has a mass of y units. Show that the mass-to-mass ratio of X to Y is constant.

Answer:

Imagine a sample containing n X atoms. If the count-to-count ratio of X-to-Y is 1:2, then this sample must have $2n$ Y atoms:

$$\frac{\text{count}_x}{\text{count}_y} = \frac{\cancel{n}}{2\cancel{n}} = \frac{1}{2}$$

If each X atom has a mass of x units and each Y atom has a mass of y units, then the mass-to-mass ratio would then be:

$$\frac{\text{mass}_x}{\text{mass}_y} = \frac{\cancel{n}x}{2\cancel{n}y} = \frac{x}{2y}$$

Since x and y are constants, $x/2y$ is also a constant; the mass-to-mass ratio of X to Y is, therefore, constant regardless of what n is.

► Example

In the preceding example, show that the percentage of X (by mass) in the compound is also constant.

Answer:

The ratio of the mass of X to the total mass is

$$\frac{\text{mass}_x}{\text{mass}_x + \text{mass}_y} = \frac{n x}{n x + 2 n y} = \frac{\cancel{n}x}{\cancel{n}(x + 2y)} = \frac{x}{x + 2y}$$

which is also a constant since x and y are constants. If we multiply this value by 100, we get the percentage of X in the compound (by mass), which is also a constant.

9.2.3 Law of Multiple Proportions

Dalton himself formulated the *Law of Multiple Proportions*, which says that if two elements can form more than one compound, the ratio of their mass ratios can be reduced to a ratio of small whole numbers.

► Example

Verify that the ratio of C-to-H mass ratios for CH_4 and C_2H_4 is a small whole-number ratio.

Answer:

Assume that the mass of each C atom is c and that the mass of each H atom is h. The C-to-H mass ratio in CH_4 is:

$$\frac{\text{mass}_c}{\text{mass}_h} = \frac{c}{4h}$$

while the C-to-H mass ratio in C_2H_4 is:

$$\frac{\text{mass}_C}{\text{mass}_H} = \frac{2c}{4h}$$

The ratio of mass ratios is:

$$\frac{\left(\frac{c}{4h}\right)}{\left(\frac{2c}{4h}\right)}$$

which simplifies to $1/2$, a ratio of two whole numbers.

► Example

A compound of elements X and Y is found to be 85.71% X by mass. According to the Law of Multiple Proportions, which of the following is a more plausible mass percent of X for another compound of X and Y? A. 80.00%, B. 84.32%

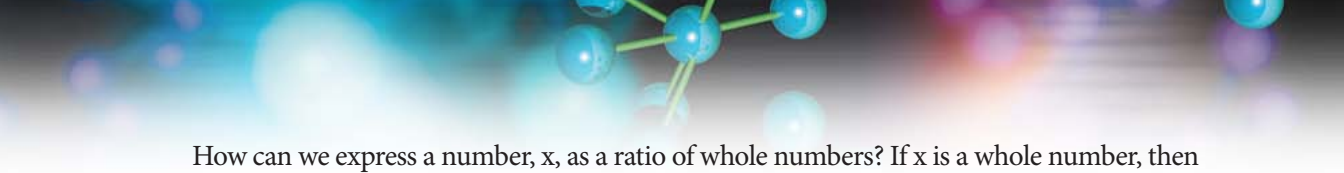
Answer: A

First, we determine the X-to-Y mass ratios.

- For the known compound, assuming a 100 g sample:
mass of X = 85.71% of 100g = 85.71 g
mass of Y = 100g – 85.71 g = 14.29 g
X-to-Y mass ratio: $85.71/14.29 = 5.998$
- For choice A, assuming a 100 g sample:
mass of X = 80.00% of 100 g = 80.00 g
mass of Y = 100 g – 80.00 g = 20.00 g
X-to-Y mass ratio: $80.00/20.00 = 4.000$
- For choice B, assuming a 100 g sample:
mass of X = 84.32% of 100 g = 84.32 g
mass of Y = 100 g – 84.32 g = 15.68 g
X-to-Y mass ratio: $84.32/15.68 = 5.378$

Then, we calculate the ratio of mass ratios.

- For the known compound and the sample in choice A:
 $5.998/4.000 = 1.500$, which is $3/2$ (a small whole number ratio)
- For the known compound and the sample in choice B:
 $5.998/5.378 = 1.115$; the closest possible ratio of small whole numbers is $10/9$ (which is equal to 1.111)



How can we express a number, x , as a ratio of whole numbers? If x is a whole number, then it already is; it is a ratio of that whole number to 1. If it is not a whole number, then we look for a whole number (n) such that nx is a whole number; the whole number ratio is nx/n .

► Example

Express 1.199 as a ratio of whole numbers.

Answer: $6/5$

We just need to find n , such that $(n)(1.199)$ is a whole number.

Try 2. $2(1.199) = 2.398$, not a whole number.

Try 3. $3(1.199) = 3.597$, not a whole number.


Try 4. $4(1.199) = 4.796$, not a whole number.

Try 5. $5(1.199) = 5.995$, close enough; round off to 6.

The ratio is $6/5$.

9.3 The Discovery of the Electron

Theories evolve as we discover new information. Some of Dalton's assumptions about atoms are no longer accepted. Atoms are, in fact, divisible. We now know that they are made up of even smaller particles called protons, neutrons, and electrons. The discovery of the electron is credited to Joseph John Thomson, although our experience with it dates back to the time of Thales of Miletus (600 BC), where it was found that rubbing amber against fur makes them attract each other. We now interpret this phenomenon in terms of electrons being transferred from fur to amber. The fur becomes positively-charged and the amber becomes negatively-charged. In 1600, William Gilbert discovered that amber was not the only material that can attract other materials when rubbed; he coined the word *electric* (from *elektron*, the Greek word for amber) and referred to materials that attract each other when rubbed as electrically charged. In 1629, Niccolo Cabeo discovered that electrically charged materials can also repel each other. This led to the notion of two kinds of charge; like charged materials repel each other, materials with unlike charge attract each other. In 1733, Charles du Fay proposed two kinds of charge: resinous and vitreous. By his definition, vitreous charges are transferred to a glass rod when it is rubbed against silk, and resinous charges are transferred to amber when it is rubbed against fur. We now know that what du Fay called resinous charges are negatively charged electrons. We also now know that when glass is rubbed against silk, it becomes positively charged, not because positively charged particles (vitreous charge) are transferred to the glass, but because (negatively-charged) electrons move out of the glass. The idea of just one type of charged particle being transferred when materials are rubbed is credited to Benjamin Franklin (1752), although he assumed that the charge that was transferred was positive.



Measurement of charges is attributed to Charles Augustin de Coulomb who formulated (in 1785) the law that now bears his name: the force between two charged particles is directly proportional to the product of the magnitudes of the charge and inversely proportional to the square of the distance between them. The SI unit for electrical charge is Coulomb (C).

► Example

At the same separation, compare the force in the following cases: Case A. between an electron and a nucleus with a +1 charge, and Case B. between an electron and a nucleus with a +2 charge.

Answer: The force is stronger in case B by a factor of 2. The charge of an electron is -1 . So, in case A, the product of the magnitude of the charges is $(1)(1) = 1$. In case B, its $(1)(2) = 2$. If the product is doubled, the force is also doubled; this is what we mean when we say that the force is directly proportional to the product of the magnitudes of the charges.

► Example

What happens to the force between two charged particles if their separation is doubled?

Answer: Since the distance doubled ($\times 2$), the force $1/4$ of the original value. If the distance is multiplied by 2, the force is divided by 2^2 . This is what we mean when we say that the force is inversely proportional to the square of the distance.

J. J. Thomson used cathode ray tubes (CRT) in his experiments (1897). Inside a CRT, a piece of metal (the cathode) is subjected to high voltage. As a result, a beam of particles, which Thomson called corpuscles, is ejected from the metal. The CRT beams behaved the same way (when subjected to a magnet or to electrically charged plates) regardless of the nature of material used as cathode. This means that whatever these particles are, they are found in all atoms. We now know that the particles in the beam are electrons; the name “electron” was coined by G. Johnstone Stoney. In J. J. Thomson’s CRT experiments, the charge-to-mass ratio for the electron, but not the mass itself, was determined.

Robert Millikan’s oil-drop experiment (1909) established the charge of the electron. In his experiments, Millikan found that when he charged oil droplets, the charges were all multiples of -1.60×10^{-19} C. This suggested that -1.60×10^{-19} C is the smallest possible charge and this is the charge of each electron.

► Example

If we were to repeat Millikan's experiment, which of the following values for the charge of an oil droplet are we least likely to observe?

- A. $-1.122 \times 10^{-18} \text{ C}$
- B. $-1.553 \times 10^{-18} \text{ C}$
- C. $-1.759 \times 10^{-18} \text{ C}$

Answer: B

The values we would expect to get should be very close to an integer multiple of the charge of an electron, which $-1.60 \times 10^{-19} \text{ C}$. To check if the given choices are integer multiples, we divided each one by $-1.60 \times 10^{-19} \text{ C}$.

- A. $(-1.122 \times 10^{-18} \text{ C}) / (-1.60 \times 10^{-19} \text{ C}) = 7.01 \rightarrow 7$
- B. $(-1.553 \times 10^{-18} \text{ C}) / (-1.60 \times 10^{-19} \text{ C}) = 9.70$
- C. $(-1.759 \times 10^{-18} \text{ C}) / (-1.60 \times 10^{-19} \text{ C}) = 10.99 \rightarrow 11$

Among the choices given, choice B is farthest from being an integer multiple.

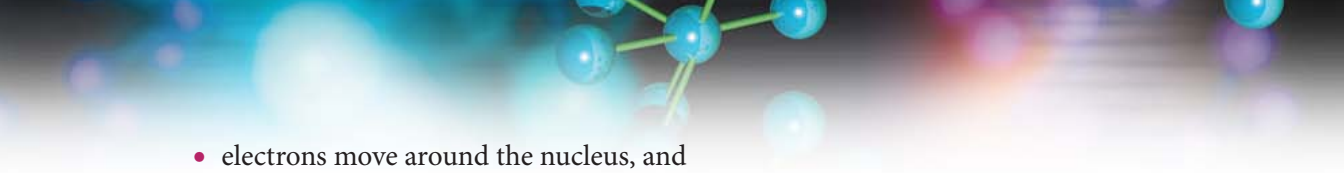
Based on J. J. Thomson's measured charge-to-mass ratio and Millikan's measured charge, the mass of the electron was found to be $9.11 \times 10^{-31} \text{ kg}$, much smaller than the mass of the lightest known atom (hydrogen).

With the discovery of the electron, the *plum pudding model* was proposed for the atom. Instead of the structureless, indivisible spheres that Dalton envisioned, atoms are now proposed to be positively charged spheres with negatively charged electrons embedded in them, just like plums in a pudding.

9.4 The Discovery of the Nucleus

The work of Ernest Rutherford provided the next major advancement in our knowledge about atoms. In his experiments (1909), Rutherford bombarded a piece of gold foil by alpha particles. Alpha particles are high speed particles produced by radioactive materials; an alpha particle is essentially a helium nucleus (2 protons and 2 neutrons). If the plum pudding model were correct, then the mass of an atom would be spread evenly throughout the space occupied by the atom and *all* of the alpha particles would be expected to pass through with very minor deflection (like bullets through a tissue paper). As it turned out, *most* (not all) of the alpha particles passed through the gold foil with very minor deflection. *A very small fraction of the particles were either deflected at very large angles or bounced back ("backscattered")*. This led to the proposition of the currently accepted *nuclear model* for the atom, where:

- the mass of atom is concentrated in a very tiny spot (the nucleus),
- the nucleus is positively charged,

- 
- electrons move around the nucleus, and
 - the space where electrons move about is much, much larger than the space occupied by the nucleus (the diameter of the region where electrons move is at least 1000 times larger than the diameter of the nucleus).

The nuclear model explains Rutherford's experimental results. Most of the alpha particles passed through because the gold foil is mostly empty space; the regions occupied by the nuclei are very, very small compared to the spaces between them. The very small fraction of alpha particles that pass near the nuclei would be deflected at large angles. The alpha particles that are backscattered are the ones that collide head-on with the nuclei.

9.5 The Discovery of the Neutron

The discovery of the neutron is credited to Sir James Chadwick. The discovery was made in 1932, years after Rutherford discovered the nucleus. Neutrons were more difficult to detect because they are electrically neutral. Electrically charged particles like electrons and protons are easier to detect because they respond to magnets and electrically charged plates.

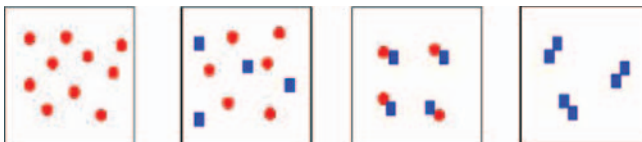
Chadwick bombarded beryllium atoms with alpha particles. He showed that the resulting radiation was a beam of neutral particles that have a mass of one amu.

TEST YOURSELF

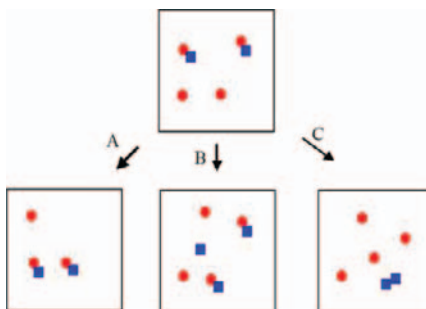
For answers and other study resources, see:

<http://i-assign.com/ebook/answers/chapter9.htm>.

1. Assume circles and squares in the figures below represent atoms. According to Dalton's atomic theory, which of the figures below best represents a sample of a compound?



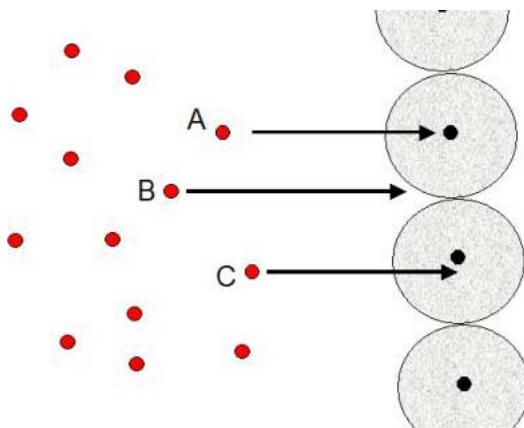
2. Assume that circles and squares in the figure below represent atoms. According to Dalton's theory, which of the changes indicated is possible?



3. Consider the pictorial representation shown below for the molecular composition of a mixture. Using Dalton's atomic theory, the figure represents a mixture of...
- A. an element and two compounds
 - B. two elements and a compound
 - C. three compounds

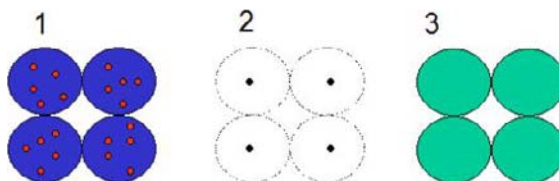


4. A compound decomposes (breaks apart) into elements “X” and “Y”. If the decomposition of 5.0 g of the compound produces 2.0 g of element “X”, how much of element “Y” is also produced?
- A. 2.0 g B. 3.0 g
C. 5.0 g D. impossible to tell
5. Shown below is a diagram illustrating Rutherford’s alpha scattering experiment. Alpha particles are represented by red circles. Which of the three labeled alpha particles (A, B, or C) will have the most typical trajectory?

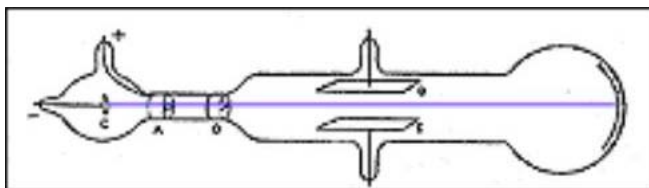


6. Which of these is true?
- A. Dalton assumed that atoms are made up of electrons, protons, and neutrons
- B. J.J. Thomson determined the charge and mass of electrons
- C. In Rutherford’s alpha scattering experiment, all of the alpha particles passed through the gold foil
- D. The alpha particles used in Rutherford’s experiment are positively charged particles.

7. Match the pictorial representations showing four neighboring atoms to the scientist most closely associated with the atomic model.



- A. 1-Dalton, 2-J.J.Thomson, 3-Rutherford
 B. 1-J.J.Thomson, 2-Dalton, 3-Rutherford
 C. 1-J.J.Thomson, 2-Rutherford, 3-Dalton
 D. 1-Rutherford, 2-J.J.Thomson, 3-Dalton
8. Which of these scientists is most closely associated with the laboratory apparatus shown below?



- A. John Dalton, B. J.J. Thomson,
 C. Ernest Rutherford, D. James Chadwick

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Quantum Theory

Towards the end of the 19th century, experiments involving light interacting with atoms and molecules showed “anomalous” results that could not be explained by classical physics. *Classical* physics refers to the physics developed by Isaac Newton, James Maxwell, and others prior to the 20th century. Describing motion using Newton’s laws of motion is called Newtonian mechanics or classical mechanics. Classical principles that describe electricity and magnetism are based on the work of James Maxwell.

Quantum mechanics and *Relativity* were developed to address failures of classical physics in describing the world of the very small and the world of the very fast, respectively. Quantum mechanics and relativity are considered as the two major branches of *modern physics*. The currently accepted model of the atom is best described by quantum mechanics.

10.1 Electromagnetic Radiation

Light is also known as electromagnetic radiation. Much of the behavior of light can be explained by thinking of it as a wave. However, towards the end of the 19th century, scientists observed phenomena that could not be explained by the wave model. In these cases, we have to think of light as a stream of particles, which we now call photons.

10.2 The Wave Model

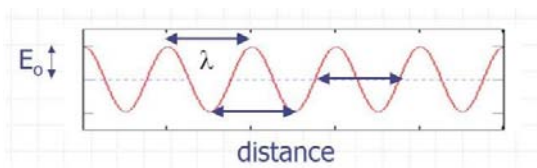
Earlier studies dealing with light have led scientists to the conclusion that light is an *electromagnetic wave*. Let us try to understand what these two words mean.

A *wave* is a periodic (repeating) disturbance that transfers energy from one place to another. Imagine dropping a rock into a body of water. A water wave is produced (ripples travel outward from where the rock fell) and an object floating elsewhere will bob up and down as the wave passes through it. We say that the energy from the rock has been transmitted to the object.

The term *electromagnetic* means that the disturbance:

- is due to oscillation of charged particles.
- exerts a force on any charged particle that is in its way.

Figure 1. Electric Component of Electromagnetic Wave



The things that are “waving” in an electromagnetic wave are electric and magnetic fields. The plot in Figure 1 illustrates how the electric field strength (E) associated with the wave varies vs. distance. Perpendicular to each electric field wave, is a magnetic field wave.

The value of the *electric field strength* at a given location refers to the strength of the force that a particle (with a charge of 1 Coulomb) would “feel” at that location; positive and negative values indicate the direction of the force. The SI unit for the electric field strength is Newton per Coulomb, N C^{-1} . The electric field is strongest at the *crests* (maximum E) and *troughs* (minimum E); the magnitude of the electric field strength at these locations is shown in Figure 1 as E_0 , and is called the *amplitude* of the wave. Locations where the magnitude of the electric field is zero are called *nodes*. The *wavelength*, represented by the Greek letter lambda (λ) in Figure 1, refers to the distance between two consecutive crests. This is also the distance between two consecutive troughs, or the distance between two nodes that are separated by one node.

10.1.1 Physical Interpretation of Wavelength

The wavelength of an electromagnetic radiation is related to what we perceive as the color of the light. The term *visible spectrum* refers to the range of possible wavelengths that we can see, 400 nm to 800 nm. The symbol nm stands for nanometer, or 10^{-9} m. The mnemonic ROYGBIV (Red, Orange, Yellow,...) relates wavelength to color. Red light is on the long wavelength end of the visible spectrum (630–800 nm), whereas violet is on the short wavelength end (about 400 nm).

► Example

Which color of light corresponds to longer wavelength: red or blue?

Answer: Red

Most electromagnetic radiation is invisible to us. The term electromagnetic spectrum refers to the entire range of possible wavelengths. Electromagnetic radiation is classified according to wavelength (shortest to longest) into gamma rays, x-rays, ultraviolet, visible, infrared, microwave, and radiowave.

► Example

Which type of electromagnetic radiation corresponds to longer wavelength: microwave or x-ray?

Answer: microwave

10.1.2 Physical Interpretation of Frequency

Electromagnetic waves travel at a speed of 2.998×10^8 m/s. For most calculations, we can round this off to 3.00×10^8 m/s. We refer to this as the *speed of light* and, typically, represent this by the letter c . When the wave has traveled a distance equal to its wavelength, we say that it has completed one cycle. The time it took for this to happen is called the period (T). The number of cycles completed per second is called the *frequency* of the wave and is just equal to $1/T$; frequency is commonly represented by the Greek letter nu (ν). Since speed is distance traveled per unit time, the speed of the wave is the distance traveled in one cycle (λ) divided by the time for one cycle. Therefore:

$$c = \frac{\lambda}{T} = \lambda \left(\frac{1}{T} \right) = \lambda \nu$$

We can rearrange this equation to:

$$\nu = \frac{c}{\lambda}$$

and see that the shorter the wavelength, the higher the frequency. Therefore, frequency is also associated with what we perceive as color. The unit for frequency is reciprocal second (s^{-1}) or Hertz (Hz).

► Example

Calculate the frequency of green light that has a wavelength of 500.0 nm.

Answer: $6.00 \times 10^{14} \text{ s}^{-1}$, or 6.00×10^{14} Hz

We simply plug in the speed of light and wavelength into the formula that relates frequency, speed of light, and wavelength. To avoid problems with units, express all quantities in base SI units. Thus, we plug in 500.0 nm as 500.0×10^{-9} m.

$$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^8 \text{ m s}^{-1}}{500.0 \times 10^{-9} \text{ m}} = 6.00 \times 10^{14} \text{ s}^{-1}$$

► Example

Which color of light corresponds to higher frequency, red or blue?

Answer: blue

Blue has shorter wavelength, higher frequency.

10.1.3 Physical Interpretation of Amplitude

The amplitude of the wave, E_0 , is related to what we perceive as the intensity of light. Intensity, S , is defined as the energy transported per unit time, per unit area, and is given by the equation:

$$S = \frac{\text{Energy}}{\text{Time} \cdot \text{Area}} = \frac{\text{Power}}{\text{Area}} = \frac{1}{2} \epsilon_0 c E_0^2$$

where, ϵ_0 (“epsilon naught”, $8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$) is the constant known as the permittivity of vacuum and c is the speed of light. The unit for intensity is Joule per second per square meter ($\text{J s}^{-1} \text{ m}^{-2}$). A Joule per second is a unit for power, the energy delivered per unit time, and is also called a Watt (W). So, the unit for intensity can also be written as W m^{-2} .

► Example

A 5.00 mW laser beam has a cross sectional area of 2.00 mm². What is the intensity of the beam? Calculate the amplitude of electric field component of the electromagnetic wave.

Answer: $S = 2.50 \times 10^3 \text{ W m}^{-2}$, $E_0 = 1.37 \times 10^3 \text{ N C}^{-1}$

Intensity is power per unit area; we are given the power (5.00 mW) and the area (2.00 mm²). It is best to express these quantities in terms of unprefix units when doing calculations.

1 mW = 10^{-3} W and 1 mm = 10^{-3} m.

$$S = \frac{\text{Power}}{\text{Area}} = \frac{5.00 \times 10^{-3} \text{ W}}{2.00 (10^{-3} \text{ m})^2} = 2.50 \times 10^3 \text{ Wm}^{-2}$$

Rearranging the equation that relates intensity to amplitude, we can solve for the amplitude as

$$\begin{aligned} E_0 &= \sqrt{\frac{2S}{\epsilon_0 c}} = \sqrt{\frac{2(2.50 \times 10^3 \text{ Wm}^{-2})}{(8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2})(2.998 \times 10^8 \text{ m s}^{-1})}} \\ &= 1.37 \times 10^3 \text{ N C}^{-1} \end{aligned}$$

Here is how the units for the electric field strength works out to N C^{-1} .

$$\begin{aligned}\sqrt{\frac{\text{W m}^2}{\text{C}^2 \text{ N}^{-1} \text{ m}^2 \text{ s}^{-1}}} &= \sqrt{\frac{\text{J s}^{-1}}{\text{C}^2 \text{ N}^{-1} \text{ m s}^{-1}}} = \sqrt{\frac{\text{N m}}{\text{C}^2 \text{ N}^{-1} \text{ m}}} \\ &= \sqrt{\text{N C}^{-2} \text{ N}^{(-1)}} = \sqrt{\text{N}^2 \text{ C}^{-2}} = \text{N C}^{-1}\end{aligned}$$

Note that a Joule (J) is equivalent to a Newton meter (N m).

10.3 The Particulate Model

Towards the end of the 19th century, experiments dealing with light showed behaviors that are inconsistent with the notion of light as an electromagnetic wave. These experiments deal with the following phenomena: blackbody radiation, photoelectric effect, atomic and molecular spectra.

In all of these, the “anomaly” is resolved by assuming that the energies of light and matter are *quantized*. Thus, the theory that was eventually developed, based on these phenomena, came to be known as *quantum theory*. When we say something is quantized, it means that its values are restricted; it cannot have just any value. In the case of electromagnetic radiation, it turns out that, in these “anomalous” cases, we have to think of the energy as being carried by a stream of particles, now called photons. The energy carried by each photon is given by:

$$E_{\text{photon}} = h\nu = \frac{hc}{\lambda}$$

where h is a very small number called Planck’s constant. We say that light energy is quantized because it is only available in multiples of $h\nu$. The value of Planck’s constant is 6.626×10^{-34} J s. Max Planck discovered this constant in trying to explain blackbody radiation and it turned out to be a universal constant; the same constant appears in the equations that were successfully used to explain the other phenomena listed above.

► Example

Which has more energetic photons: radiowave or x-ray?

Answer: x-rays

X-rays have very short wavelengths, very high frequency, very energetic photons. This is the reason why x-rays are considered dangerous. One should not have too much exposure to x-rays. X-ray photons are energetic enough that they can “knock off”

electrons from atoms in your body, which could lead to all sorts of chemical changes. X-rays are called ionizing radiation. Magnetic resonance imaging (MRI, the other major imaging technique used in medicine) uses radiowaves, which are on the other end of the electromagnetic spectrum. Radiowaves have very low energy photons.

► Example

Calculate the energy of each photon of red light with a wavelength of 632 nm.

Answer: $3.14 \times 10^{-19} \text{ J}$

$$E_{\text{photon}} = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m s}^{-1})}{632 \times 10^{-9} \text{ m}} \\ = 3.14 \times 10^{-19} \text{ J}$$

Note that we replaced nm by 10^{-9} m .

Because h is a very small number, photon energies in Joules are also very small numbers. It is often convenient to express photon energies in terms of a smaller energy unit, the electron volt (eV): $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$.

► Example

A photon has an energy of $3.14 \times 10^{-19} \text{ J}$. Express this value in eV.

Answer: 1.96 eV

$$3.14 \times 10^{-19} \cancel{\text{ J}} \times \left(\frac{1 \text{ eV}}{1.602 \times 10^{-19} \cancel{\text{ J}}} \right) = 1.96 \text{ eV}$$


► Example

The frequency of radiation used in a microwave oven is 2.45 GHz. If a 600.0 W oven is operated for 60.0 s, how many photons are generated.

Answer: 2.22×10^{28} photons

1 GHz = 10^9 Hz or 10^9 s^{-1} . So, the energy of one photon is

$$E_{\text{photon}} = hv = (6.626 \times 10^{-34} \text{ J s})(2.45 \times 10^9 \text{ s}^{-1}) = 1.62 \times 10^{-24} \text{ J}$$



A Watt (W) is a unit of power, which is energy per unit time: $1 \text{ W} = 1 \text{ J s}^{-1}$. Therefore, if we multiply the wattage by the time in seconds, we get the total energy generated by the oven:

$$E_{\text{total}} = (600.0 \text{ J s}^{-1}) (60.0 \text{ s}) = 3.60 \times 10^4 \text{ J}$$

If we have N photons and multiply it by the energy of each photon, we get the total energy. In other words:

$$E_{\text{total}} = N E_{\text{photon}}$$

or:

$$N = \frac{E_{\text{total}}}{E_{\text{photon}}} = \frac{3.60 \times 10^4 \text{ J}}{1.62 \times 10^{-24} \text{ J}} = 2.22 \times 10^{28}$$

10.4 The Photoelectric Effect

The photoelectric effect is one of the phenomena that could not be explained with the notion that light is a wave. A *photoelectron* is an electron ejected from a metallic surface when the surface is exposed to light. It was found that:

- there is a minimum frequency (ν_0) of light needed to cause electrons to be ejected; the threshold frequency depends on the nature of the metallic surface.
- the kinetic energy of the electrons ejected depends on the frequency, but not on the intensity of the light; this was puzzling because the intensity of light is the amount of energy it delivers per unit time per unit area.
- if electrons are ejected, more of them are ejected if the light is made more intense.

Albert Einstein explained the observations as follows. The kinetic energy of the ejected electron is the difference between the energy of the photon and the energy needed to dislodge the electron from the metal. If the individual photons do not have sufficient energy to dislodge electrons, no photoelectrons will be observed regardless of how intense the radiation is. If the photon energies are sufficient, then a higher intensity would mean more photons and, consequently, more photoelectrons produced. But the kinetic energy of the electrons depends only on the photon energy (hence, on the frequency, not on the intensity). Based on the data, Einstein deduced that

- the photon energy is $h\nu$, where h is the same constant that Planck earlier discovered when trying to explain blackbody radiation.
- the minimum photon energy needed to dislodge the electron, called the work function of the metal, is $h\nu_0$.

► Example

The work function for Al is 4.08 eV. Will photoelectrons be ejected if it is exposed to ultraviolet radiation of frequency 300.0 nm? If so, what would be the kinetic energy of the photoelectrons?

Answer: Yes, the kinetic energy of the photoelectron would be 0.05 eV

The photon energy for 300.0 nm is:

$$E_{\text{photon}} = \frac{hc}{\lambda} = \frac{(6.626 \cdot 10^{-34} \text{ J s}) (2.998 \cdot 10^8 \text{ m s}^{-1})}{300.0 \cdot 10^{-9} \text{ m}}$$
$$= 6.622 \cdot 10^{-19} \text{ J}$$

which corresponds to 4.134 eV. The energy of the photoelectron would be the difference between the photon energy and the energy needed to remove the electron:

$$\text{KE of photoelectron} = 4.134 \text{ eV} - 4.08 \text{ eV} = 0.05 \text{ eV}$$

10.5 Atomic and Molecular Spectra

When light is passed through a prism, the prism causes the waves corresponding to different wavelengths to bend at different angles. If the light comes from a source where there is a very high concentration of particles (atoms, molecules or ions), we tend to get a continuous band of colors, the familiar rainbow of colors. If we pass that light through a sample that has a very low concentration of particles before we pass it through the prism, we are likely to see a pattern of dark lines interspersed within what would otherwise be a continuous band of colors; see Figure 2. We say that light waves (with wavelengths corresponding to the missing colors) were absorbed by the particles in the sample. Thus, the observed pattern is known as the absorption spectrum of the sample. Figure 2 shows the *absorption spectrum* of hydrogen atoms.

If we were to examine light from a source where the concentration of particles is very low, we are not likely going to get a continuous band of colors. If we project the light that passes through the prism onto a screen, we would see a pattern of bright colored lines with dark regions in between. The pattern depends on what atoms or molecules are

Figure 2. Absorption Spectrum of Hydrogen



Figure 3. Emission Spectrum of Hydrogen



Figure 4. Absorption Spectrum of Sodium



producing the light, and is called the atom or molecule's emission spectrum. The *emission spectrum* from hydrogen atoms is shown in Figure 3.

Each atom or molecule has a characteristic spectrum that can serve as its “fingerprint” for identification purposes. Figure 4 shows the absorption spectrum of sodium.

Spectra from atoms tend to have sharper lines; thus, they are often referred to as *line spectra*.

How come atoms and molecules do not absorb or emit a continuous band of colors? The explanation provided by Niels Bohr is as follows:

- Energies of atoms and molecules are quantized. They cannot have just any amount of energy.
- Transitions between allowed energy levels can occur when a photon is absorbed or released.
- The energy of photon must be equal to the difference in energy between two allowed levels (this is known as the *Bohr frequency condition*). Since the energies are restricted, this means that the energy differences are also restricted. Thus, not every photon energy can be observed, which means that not every wavelength or frequency can be observed.

$$\Delta E = E_{\text{photon}} = h \left(\frac{c}{\lambda} \right)$$

► Example

Theory predicts that the two lowest allowed energy levels of hydrogen are -13.6 eV and -3.40 eV, respectively. What is the energy of the photon that will be absorbed by a hydrogen atom for it to be excited from -13.6 eV to -3.40 eV? What wavelength of light does this correspond to?

Answer: 121.6 nm

$$E_{\text{photon}} = \Delta E = (-3.40 \text{ eV}) - (-13.6 \text{ eV}) = 10.2 \text{ eV}$$

We rearrange:

$$E_{\text{photon}} = h \left(\frac{c}{\lambda} \right)$$

to solve for λ :

$$\lambda = \frac{h c}{E} = \frac{(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m s}^{-1})}{10.2 (1.602 \times 10^{-19} \text{ J})} = 1.22 \times 10^{-7} \text{ m}$$

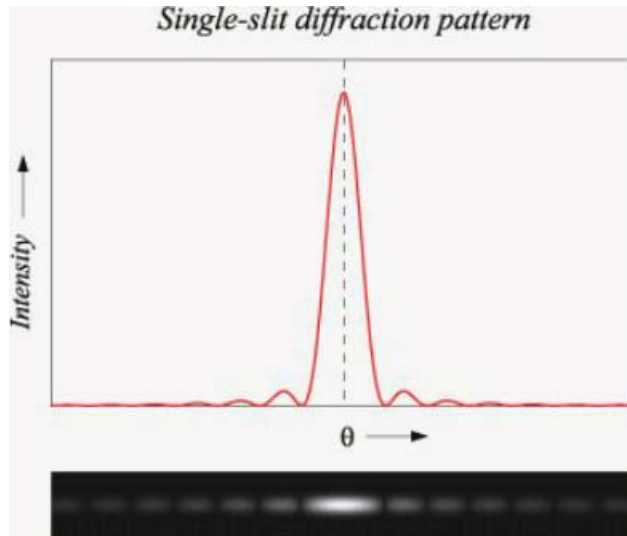
or 122 nm. Note that we have substituted 1.602×10^{-19} J for eV so that our answer comes out in meters (m). This spectral line is observed experimentally, and is known as the Lyman alpha line.

10.6 Matter Waves

Light exhibits wave-like behavior, as well as particle-like behavior. The term *wave-particle duality* is used to describe this dual nature of light. Nature tends to be symmetrical, so it makes sense to expect that what we normally consider as particles (like electrons) would also exhibit wavelike behavior. In the 1920s, Louis de Broglie suggested that matter, which we normally think of as being made of particles, may also exhibit wave-like behavior. In 1925, Davisson and Germer provided experimental support for this idea: diffraction patterns were observed for a beam of electrons. *Diffraction* is a phenomenon associated with waves. Figure 5 shows what happens when light is passed through the narrow slit, and observed on a wall behind the slit.

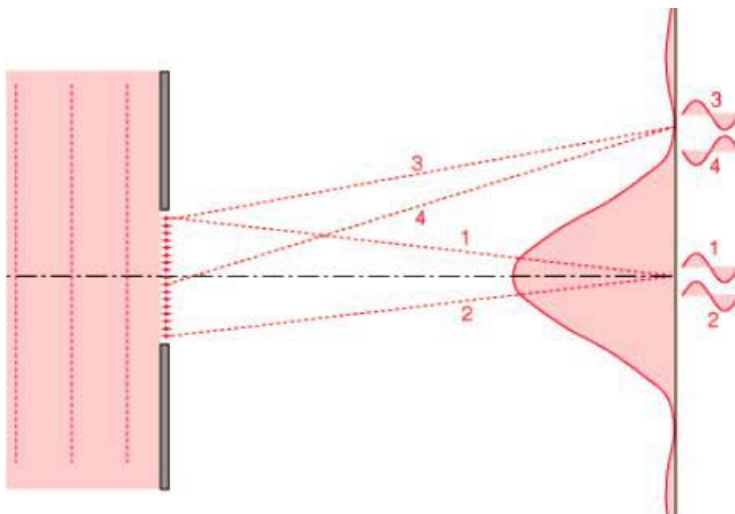
Instead of showing up only around where the slit is located, the light spreads out. It spreads out more the narrower we make the slit. We also observe dark spots in between bright spots. This can only be explained if we think of light as a wave; see Figure 6. As waves emerge from the barrier (through the slit), they bend. As a result some waves will have farther to travel than others before they hit the wall on the other side. At certain

Figure 5. Single Slit Diffraction



from <http://en.wikipedia.org/wiki/File:Diffraction1.png> GNU Free Documentation License

Figure 6. Explaining Single Slit Diffraction



from <http://hyperphysics.phy-astr.gsu.edu/hbase/phyopt/sinlitd.html#c1>

angles, the shifting of the waves results in what is known as *destructive interference* and we see a dark spot on the wall where this occurs.

It is now generally accepted that wave characteristics apply to all matter. The so-called *de Broglie wavelength* (λ) associated with a particle is inversely proportional to the momentum of the particle. *Momentum* is the product of mass (m) and speed (v).

$$\lambda = \frac{h}{p} = \frac{h}{m v}$$

The proportionality constant is Planck's constant (h), which is a very small number. Because of this, wave behavior is only discernible for very small particles (very small masses). Diffraction, for example, is observed when the particle encounters obstacles that are separated by a distance comparable to its de Broglie wavelength. For large masses, the de Broglie wavelength tends to be very, very small to be detectable.

► Example

Calculate the de Broglie wavelength of a 1.00 kg object moving at 1.00 m/s.

Answer: 6.63×10^{-34} m

$$\lambda = \frac{h}{m v} = \frac{6.626 \times 10^{-34} \text{ J s}}{(1.00 \text{ kg})(1.00 \text{ m s}^{-1})} = 6.63 \times 10^{-34} \text{ m}$$

This is very, very, very small. This is much smaller than the diameter of a typical nucleus (10^{-13} – 10^{-14} m), or even an electron (10^{-18} m). It is undetectable. We expect, in this case, that classical physics would adequately describe the particle.

Note: here is how the unit in the answer works out to meters (m).


$$\frac{\boxed{\text{J s}}}{\text{kg m s}^{-1}} = \frac{\boxed{\text{kg m}^2 \text{ s}^{-2} \text{ s}}}{\text{kg m s}^{-1}} = \frac{\text{kg m m s}^{-1}}{\text{kg m s}^{-1}} = \text{m}$$

► Example

Calculate the de Broglie wavelength of an electron (mass = 9.11×10^{-31} kg) moving at a speed of 1.00×10^6 m s⁻¹.

Answer: 7.27×10^{-10} m

$$\lambda = \frac{h}{m v} = \frac{6.626 \times 10^{-34} \text{ J s}}{(9.11 \times 10^{-31} \text{ kg})(1.00 \times 10^6 \text{ m s}^{-1})} = 7.27 \times 10^{-10} \text{ m}$$



This wavelength is comparable to x-rays and to the distance between the nuclei of adjacent atoms in a solid, which is typically about 1-2 Angstroms; one Angstrom is 10^{-10} m. We expect the electrons here to exhibit wavelike behavior similar to x-rays.

10.7 The Uncertainty Principle

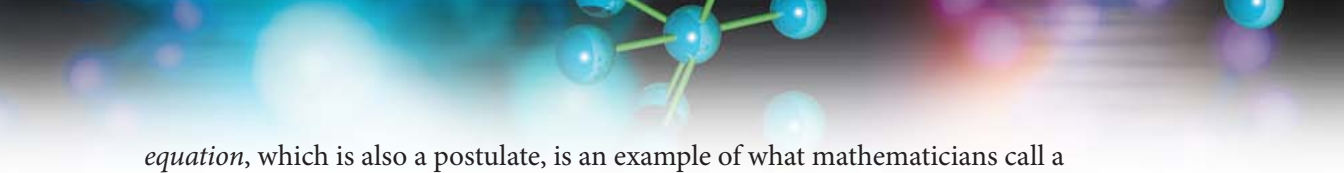
The Uncertainty Principle is a consequence of wave-particle duality. It says that it is impossible to precisely determine the location and velocity of particles at the same time. The uncertainties are inconsequential in our macroscopic world, but tend to be significant in the world of the very small. For example, to see anything, you need light. Light bouncing off an object travels to the detector (such as your eyes), which tells you where the object is located. If we were to try to locate an electron, we would need to bounce a photon off it. Since the photon behaves like a particle, the act of locating an electron affects the electron's motion. The impact is insignificant for macroscopic objects.

We could try to precisely locate electrons by passing them through a narrow slit. The narrower we make the slit, the more we know about the location of the electrons that pass through the slit. However, we find that the narrower we make the slit, the less we know about the direction of motion as the electrons emerge from the slit; this manifested by the spreading out of the observed diffraction pattern. This means we lose information about the velocities of the electrons by attempting to more precisely locate them.

Wave-particle duality and the uncertainty principle resolve the problem regarding the stability of the nuclear atom. Classical mechanics predicts that the electron will crash into the nucleus and this will happen so fast that the nuclear structure suggested by Rutherford's experiment could not be stable. The uncertainty principle suggests that the closer an electron gets to the nucleus, the less uncertain we would be about its location, the more uncertain we would be about its velocity (how fast it is moving and where it is headed), just like the electron beam that goes through a narrow slit spreads out more the narrower we make the slit.

10.8 Quantum Mechanics

By the 1920s, it became evident that classical physics is just an approximation. This approximation happens to work well in the macroscopic world we deal with every day. However, a more general theory is needed in order to account for observations we make on the world of the very small. Thus, quantum mechanics was invented. Quantum Mechanics, as formulated by Erwin Schrodinger, postulates (assumes) that a mathematical function (called the *wavefunction*) is associated with particles and that all accessible information about the system can be obtained from this wavefunction. The *Schrodinger*



equation, which is also a postulate, is an example of what mathematicians call a differential equation; when we solve it, we get a function (the wavefunction). Quantum Mechanics is consistent with Heisenberg's Uncertainty Principle. It can be described as a *probabilistic* theory, as opposed to one that is deterministic. In Quantum Mechanics, we do not try to locate particles; we only try to calculate probabilities or likelihood of finding particles in whatever region we are interested in.

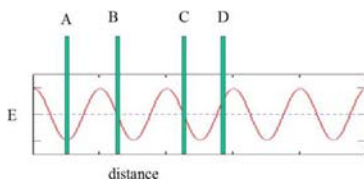
For the macroscopic world, Quantum Mechanics makes essentially the same predictions as classical physics (although it would be more cumbersome to use it in this case since classical physics would work just fine). Otherwise, it would be unacceptable. The requirement that Quantum Mechanics should be consistent with classical physics where classical physics is known to be valid is called the *Bohr Correspondence Principle*.

TEST YOURSELF

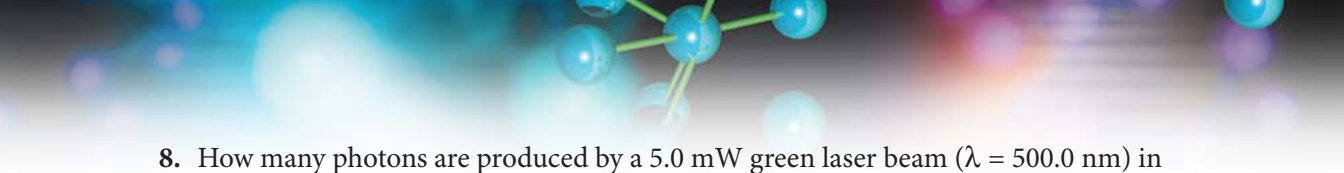
For answers and other study resources, see:

<http://i-assign.com/ebook/answers/chapter10.htm>.

1. Illustrated below is a snapshot of the electric field component of an electromagnetic wave as it travels through space. At which of the locations indicated would a charged particle experience the strongest force?



2. Which of the following wavelengths is associated with the electromagnetic radiation that humans can see?
A. 500 nm B. 300 nm C. 0.0005 cm
3. Which of the following regions of the electromagnetic spectrum has the longest wavelengths?
A. x-rays B. visible C. microwave D. radiowave
4. What is the frequency of the electromagnetic wave with a wavelength of 250 nm?
A. 1.2×10^6 Hz B. 1.2×10^{15} Hz C. 6.0×10^{14} Hz
5. What is the energy of a photon of ultraviolet radiation with a wavelength of 250 nm?
A. 5.0 eV B. 2.5 eV C. 4.0×10^{-2} eV
6. Which of the following regions of the electromagnetic spectrum has the most energetic photons?
A. x-rays B. visible C. microwave D. radiowave
7. Which of the following characteristics of electromagnetic radiation is not associated with what we perceive as color?
A. wavelength B. frequency C. wave speed D. photon energy

- 
8. How many photons are produced by a 5.0 mW green laser beam ($\lambda = 500.0 \text{ nm}$) in 20.0 s?
9. Theory predicts that the allowed energies of hydrogen are given by the formula:
- $$E = (-13.6 \text{ eV}) / n^2, \text{ where } n = 1, 2, 3, \dots$$
- which of these photon energies cannot be absorbed by a hydrogen atom that has an energy of -13.6 eV ?
- A. 5.1 eV B. 12.1 eV C. 13.6 eV
10. The average speed of N_2 molecules at 298K is 475 m s^{-1} . Calculate the de Broglie wavelength of the average N_2 molecule (mass = $4.65 \times 10^{-26} \text{ kg}$). Would you expect a beam of N_2 molecules moving at 475 m s^{-1} to be diffracted when it encounters atoms that are about 10^{-10} m apart?

Atomic Orbitals

In this chapter, we examine the quantum mechanical description of electrons in atoms and monatomic ions.

11.1 Wavefunctions and Orbitals

One of the postulates of modern quantum theory is that anything that can be known about an atom or molecule can be obtained from a mathematical function, called a *wavefunction*, which is customarily represented by the Greek letter psi (ψ). This, of course, assumes that Mother Nature gives us access to this information. The wavefunction is determined by solving what is known as the *Schrodinger equation*.

► Example

True or False. If we know ψ for an electron in an atom, then at any given time, we can use ψ to precisely determine where it is, how fast it is moving, and in which direction it is headed.

Answer: False

Experimental evidence suggests that it is not possible to precisely determine, at the same time, both velocity and location of an electron. This is known as Heisenberg's Uncertainty Principle. This is the reason why the notion of electrons moving around in well-defined orbits around the nucleus is no longer acceptable.

An *orbital* is a wavefunction that gives us information about an electron. It depends on location. It is customary to refer to an electron as being “*in an orbital*” or as “*occupying an orbital*,” as if orbitals are actual physical entities. When we say this, what we really mean is that *information about the electron can be obtained by performing mathematical operations on the function that defines the orbital*, which is quite a mouthful. The simplest, yet accurate, way of stating this idea is to say that the electron is being “*assigned to an orbital*.”

11.2 Quantum Numbers

For each atom, ion, or molecule, quantum theory gives us an infinite set of orbitals that we can use to describe the electrons. It is convenient to refer to these orbitals by a set of numbers (called *quantum numbers*) that is unique for each orbital. Quantum numbers, which arise when we solve the Schrodinger equation, are restricted numbers; they cannot have just any value. The restrictions are as follows:

- n , the *principal quantum number*, can only be a positive integer: $n = 1, 2, 3, \dots$
- l (“ell”), the *orbital angular momentum quantum number* (also known as azimuthal quantum number or orbital quantum number) can only be a non-negative integer that is less than n : $l = 0, 1, \dots, n - 1$
- m (or m_l , “em sub ell”), the *magnetic quantum number* can only be an integer from $-l$ to $+l$.

► Example

Which of the following is an allowed value for the quantum number n ?

- A. 0 B. 0.5 C. 2 D. -3

Answer: C. 2

The number 0.5 is not allowed because it is not an integer. The numbers 0 and -3 are integers but they are not positive.

► Example

Which of the following is an allowed value for the quantum number l if $n = 2$?

- A. -1 B. 1.2 C. 0 D. 2

Answer: C. 0

If $n = 2$, the only allowed values of l are 0 and 1.

► Example

Which of the following is an allowed value for the quantum number m if $n = 3$ and $l = 2$?

- A. -3 B. 1.5 C. 2 D. 3

Answer: C. 2

If $l = 2$, then, the only allowed values of m are -2, -1, 0, 1, and 2.

11.3 Shells and Subshells

Orbitals can be classified into *shells* or *levels*. All orbitals that have the same principal quantum number (n) are said to belong to the same shell or level.

Orbitals can also be classified into *subshells* or *sublevels*. All orbitals in the same shell that have the same orbital angular momentum quantum number (l) are said to belong to the same sublevel or subshell.

Subshells are often specified by writing a code letter for l next to the value of n . This is known as the *spectroscopic notation*. The code letters are:

- s if $l = 0$
- p if $l = 1$
- d if $l = 2$
- f if $l = 3$
- g if $l = 4$

► Example

What is spectroscopic notation for the subshell with $n = 2$ and $l = 1$?

Answer: 2p

The number 2 is the value of n . The letter p is the code letter for $l = 1$. We call this subshell the “2p subshell.”

► Example

How many orbitals belong to a d subshell?

Answer: 5

The letter d is the code letter for $l = 2$. For $l = 2$, the allowed values of m are -2 , -1 , 0 , 1 , and 2 . Each of these corresponds to one orbital.

In general, the number of orbitals that belong to the same subshell is equal to $2l + 1$:

- If $l = 0$, $2(0) + 1 = 1$; there is only one orbital in an s subshell.
- If $l = 1$, $2(1) + 1 = 3$; there are three orbitals in a p subshell.
- If $l = 2$, $2(2) + 1 = 5$; there are five orbitals in a d subshell.
- If $l = 3$, $2(3) + 1 = 7$; there are seven orbitals in an f subshell.

We can also say that s orbitals come in sets of 1, p orbitals come in sets of 3, d orbitals come in sets of 5, etc. Each orbital in a subshell has a unique m quantum number.

We can use spectroscopic notation to refer to a subshell or to any one of the orbitals in that subshell. So, when we say “2p orbital,” we mean any one of the three orbitals in the 2p subshell. If we want, we can specify the m , as in $2p_{+1}$; this would be the orbital in the 2p subshell that has $m = +1$.

► Example

How many orbitals belong to the $n = 2$ shell? List them.

Answer: 4

The possible sets of quantum numbers for $n = 2$ are:

n	l	m
2	0	0
2	1	-1
2	1	0
2	1	+1

One of the orbitals is in the 2s subshell ($n = 2, l = 0, m = 0$). This orbital is called the 2s orbital.

Three of the orbitals are in the 2p subshell ($n = 2, l = 1$). The m quantum number distinguishes the orbitals. These orbitals are called $2p_{+1}$, $2p_0$ and $2p_{-1}$.

In general, the n th shell has n^2 orbitals:

- For $n = 1, n^2 = 1$; there is only one orbital ($n = 1, l = 0, m = 0$).
- For $n = 2, n^2 = 4$; there are 4 orbitals; 1 in the 2s, 3 in the 2p; $1 + 3 = 4$.
- For $n = 3, n^2 = 9$; there are 9 orbitals: 1 in the 3s, 3 in the 3p, 5 in the 3d; $1 + 3 + 5 = 9$.

11.4 Information from Orbitals

The value of ψ itself, which could be a complex number, has no physical significance. To obtain information about the electron, we need to perform mathematical operations on ψ , depending on what information we need.

11.4.1 Probability of Finding Electron

The square of the absolute value of ψ is assumed to be a probability density function; this assumption is called the *Born Postulate*. From this, we can calculate the probability of finding the electron in any particular region.

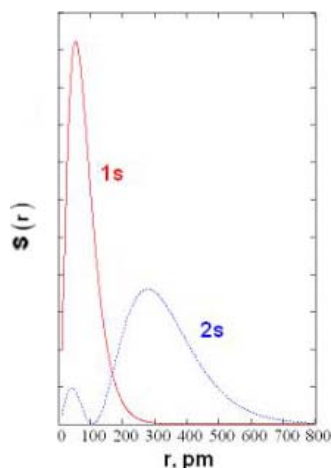
From ψ , we can obtain the so-called *radial distribution function* or *surface density function*, $S(r)$, which tells us how the probability of finding the electron depends on the distance (r) from the nucleus, as illustrated in Figure 1 for the 1s and 2s orbitals of hydrogen. The value of r where the radial distribution reaches a maximum value corresponds to the most probable distance of the electron from the nucleus. Examining Figure 1 carefully, we find that if the electron is described by the 1s orbital, its most probable distance from the nucleus is 52.9 pm. If the electron is in the 2s orbital, its most probable distance is farther away.

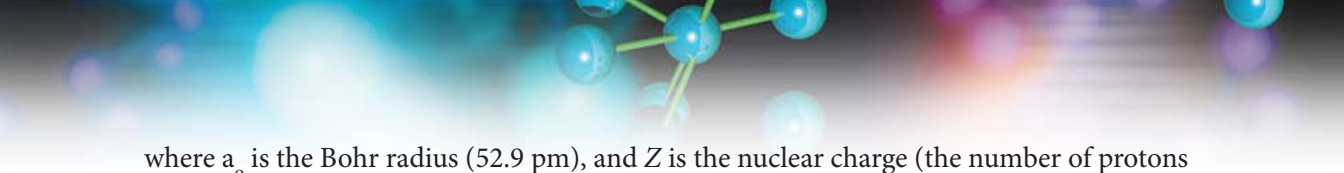
The most probable distance of the 1s electron of H, 52.9 pm, is called the Bohr radius. It is the same distance that Bohr, in an earlier model, predicted to be the first allowed orbit for the electron in a hydrogen atom. Bohr's model is no longer accepted because it assumes well-defined circular orbits for electrons, which is inconsistent with the Heisenberg uncertainty principle. With modern quantum theory, we now say that the Bohr radius is just the most probable distance of the electron from the nucleus for an electron in the 1s orbital of hydrogen; the electron can actually be anywhere from very close to the nucleus to very far away.

We can deduce from Figure 1, that on average, the electron would be closer to the nucleus if it is in the 1s orbital than if it is in the 2s orbital. We can actually calculate the average distance, $\langle r \rangle$, of an electron from the nucleus if it is the only electron in the atom or ion:

$$\langle r \rangle = n^2 \left[1 + \frac{1}{2} \left[1 - \frac{l(l+1)}{n^2} \right] \right] \frac{a_0}{Z}$$

Figure 1. Radial Distribution Function for H (1s and 2s)





where a_0 is the Bohr radius (52.9 pm), and Z is the nuclear charge (the number of protons in the nucleus). For atoms with more than one electron, we can estimate $\langle r \rangle$ by replacing the nuclear charge Z by an effective nuclear charge Z_{eff} , a smaller number, since the electron is not going to feel the “full force” of the nucleus due to the presence of other electrons.

► Example

For which of these orbitals is the distance of the electron, on average, farthest from the nucleus?

- A. 2s of H B. 2p of H C. 2s of He^+

Answer: A

- If we plug in n , l , and Z into the formula for $\langle r \rangle$, we find that
- For H, 2s: $Z = 1$, $n = 2$, $l = 0$: $\langle r \rangle = 6 a_0$
- For H, 2p: $Z = 1$, $n = 2$, $l = 1$: $\langle r \rangle = 5 a_0$
- For He^+ , 2s: $Z = 2$, $n = 2$, $l = 0$: $\langle r \rangle = 3 a_0$

Comparing 2s and 2p in H, we find that the electron will (on average) be farther from the nucleus in the 2s orbital.

Comparing 2s in He^+ and 2s in H, we find that the electron will (on average) be farther from the nucleus in H. In He^+ , there are 2 protons in the nucleus pulling the electron in; in H, there is only one proton.

In general, the average and most probable distance depends on Z , n and l :

- For the same Z and l , the larger the n , the larger the average distance.
- For the same Z and n , the larger the l , the smaller the average distance.
- For the same n and l , the larger the Z , the smaller the average distance.

Comparisons of most probable distances will show the same pattern.

We can use ψ to generate plots that would help us visualize the probability of finding the electron. In Figure 2, the probability of finding the electron assigned to a $3p_0$ orbital is represented by an electron cloud (or charge cloud); regions where the cloud is thicker represent regions where the probability of finding the electron is higher.

A more commonly used representation is called a *boundary surface* plot; see Figure 3. A 3-dimensional surface is drawn such that the probability of finding the electron (being described by the orbital) is low outside the surface. The surface is chosen so that $|\psi|^2$ is

constant anywhere on the surface. The algebraic sign (+ or -) of the function is oftentimes indicated, or color-coded. The shape of the boundary surface resembles the shape of the electron cloud and depends on the quantum numbers l and m . The s orbitals are spherically symmetrical. The p orbitals can be described as consisting of two lobes. The size of the surface depends on the quantum number n ; the larger the n , the farther the surface extends from center (where the nucleus is located).

Evaluation of orbitals with nonzero m generally yields complex numbers. It is common practice to combine orbitals with the same $|m|$ so that an equivalent pair of orbitals that yield real numbers are obtained. For example, the $2p_{+1}$ and $2p_{-1}$ orbitals can be combined so that we do not need to deal with complex numbers; the resulting orbitals are called $2p_x$ and $2p_y$. The p orbitals shown in Figure 3 are labeled p_x , p_y and p_z , instead of p_{+1} , p_{-1} and p_0 . The $2p_z$ is, in fact, another name for $2p_0$. Similarly, for $l = 2$, combinations of d_{+1} and d_{-1} orbitals give rise to d_{xz} and d_{yz} orbitals; combinations of d_{+2} and d_{-2} orbitals give rise to $d_{x^2-y^2}$ and d_{xy} orbitals; the d_{z^2} orbital is identical to the d_0 orbital ($l = 2, m = 0$).

Figure 2. Electron Cloud Representation of the $3p_0$

from http://www.jce.divched.org/JCEDLib/LivTexts/pChem/JCE2005p1880_2LTXT/QuantumStates/Bookfolder/L25OrbitalShapes.htm

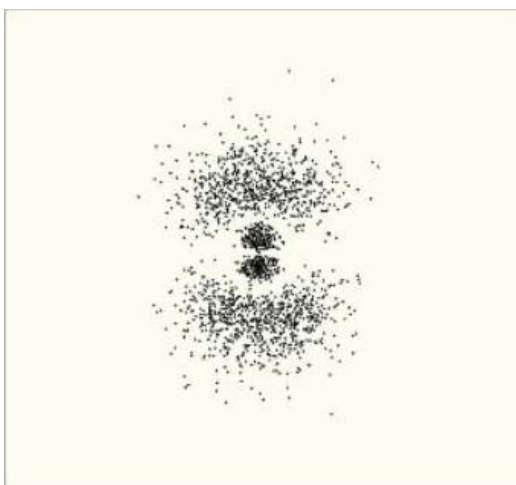
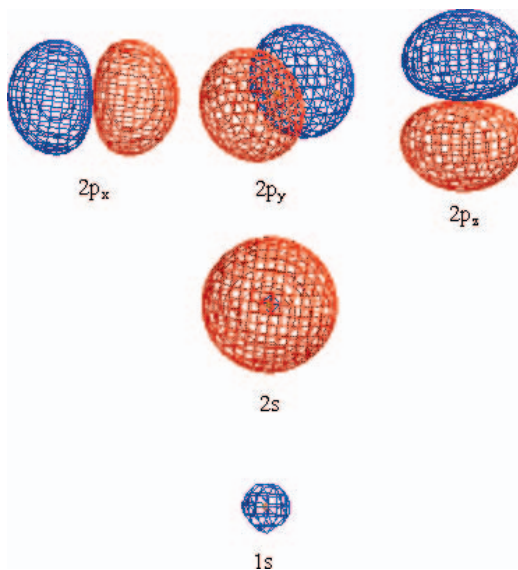


Figure 3. Boundary Surface Plots of Real Orbitals

from <http://www.chm.davidson.edu/ronutt/che115/AO.htm>



11.4.2 Orbital Energies

An orbital gives us information about the energy of an electron. For hydrogen and ions with only one electron (such as He⁺), the formula for orbital energy predicted by modern quantum theory is:

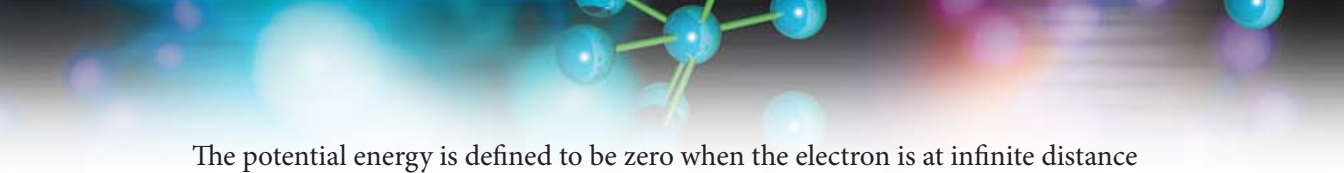
$$E = -R_H \left(\frac{Z}{n} \right)^2$$

where R_H is called the Rydberg constant (13.6 eV or 2.18×10^{-18} J), n is the principal quantum number, and Z is the nuclear charge (in atomic units; the number of protons in the nucleus).

► Example

In a hydrogen atom, which orbital describes an electron with higher energy: 3s or 3p?

Answer. In both cases, $n = 3$. So the orbital energy is the same.



The potential energy is defined to be zero when the electron is at infinite distance from the nucleus. Therefore, a negative value for the energy means that the electron must gain energy from somewhere in order for it to escape from the atom. The minimum energy required is called the *ionization energy* and it is simply $-E$. In other words, the ionization energy (IE) is:

$$\text{IE} = -E = R_{\text{H}} \left(\frac{Z}{n} \right)^2$$

If the energy available is more than the minimum required, the excess energy becomes kinetic energy of the freed electron. An experimental technique known as photoelectron spectroscopy allows us to verify predictions of quantum theory; patterns in the measured kinetic energies of the electrons removed from atoms and molecules give us information about the orbital energies.

► Example

What is the minimum energy needed to remove an electron from the 2s orbital of H? If this electron were to encounter a photon with energy of 5.0 eV, what would be its kinetic energy once it leaves the atom?

Answer: 3.4 eV, 1.6 eV

The energy of the electron in the 2s orbital of H is:

$$E = -R_{\text{H}} \left(\frac{Z}{n} \right)^2 = -(13.6 \text{ eV}) \left(\frac{1}{2} \right)^2 = -3.40 \text{ eV}$$

since $Z = 1$ and $n = 2$.

This means it has to gain at least 3.40 eV to be able to leave the atom.

The photon energy is 5.0 eV: $5.0 \text{ eV} - 3.4 \text{ eV} = 1.6 \text{ eV}$.

The extra 1.6 eV of energy becomes kinetic energy of the freed electron.

► Example

From which orbital would it be hardest to remove an electron?

- A. 1s of H B. 1s of He^+ C. 2s of He^+

Answer: B

- For 1s of H, $Z = 1$, $n = 1$: $E = -13.6 \text{ eV} (1/1)^2 = -13.6 \text{ eV}$
 $\text{IE} = 13.6 \text{ eV}$

- For 1s of He⁺, Z = 2, n = 1: E = -13.6 eV (2/1)²
= -54.4 eV, IE = +54.4 eV
- For 2s of He⁺, Z = 2, n = 2: E = -13.6 eV (2/2)²
= -13.6 eV, IE = +13.6 eV

From orbital energies, we can calculate the energy of photons that can be absorbed or emitted. The energy of the photon must be equal to the difference between allowed energies; this is called the *Bohr frequency condition*.

$$E_{\text{photon}} = \Delta E$$

We can also calculate the wavelength of the light (λ) since:

$$E_{\text{photon}} = \frac{h c}{\lambda}$$

► Example

What is the energy of the photon released when an electron in the 3p orbital of H loses energy and ends up in the 2s orbital? What is the color of the light produced?

Answer: 1.89 eV or 3.03×10^{-19} J, red light

The energy of the photon must be equal to the difference in the orbital energies for 3p and 2s.

$$\begin{aligned} E_{\text{photon}} &= E_{3p} - E_{2s} = \left[-R_H \left(\frac{1}{3} \right)^2 \right] - \left[-R_H \left(\frac{1}{2} \right)^2 \right] \\ &= -R_H \left(\frac{1}{9} - \frac{1}{4} \right) = 1.89 \text{ eV} = 3.03 \times 10^{-19} \text{ J} \end{aligned}$$

where we used 13.6 eV or 2.18×10^{-18} J for the Rydberg constant (R_H). To calculate the wavelength, it is preferable to use the value of the photon energy in the SI unit (J).

$$\begin{aligned} \lambda &= \frac{hc}{E_{\text{photon}}} = \frac{(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m s}^{-1})}{3.03 \times 10^{-19} \text{ J}} \\ &= 6.56 \times 10^{-7} \text{ m} = 656 \text{ nm} \end{aligned}$$

For atoms with more than one electron, calculating the actual energy of the orbitals is complicated; we can approximate by replacing the nuclear charge Z by an effective nuclear charge (Z_{eff}). The effective nuclear charge will depend on the quantum number l . Therefore the orbital energy will depend on both quantum numbers n and l .

11.4.3 Magnetic Properties

Any type of curved motion of a charged particle generates a magnetic field. Thus, the motion of electron around the nucleus generates a magnetic field. The magnetic quantum number, m , gives us information about the magnetism generated by the electron.

Imagine an electron moving around in a circle as illustrated in Figure 4. A particle that is moving in a circle is said to have an angular momentum vector that is pointing perpendicular to the plane of the circle; for the motion indicated in Figure 4, the red arrow indicates the direction of the *angular momentum vector*. If the particle happens to be an electron, then it is said to have a *magnetic moment vector* that is pointing in the direction opposite that of the angular momentum vector. In other words, if an electron were moving as shown in Figure 4, we can imagine that there is a tiny invisible bar magnet in the middle of the circle and the red arrow would be pointing to the south pole of that magnet.

The magnetic moment, μ , a measure of the strength of the magnetism, depends on the area of the circle and how fast the charged particle is moving; it is quantized and the allowed values depend on the orbital quantum number l :

$$\mu = \sqrt{l(l+1)}\mu_B$$

where μ_B is a constant called the Bohr magneton. However, because of the Uncertainty Principle, the direction of the magnetic moment vector is not well defined. In other words, we do not exactly know where the red arrow in Figure 4 would be pointing. We do know that the angle it makes with the z-axis depends the quantum number m . Therefore, for a given l , we say that there are $2l + 1$ ways that the magnetism (due to the orbital motion of the electron) can be oriented, as illustrated in Figure 5 for $l = 2$. The five possible orientations correspond to the five possible values of the magnetic quantum number, m , for $l = 2$. Each of the arrows shown in Figure 5 represents a possible orientation of the

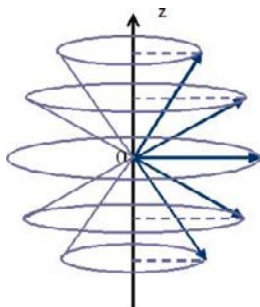
Figure 4. Angular Momentum of Particle Moving in a Circle

From <http://hyperphysics.phy-astr.gsu.edu/hbase/magnetic/magmom.html#c1>



Figure 5. Five Possible Orientations of Magnetic Moment for $l = 2$

adapted from http://physchem.ox.ac.uk/~hill/tutorials/qm2_tutorial/am/index.html



north-south line of the magnetism. The arrow should not be taken as stationary; it could be anywhere on the cone that is superimposed on it in the sketch. We say that it is *precessing* about the z -axis on this cone of uncertainty.

► Example

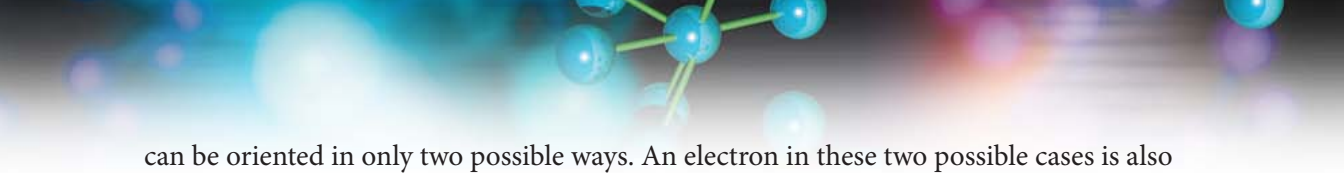
How many ways can the magnetism due to the orbital motion of an electron in a $2p$ subshell be oriented?

Answer: 3

Since p is the code letter for $l = 1$, there are three possible values for m for an electron in the $2p$ subshell: $m = -1$, 0 , or $+1$. These correspond to the three $2p$ orbitals that could be used to describe the electron, and these correspond to the three different ways that the magnetism due to the orbital motion can be oriented.

11.5 Electron Spin

The magnetic properties of atoms suggest that electrons have an intrinsic magnetism, *in addition* to the magnetism that is generated by their motion around the nucleus. By intrinsic, we mean that they are magnetic just by being electrons. Since magnetism is associated with a circular type of motion of a charged particle, it is useful to imagine the intrinsic magnetism of an electron as resulting from a spinning motion. The motion of an electron around the nucleus is analogous to that of a planet revolving around the sun, while electron spin is analogous to the rotation of the planet around its own axis. To be consistent with experimental results, we have to assume that the magnetism due to electron spin



can be oriented in only two possible ways. An electron in these two possible cases is also referred to as having a *spin quantum number*, m_s , of either $+1/2$ (*spin up*) or $-1/2$ (*spin down*). Thus, an electron in an atom is completely described by specifying four quantum numbers (n , l , m , m_s). The quantum numbers n and l tell us the shell and subshell, the quantum number m tells us which orbital, and m_s tells us the spin.

► Example

How many ways can the magnetism due to spin of an electron in a 3d orbital be oriented?

Answer: 2

For any electron, there are only two ways that the magnetism due to spin can be oriented. We refer to these ways as “spin up” ($m_s = +1/2$) and “spin down” ($m_s = -1/2$).

11.6 Pauli's Exclusion Principle

There is a limit to the number of electrons that we can assign to an orbital, and that limit is 2. If we do assign two electrons to an orbital, one must be “spin up”, the other must be “spin down.” This is known as Pauli's Exclusion Principle. Another way of stating Pauli's Exclusion Principle is to say that “no two electrons in an atom can have the same set of quantum numbers.” If two electrons have the same n , l , and m (same orbital), they must have opposite spins (one must have $m_s = +1/2$, the other must have $m_s = -1/2$)

► Example

How many electrons can be assigned to a 4p orbital?

Answer: 2

For *any* orbital, the limit is 2; one electron has $m_s = +1/2$, the other has $m_s = -1/2$.

► Example

How many electrons can be assigned to 4p orbitals?

Answer: 6

The 4p orbitals come in sets of 3, and a maximum of 2 electrons can be assigned per orbital. All six will have $n = 4$, $l = 1$. They will differ in m and m_s values; the six possible (m, m_s) values: $(1, 1/2)$, $(0, 1/2)$, $(-1, 1/2)$



and

$(1, -1/2)$, $(0, -1/2)$, $(-1, -1/2)$.

The first three are “spin up”; the other three are “spin down.”

► **Example**

How many electrons can be assigned to a 4p **subshell**?

Answer: 6

A 4p subshell consists of three 4p orbitals. Maximum “occupancy” is 2 electrons per orbital; $2 \times 3 = 6$.

► **Example**

How many electrons can be assigned to the $n = 3$ **shell**?

Answer: 18

In the $n = 3$ shell, there are 3 subshells (3s, 3p, 3d).

The 3s subshell consists of 1 orbital.

The 3p subshell consists of 3 orbitals.

The 3d subshell consists of 5 orbitals.

The total number of orbitals is $1 + 3 + 5$, or 9.

Maximum occupancy is 2 electrons per orbital; $2 \times 9 = 18$

In general, since there are n^2 orbitals in the n th shell, the number of electrons that can be assigned to a shell is $2n^2$.




TEST YOURSELF

For answers and other study resources, see:

<http://i-assign.com/ebook/answers/chapter11.htm>

- Which of the following are allowed values of the quantum numbers n and l , respectively?
A. 1.5 and 0 B. 3 and 3 C. 2 and 1 D. 0 and 1
- Which of the following is not an allowed value of the magnetic quantum number (m) for an electron in a 3d orbital?
A. 3 B. 2 C. 0 D. -1
- What is the value of the orbital quantum number for an electron in a 3p orbital?
A. 0 B. 1 C. 2 D. 3
- Which of the following is not a valid name for an atomic orbital?
A. 1s B. 2s C. 2d D. 3p
- How many ways can the intrinsic magnetism of an electron in a 4d orbital be oriented?
A. 2 B. 3 C. 5 D. 10
- What is the maximum number of electrons that can be assigned to a 2p orbital of an atom?
A. 2 B. 3 C. 6 D. 10
- How many sets of quantum numbers can an electron in a 4p subshell have?
A. 2 B. 3 C. 6 D. 10
- Which of the following can accommodate the most number of electrons?
A. a 4f orbital B. the 3d subshell C. the $n=2$ shell D. a 3d orbital
- How many ways can the magnetism generated by the orbital motion of an electron in a 3p orbital be oriented?
A. 1 B. 3 C. 5 D. 7

- 
10. Calculate the wavelength required to remove an electron from the 1s orbital of Li^{2+} if the electron is to have a kinetic energy of 2.0 eV.
11. Calculate the energy needed to excite an electron from the 1s orbital to the 2p orbital of H.
12. Atomic orbitals are mathematical functions that allow us to determine all of the following except ...
- A. the location and velocity of an electron at any given time
 - B. the probability of finding an electron in any given region
 - C. how an atom would behave in a magnetic field
 - D. the energy needed to remove an electron from an atom

Electron Configuration

12.1 Ground and Excited Configurations

The term *electron configuration* refers to a listing of the number of electrons assigned to subshells of an atom. The number of electrons assigned to each subshell is indicated as a superscript next to the name of the subshell; unwritten numbers are implied to be 1. If no electron is assigned to a subshell, the name of the subshell is omitted.

► Example

What does the electron configuration $1s^2 2s^2 2p^1$ represent?

Answer: The configuration $1s^2 2s^2 2p^1$ refers to assignment of 5 electrons to three different subshells: 2 electrons are assigned to the 1s subshell, 2 electrons are assigned to the 2s subshell and one electron is assigned to the 2p subshell. This electron configuration can also be written as $1s^2 2s^2 2p$.

► Example

Which atom or ion can have an electron configuration of $1s^2 2s^2 2p^1$?

Answer: Strictly speaking, any monatomic species that has 5 electrons, such as B, C^+ , N^{2+} , Be^- , Li^{2-} .

The term *ground state configuration* refers to the most stable (lowest energy) way of assigning the electrons. All other ways are higher energy or *excited state configurations*. Excited state configurations are unstable and can be formed when an atom absorbs light or collides with other particles. Excited atoms eventually revert to their ground state configuration either by giving off light or as a result of collisions with other particles. If ground or excited is not specified, we assume that the term electron configuration refers to the ground state.



► Example

Which of the following is an excited electron configuration of H?

- A. $1s^1$ B. $1s^2$ C. $2p$ D. none of these

Answer: C. $2p$

- The configuration $1s^1$ means one electron assigned to the $1s$ orbital (subshell). This is the ground state of H because the electron has the lowest energy if assigned to the $1s$ orbital.
- The configuration $1s^2$ implies two electrons. H has only one electron.
- The configuration $2p$ means one electron assigned to the $2p$ subshell; we can write this as $2p^1$. This would be an excited state since an electron will not have its lowest possible energy in the $2p$ subshell.

► Example

Write ground and excited electron configurations for He.

Answer:

A helium atom has 2 electrons. Therefore, we need to list how these 2 electrons are to be assigned.

- The ground state configuration has both electrons assigned to the lowest energy subshell, which is the $1s$ subshell: $1s^2$
- Any other way of assigning the two electrons would be an excited state. Examples of excited state of He: $1s^12s^1$, $1s^12p^1$, $2s^2$, $2s^12p^1$, etc.

12.2 Orbital Energies and the Aufbau Principle

One may be tempted to think that the ground state configuration is obtained by simply assigning all electrons to the $1s$ subshell. That would be incorrect because there is a limit to the number of electrons that can be assigned to an orbital and there is only one orbital in the $1s$ subshell. Pauli's Exclusion Principle says that no more than two electrons can be assigned to an orbital.

► Example

When writing electron configurations, what is the maximum number of electrons that can be assigned to the 2p subshell?

Answer: 6

There are three orbitals in the 2p subshell. The maximum number of electrons that can be assigned to any orbital is 2: $3 \times 2 = 6$.

For atoms with more than one electron, the ground state configuration is obtained by using the *Aufbau principle*: *assign electrons to lowest energy orbitals first*. Whereas orbital energy depends only the principal quantum number (n) for H and ions with only one electron, this is not the case for atoms or ions with more than one electron, where it also depends on the orbital angular momentum quantum number (l). The reason for this is that in atoms with more than one electron, each electron will be shielded from the nuclear charge by the other electrons, and the extent of shielding is different for electrons in different subshells. In H and atoms and ions with only one electron, there is no shielding; the orbital energy is the same for all subshells (within the same shell). It turns out that, in a typical atom:

- Orbitals with higher ($n + l$) have higher energies.
- For orbitals with the same ($n + l$), the orbitals with higher n have higher energies.

► Example

In a typical atom, arrange the following orbitals in order of increasing energy: 3p, 4s, and 3d.

Answer: $3p < 4s < 3d$

Compare ($n + l$) values:

- 3p, $n = 3$, $l = 1$, $n + l = 4$
- 4s, $n = 4$, $l = 0$, $n + l = 4$
- 3d, $n = 3$, $l = 2$, $n + l = 5$

Therefore, among these, 3d has the highest energy. For 3p and 4s, which have the same ($n + l$) value, 4s has a higher energy because it has the higher n .

We can use the periodic table as a memory aid for the typical order of filling of orbitals, as shown in Figure 1. The order is: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p.

Figure 1. Using The Periodic Table to Remember Typical Order of Orbital Filling

PERIODIC TABLE OF THE ELEMENTS												
1 1A												18 8A
1s												
2s											2p	
3s	3B	4B	5B	6B	7B	8B	9B	10B	11B	12B	3p	
4s	3d										4p	
5s	4d										5p	
6s	5d										6p	
7s	6d										7p	
											4f	
											5f	

Keep these in mind when using the memory aid:

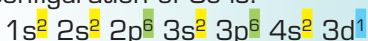
- The *s block* (shown in green) spans 2 columns. We can assign a maximum of 2 electrons to an *s* subshell since an *s* subshell consists of only one orbital.
- The *p block* (shown in purple) spans 6 columns. We can assign a maximum of 6 electrons to a *p* subshell since there are 3 orbitals in a *p* subshell and each orbital can be assigned to a maximum of 2 electrons: $3 \times 2 = 6$.
- The *d block* (shown in blue) spans 10 columns. We can assign a maximum of 10 electrons to a *d* subshell since there are 5 orbitals in a *d* subshell and each orbital can be assigned to a maximum of 2 electrons: $5 \times 2 = 10$.
- The *f blocks* (shown in yellow and red) span 14 columns. We can assign a maximum of 14 electrons to an *f* subshell, up to 2 for each of the 7 orbitals in the subshell.

Example

Write the ground state electron configuration for Scandium (Sc).

Answer: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$

First, we determine the atomic number of Sc. We can refer to a periodic table and find that it is 21. The number of electrons in an atom is equal to the number of protons, which is equal to the atomic number. Therefore, we need to assign 21 electrons to orbitals following the Aufbau principle. The ground state electron configuration of Sc is:

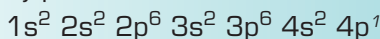


The numbers in the superscripts should add up to 21. Note that $2p^6$ does not mean that we are putting 6 electrons in a $2p$ orbital. What it means is that we are putting 6 electrons in *the* $2p$ subshell, which consists of 3 orbitals.

► Example

Write an excited state electron configuration for Scandium (Sc).

Answer: one of many possible answers is



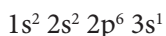
To write an excited state configuration, all we have to do is not follow the Aufbau principle. But we must still follow Pauli's principle (no more than 2 electrons per orbital). In the answer given here, we put the last electron in a higher energy orbital (in the $4p$ subshell) instead of the $3d$ subshell.

12.3 Patterns in Electron Configuration and the Periodic Table

Consider the electron configurations of Ne and Na. Neon (Ne) has 10 electrons and its electron configuration is:



Sodium (Na) has 11 electrons, one more than Ne. Its electron configuration is



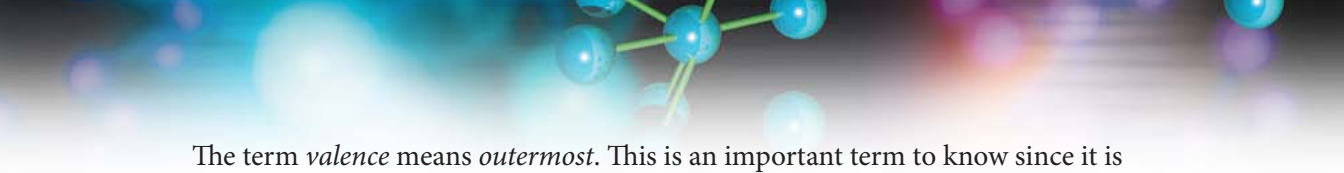
which is oftentimes abbreviated as:



The symbol $[\text{Ne}]$ is an abbreviation for $1s^2 2s^2 2p^6$ and refers to what we call a *noble gas core* or, more specifically, the *neon core*. It is very convenient to write electron configurations for atoms this way: specify the noble gas core, then write the configuration for the remaining electrons. A list of ground state electron configurations written this way can be found at the NIST Atomic Spectral Database, and is partially reproduced in Table 1. Note that $[\text{He}]$ is the noble gas core for all elements in the second row of the periodic table (elements 3 through 10); $[\text{Ne}]$ is the noble gas core for the third row (elements 11 through 18); $[\text{Ar}]$ is the noble gas core for the fourth row, etc.

Table 1. Electron Configurations of First 92 Elements from NIST Atomic Spectral Database <http://physics.nist.gov/PhysRefData/DFTdata/configuration.html>

1	H	1s ¹	32	Ge	[Ar] 3d ¹⁰ 4s ² 4p ²	63	Eu	[Xe] 4f ⁷ 6s ²
2	He	1s ²	33	As	[Ar] 3d ¹⁰ 4s ² 4p ³	64	Gd	[Xe] 4f ⁷ 5d ¹ 6s ²
3	Li	[He] 2s ¹	34	Se	[Ar] 3d ¹⁰ 4s ² 4p ⁴	65	Tb	[Xe] 4f ⁹ 6s ²
4	Be	[He] 2s ²	35	Br	[Ar] 3d ¹⁰ 4s ² 4p ⁵	66	Dy	[Xe] 4f ¹⁰ 6s ²
5	B	[He] 2s ² 2p ¹	36	Kr	[Ar] 3d ¹⁰ 4s ² 4p ⁶	67	Ho	[Xe] 4f ¹¹ 6s ²
6	C	[He] 2s ² 2p ²	37	Rb	[Kr] 5s ¹	68	Er	[Xe] 4f ¹² 6s ²
7	N	[He] 2s ² 2p ³	38	Sr	[Kr] 5s ²	69	Tm	[Xe] 4f ¹³ 6s ²
8	O	[He] 2s ² 2p ⁴	39	Y	[Kr] 4d ¹ 5s ²	70	Yb	[Xe] 4f ¹⁴ 6s ²
9	F	[He] 2s ² 2p ⁵	40	Zr	[Kr] 4d ² 5s ²	71	Lu	[Xe] 4f ¹⁴ 5d ¹ 6s ²
10	Ne	[He] 2s ² 2p ⁶	41	Nb	[Kr] 4d ⁴ 5s ¹	72	Hf	[Xe] 4f ¹⁴ 5d ² 6s ²
11	Na	[Ne] 3s ¹	42	Mo	[Kr] 4d ⁵ 5s ¹	73	Ta	[Xe] 4f ¹⁴ 5d ³ 6s ²
12	Mg	[Ne] 3s ²	43	Tc	[Kr] 4d ⁵ 5s ²	74	W	[Xe] 4f ¹⁴ 5d ⁴ 6s ²
13	Al	[Ne] 3s ² 3p ¹	44	Ru	[Kr] 4d ⁷ 5s ¹	75	Re	[Xe] 4f ¹⁴ 5d ⁵ 6s ²
14	Si	[Ne] 3s ² 3p ²	45	Rh	[Kr] 4d ⁸ 5s ¹	76	Os	[Xe] 4f ¹⁴ 5d ⁶ 6s ²
15	P	[Ne] 3s ² 3p ³	46	Pd	[Kr] 4d ¹⁰	77	Ir	[Xe] 4f ¹⁴ 5d ⁷ 6s ²
16	S	[Ne] 3s ² 3p ⁴	47	Ag	[Kr] 4d ¹⁰ 5s ¹	78	Pt	[Xe] 4f ¹⁴ 5d ⁹ 6s ¹
17	Cl	[Ne] 3s ² 3p ⁵	48	Cd	[Kr] 4d ¹⁰ 5s ²	79	Au	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ¹
18	Ar	[Ne] 3s ² 3p ⁶	49	In	[Kr] 4d ¹⁰ 5s ² 5p ¹	80	Hg	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ²
19	K	[Ar] 4s ¹	50	Sn	[Kr] 4d ¹⁰ 5s ² 5p ²	81	Tl	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ¹
20	Ca	[Ar] 4s ²	51	Sb	[Kr] 4d ¹⁰ 5s ² 5p ³	82	Pb	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ²
21	Sc	[Ar] 3d ¹ 4s ²	52	Te	[Kr] 4d ¹⁰ 5s ² 5p ⁴	83	Bi	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ³
22	Ti	[Ar] 3d ² 4s ²	53	I	[Kr] 4d ¹⁰ 5s ² 5p ⁵	84	Po	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁴
23	V	[Ar] 3d ³ 4s ²	54	Xe	[Kr] 4d ¹⁰ 5s ² 5p ⁶	85	At	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁵
24	Cr	[Ar] 3d ⁵ 4s ¹	55	Cs	[Xe] 6s ¹	86	Rn	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁶
25	Mn	[Ar] 3d ⁵ 4s ²	56	Ba	[Xe] 6s ²	87	Fr	[Rn] 7s ¹
26	Fe	[Ar] 3d ⁶ 4s ²	57	La	[Xe] 5d ¹ 6s ²	88	Ra	[Rn] 7s ²
27	Co	[Ar] 3d ⁷ 4s ²	58	Ce	[Xe] 4f ¹ 5d ¹ 6s ²	89	Ac	[Rn] 6d ¹ 7s ²
28	Ni	[Ar] 3d ⁸ 4s ²	59	Pr	[Xe] 4f ³ 6s ²	90	Th	[Rn] 6d ² 7s ²
29	Cu	[Ar] 3d ¹⁰ 4s ¹	60	Nd	[Xe] 4f ⁴ 6s ²	91	Pa	[Rn] 5f ² 6d ¹ 7s ²
30	Zn	[Ar] 3d ¹⁰ 4s ²	61	Pm	[Xe] 4f ⁵ 6s ²	92	U	[Rn] 5f ³ 6d ¹ 7s ²
31	Ga	[Ar] 3d ¹⁰ 4s ² 4p ¹	62	Sm	[Xe] 4f ⁶ 6s ²			



The term *valence* means *outermost*. This is an important term to know since it is very frequently used to describe patterns in electron configuration. What patterns do we observe when we write electron configurations?

All atoms in the same (horizontal) row of the periodic table have the same valence shell. To be more specific, the valence shell of all atoms in row n is the n^{th} shell.

► Example

In which row of the periodic table would you find an atom with an electron configuration of $[\text{Ar}] 4s^2 3d^2$?

Answer: fourth row; the valence shell is the fourth shell since the 4s orbital belongs to the fourth shell; the 3d orbital belongs to an inner shell. The atom is Ti.

If we examine Table 1, we find Ti listed with an electron configuration of $[\text{Ar}] 3d^2 4s^2$. The $3d^2$ is written before the $4s^2$. There is nothing wrong with writing the configuration either way. What matters is that the 4s is filled before the 3d. This is like saying “there are two people in room A and two people in room B.” It would be equivalent to saying “there are two people in room B and two people in room A.”

All atoms in the same group (or vertical column) of the periodic table have the same valence configuration type. If the n^{th} shell is the valence shell, then the valence configurations are:

- Group IA. ns^1 , Examples: Li: $2s^1$, Na: $3s^1$
- Group IIA. ns^2 , Examples: Mg: $3s^2$, Ca: $4s^2$
- Group IIIA. ns^2np^1 , Examples: B: $2s^22p^1$, Ga: $4s^23d^{10}4p^1$
- Group IVA. ns^2np^2 , Examples: C: $2s^22p^2$, Ge: $4s^23d^{10}4p^2$
- Group VA. ns^2np^3 , Examples: P: $3s^23p^3$, Sb: $5s^24d^{10}5p^3$
- Group VIA. ns^2np^4 , Examples: O: $2s^22p^4$, Se: $4s^23d^{10}4p^4$
- Group VIIA. ns^2np^5 , Examples: Cl: $3s^23p^5$, I: $5s^24d^{10}5p^5$
- Group VIIIA. ns^2np^6 , Examples: Ne: $2s^22p^6$ (except He: $1s^2$)
- Transition Metals. $ns^2(n-1)d^x$, where $x = 1$ to 10. Example: Sc: $[\text{Ar}] 4s^23d^1$

Examine the valence configurations above. Why do you think groups IA and IIA are collectively referred to as the “s block” elements? Why do you think groups IIIA through VIIIA (columns 13 through 18) are called the “p block” elements? Why do you think the transition metals are called the “d block” elements?

Example

Which atom has an electron configuration of $1s^2 2s^2 \dots \text{etc} \dots 4p^5$?

Answer: Bromine (Br).

The valence shell is 4. Therefore, the element belongs to period 4 (horizontal row #4). The configuration ends in $4p^5$, so this element belongs to the fifth column of the p block—column 17 (group VIIA). The configuration given is for an atom of bromine (Br).

For transition metals, the valence configuration is $ns^2(n-1)d^x$. Note that $(2 + x)$ gives us the column where the element is located in the periodic table:

- for column 3 (group IIIB): $x = 1$, or $2 + x = 3$
- for column 4 (group IVB): $x = 2$, or $2 + x = 4$
- etc.
- for column 12 (group IIB): $x = 10$, or $2 + x = 12$

However, there are exceptions; see Table 1. Notable exceptions are Cr, Ni, Cu, Nb, Ru, Rh, Pd, and Pt. A commonly used justification for these exceptions is that electrons are “shifted” in order to have half-filled (d^5) or fully-filled d subshells (d^{10}); there seems to be some stability attained with half-filled or fully-filled subshells. *But this justification is tenuous* since the exceptions are not consistent. Consider Ni, Pd, and Pt which all belong to the same column. The electron configurations are:

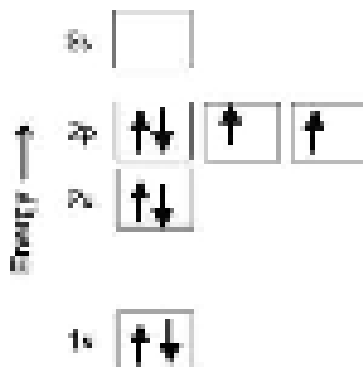
- For Ni, the electron configuration is $[\text{Ar}] 4s^2 3d^8$ (no shifting!)
- For Pd, the electron configuration is $[\text{Kr}] 4d^{10}$, instead of $[\text{Kr}] 5s^2 4d^8$; two electrons shifted; “stability of completely filled subshell” justification
- For Pt, the electron configuration is $[\text{Xe}] 6s^1 4f^{14} 5d^9$ (only one electron shifted!)

Characterizing atoms with more than one electron using orbitals is, strictly speaking, an approximation. A much more accurate theoretical treatment is beyond the scope of an introductory Chemistry textbook.

12.4 Orbital Diagrams

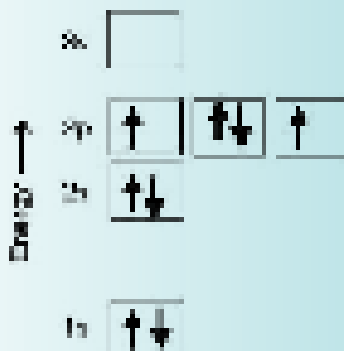
An orbital diagram gives more detailed information than an electron configuration. In an orbital diagram, electrons are represented by arrows. Boxes or blanks are used to represent orbitals. Upward-pointing arrows represent electrons with $+1/2$ spin; downward-pointing arrows represent electrons with $-1/2$ spin. Figure 2 illustrates one of many possible orbital diagrams that can be drawn for an oxygen atom, which has 8 electrons. Note that Pauli’s principle must be followed: no more than 2 electrons per orbital; if there are two electrons in an orbital, one must be spin-up, the other spin-down.

Figure 2. Orbital Diagram for an Atom with 8 Electrons



► **Example**

Which atom is represented by the following orbital diagram?



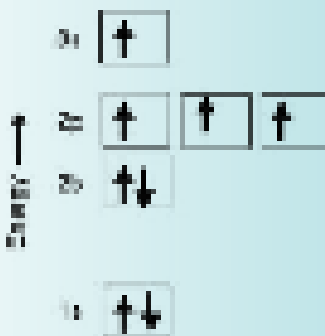
Answer: Oxygen

The diagram shows 8 arrows. Each arrow represents an electron.

The orbital diagrams shown for oxygen in the preceding example and in Figure 2 are just two of many (in this case, 15) allowed ways of distributing the electrons. These represent two of the most stable, lowest energy distributions for the ground state configuration of oxygen. To get these distributions, we fill the orbitals in the highest occupied subshell singly, with electrons of the same spin, before putting a second electron (of opposite spin) in any of the orbitals. When we do this, we are following what is known as *Hund's Rule of Maximum Multiplicity*. The justification for Hund's rule is *spin correlation*; electrons with the same spin repel each other less than electrons with opposite spins.

▶ Example

Is there anything wrong with the orbital diagram shown below?



Answer: No, there is nothing wrong with it. It would be one of many possible orbital diagrams for an *excited* configuration of an oxygen atom. An oxygen atom has 8 electrons; thus 8 arrows are drawn. Pauli's Exclusion principle is not violated; none of the orbitals have more than two electrons and the electrons have opposite spins in orbitals that have two electrons. The configuration in this case is $1s^2 2s^2 2p^3 3s^1$

If you have taken a course in probability, the number of ways of distributing is ${}_8C_4$, or 70.

$${}_8C_4 = \frac{8!}{(8-4)! 4!} = 70$$

The "8" in ${}_8C_4$ refers to the number of ways of each electron can be assigned (4 orbitals \times 2 possible spins = 8) to the partially occupied subshells. The "4" in ${}_8C_4$ refers to the number of electrons assigned to the partially occupied subshells. For the ground configuration of oxygen, $1s^2 2s^2 2p^4$, the number of ways is ${}_6C_4$, or 15.

12.5 Paramagnetism

Magnetic properties of materials are due to unpaired electrons. Materials made of atoms, molecules, or ions that have one or more unpaired electrons are said to be *paramagnetic*. An oxygen atom, as shown in section 12.4, has unpaired electrons. Oxygen atoms are like tiny magnets. They will be attracted to other magnets. Whenever the electron configuration of an atom has partially filled subshells, the atom is paramagnetic. Atoms that are not paramagnetic are said to be *diamagnetic*.



► **Example**

Explain why N atoms is paramagnetic?

Answer: The ground configuration for a nitrogen atom is $1s^2 2s^2 2p^3$. The 3 electrons in the 2p subshell are spread out over the three 2p orbitals, with parallel spins.

► **Example**

Explain why Be atoms are not paramagnetic?

Answer: The ground configuration for Be is $1s^2 2s^2$. All the subshells are completely filled. All the electrons are paired up; the magnetism due to their spins cancel each other out.



TEST YOURSELF

For answers and other study resources, see:

<http://i-assign.com/ebook/answers/chapter12.htm>.

- Which of the following is not a valid electron configuration for a lithium atom, which has 3 electrons?
A. $1s^3$ B. $1s^2 2s^1$ C. $1s^2 2p^1$ D. $1s^1 2p^1 3s^1$
- In a typical atom, which of these orbitals is filled last?
A. 3p B. 3d C. 4s D. 4p
- Which of the following is the ground state electron configuration of Sulfur?
A. $1s^2 2s^2 2p^6 2d^6$ B. $1s^2 2s^2 2p^6 3s^2 3p^4$
C. $1s^2 2s^2 2p^7 3s^1 3p^3$ D. $1s^2 2s^2 2p^6 3s^2 3p^6$
- Which of the following is the ground state electron configuration of Al?
A. $[\text{Ne}] 3s^2 3p^1$ B. $[\text{He}] 2s^2 2p^6 3s^2 3p^1$
C. $[\text{Mg}] 3p^1$ D. all of the above
- What is the ground state electron configuration for zirconium?
A. $[\text{Kr}]5s^2 5p^2$ B. $[\text{Kr}]5s^2 5d^2$ C. $[\text{Kr}]5s^2 4d^2$
- How many electrons are unpaired in the ground state of Oxygen?
A. 0 B. 1 C. 2 D. 3
- Which of the following atoms is not paramagnetic?
A. Na B. Mg C. C D. Ti

Periodic Trends in Atomic Properties

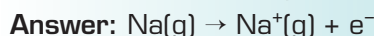
The way the periodic table is organized allows us to easily predict trends in properties of atoms. These trends can be explained using electron configurations. In this chapter, we will examine ionization energy, atomic size, and electronegativity. We will explain the observed patterns in the charges of naturally occurring ions.

13.1 Ionization Energy

The *first ionization energy* of an atom refers to the minimum energy needed to remove an electron from a neutral atom in the gas phase.

▶ Example

Write the chemical equation for the first ionization energy of Na.

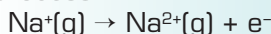


Note that the physical states of Na atoms and $\text{Na}^{\text{+}}$ ions are both gaseous.

The second ionization energy of an atom refers to the energy needed to remove a second electron. The energies needed to remove additional electrons are called the third ionization energy, fourth ionization energy, fifth ionization energy, etc.

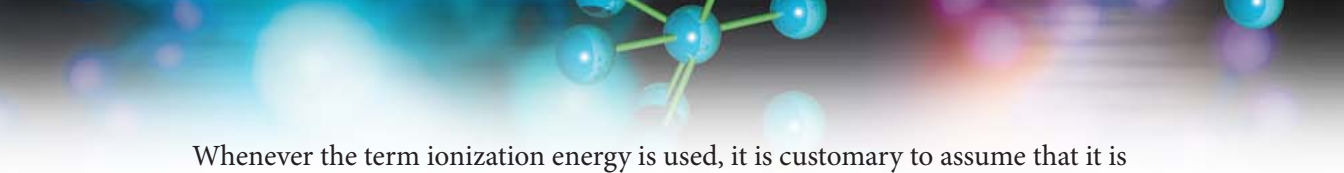
▶ Example

What is the term for the energy associated with the following process?



Answer: the second ionization energy of Na atom

This is called the second ionization energy of Na atom because $\text{Na}^{\text{+}}$ represents an atom that has already lost one electron. *We can also call it the "ionization energy of the sodium ion ($\text{Na}^{\text{+}}$)."*



Whenever the term ionization energy is used, it is customary to assume that it is referring to the first ionization energy. It is also customary to assume that the electron being removed is in the outermost shell of the atom. Higher energies would be needed to remove electrons from inner shells; in fact, measurements of the energies (using an experimental technique called photoelectron spectroscopy) needed to remove electrons from inner shells give us experimental validation of the concepts of sublevels (or subshells).

► Example

The first ionization energy of Na is the minimum energy needed to remove the electron from which orbital of Na?

Answer? 3s

The first ionization energy is the minimum energy needed to remove an electron from an atom. The minimum would correspond to the value for the easiest electron to remove and that would be the valence (outermost) electron. For Na, the electron configuration of Na is $1s^2 2s^2 2p^6 3s^1$, or [Ar] **3s¹**. Thus, the easiest electron to remove is in the 3s orbital.

A good compilation of ionization energy data can be found at webelements.com. Since the typical values in Joules are very small, ionization energies are often given in kilojoules per mole (kJ mol^{-1}). One mole of atoms is a collection of 6.022×10^{23} atoms, or about 602 billion trillion atoms. In some tabulations, eV is used; $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$.

► Example

Experimental first ionization energy of Na is reported as $495.8 \text{ kJ mol}^{-1}$. What is the minimum energy needed to remove an electron from the 3s orbital of one sodium atom?

Answer: $8.233 \times 10^{-19} \text{ J}$, or 5.139 eV

The given value is for a mole of atoms, or for 6.022×10^{23} atoms. Therefore, we divide this by 6.022×10^{23} to get the value for just one atom:

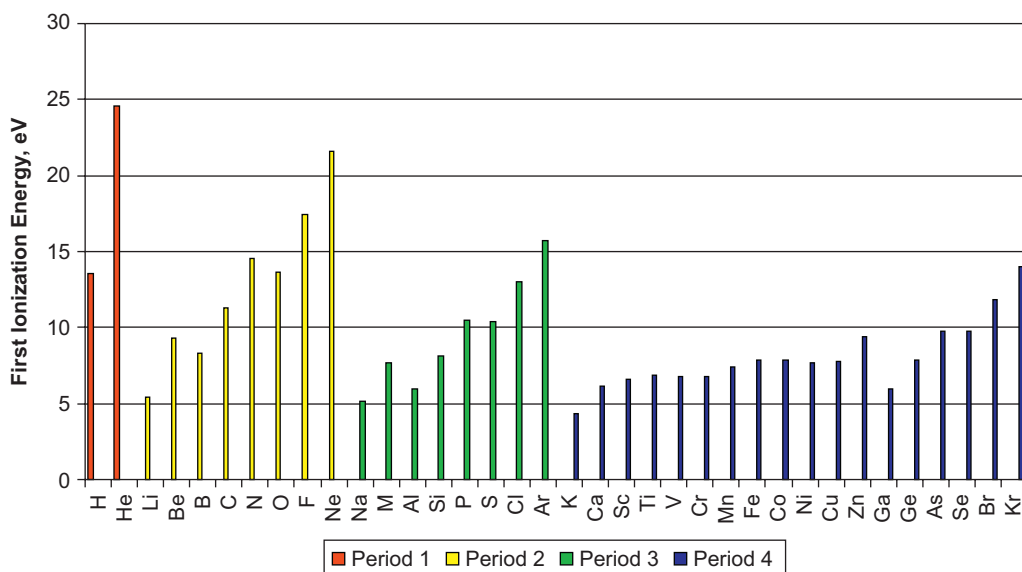
$$\frac{495.8 \times 10^3 \text{ J mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 8.233 \times 10^{-19} \text{ J}$$

$$8.233 \times 10^{-19} \text{ J} \times \frac{1 \text{ eV}}{1.602 \times 10^{-19} \text{ J}} = 5.139 \text{ eV}$$

In Figure 1, we can see that the general trends in ionization energy are:

- Across a period (horizontal row): ionization energy increases.
- Going down a group (vertical column): ionization energy decreases.

Figure 1. First Ionization Energies



A good way of summarizing the trend in ionization energy is to say that it is increasing towards the top right corner of the periodic table. Helium has the highest ionization energy. However, there are exceptions. Among the main group elements, the most notable breaks in the trend across a period are between group IIA and IIIA (columns 2 and 13), and from group VA to VIA (columns 15 and 16). There is also a break in the trend through the transition and inner transition metals.



► **Example**

In any given period, which element has the highest ionization energy?

Answer: the noble gas

It would be most difficult to remove an electron from a noble gas atom. Electrons would be easiest to remove from alkali metals (group IA).

► **Example**

From which atom is it harder to remove an electron: Na or K?

Answer: Na

Na and K are in the same column (group IA). The trend in ionization energy is decreasing going down a column. Na is above K in group IA. Therefore, the ionization energy is larger for Na. It would be harder to remove an electron from Na.

13.2 Trends in Atomic Size

The trend in atomic size is opposite that of the ionization energy. The general trend is

- Across a period (horizontal row): size decreases
- Going down a group (vertical column): size increases

► **Example**

Arrange the following in order of increase atomic size: Na, K, Cl?

Answer: Cl < Na < K. Explanation: Cl is found to the right of Na in row 3. So Cl is smaller than Na. K is below Na in group IA. So K is larger than Na.



13.3 Explaining Trends in First Ionization Energy and Atomic Size

The trend of increasing ionization energy can be explained by examining the trends in the factors that determine how hard it is to remove an atom's valence electron. Valence means "outermost."

Across a period, the number of protons in the nucleus increases. In other words, the nuclear charge increases as we go from left to right. This leads to a stronger inward pull on the outermost electrons. Therefore, this trend would tend to make it harder to remove an electron from the outermost shell.

Across a period, the number of valence electrons also increases. Since electrons repel each other, this trend would tend to make it easier to remove an electron from the outermost shell. We can think of an outer electron as being partly shielded or screened by other electrons from the pull of the nucleus.

Therefore, we can say that an outer electron feels an *effective nuclear charge* that pulls it in toward the nucleus; the stronger this effective nuclear charge, the more difficult it is to remove an electron, and the higher the ionization energy. Since the push from an additional electron is partly directed toward the nucleus while the pull from an additional proton is always directed that way, the effective nuclear charge generally increases as we go across a row (from left to right).

In general, breaks in the trend among the main group elements occur when going from an atom with a filled subshell (such as those in Group IIA; valence configuration: s^2) or from an atom with a half-filled subshell (such as those in Group VA; valence configuration: p^3) to the atom in the next group.

- Valence electrons in group IIA are in the s subshell, whereas the valence electron in group IIIA is in the p subshell. Electrons in the valence s orbitals of a group IIA atom are able to penetrate closer to the nucleus and are able to achieve a higher effective nuclear charge, compared to the electron in the valence p orbital of the neighboring group IIIA atom.
- Electrons in half-filled subshells all have the same (parallel) spins; adding one more electron would mean adding an electron with opposite spin, which would involve a significantly larger increase in electron-electron repulsions. Electrons with parallel spins repel each other less compared to electrons with opposite spins.

The break in the trend through the transition metals has to do with additional electrons going into a d subshell, which is in an inner shell; the valence configuration remains the same. For example, the electron configuration of Sc is $[\text{Ar}]4s^23d^1$, whereas Ti has an electron configuration of $[\text{Ar}]4s^23d^2$.



► Example

For which pair of atoms does a break occur in the ionization energy trend across a period: Mg and Al, Si and P, S and Cl

Answer: Mg and Al

Among main group elements, breaks occur between group IIA and IIIA and between group VA and VIA.

The trend within a group is primarily due to the size of the valence shells. Going down a group, the effective nuclear charge would be similar, but the valence shells get larger; the farther a valence electron is from the nucleus, the easier it is to remove from the atom. This follows from Coulomb's law: the attraction between the valence electron and the nucleus is inversely proportional to the square of the distance between them.

The explanation for the trends in atomic size is similar to that of ionization energy. In general, the higher the ionization energy, the more strongly a valence electron is held, the closer it would be to the nucleus, the smaller the atom.

13.4 Explaining Ion-formation Patterns

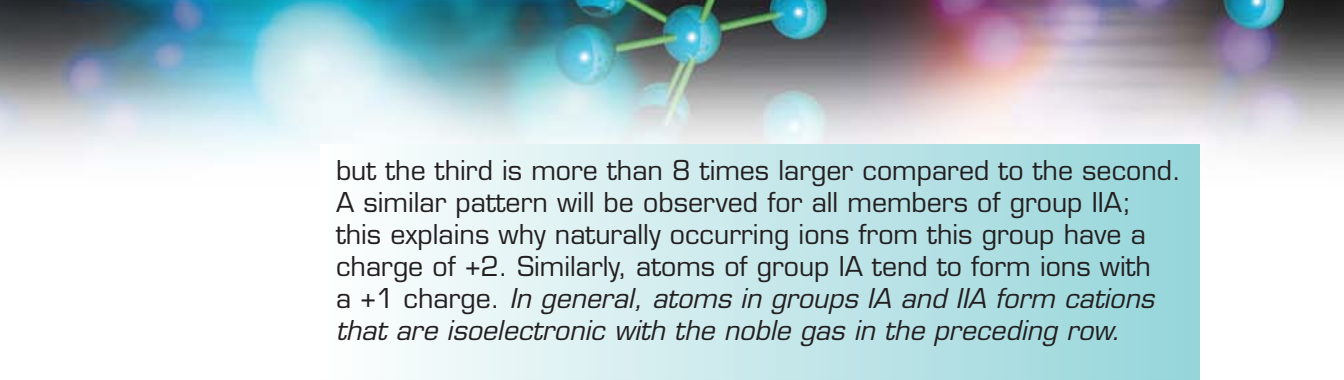
It is more difficult to remove a second electron after the first one is gone. Similarly, it is harder to take out a third one after two have been taken out. In other words, the trend in successive ionization energies is increasing. The explanation is simple: fewer electrons means lower electron-electron repulsion and a higher effective nuclear charge for the remaining electrons, making them harder to remove.

A *drastic* increase in ionization energy occurs once all the valence electrons have been taken out. This is because the remaining electrons (the core electrons) are significantly much closer to the nucleus than the valence electrons.

► Example

Predict where the drastic increase occurs in the successive ionization energies of Be.

Answer: Between the second and third ionization energies. Be has an electron configuration of $[\text{He}]2s^2$; it has two valence electrons (in the 2s orbital); after the removal of the two valence electrons, we're left with the noble gas core and it becomes drastically more difficult to remove the next one. We can look up the successive ionization energies of Be from webelements.com and find: 899.5, 1757.1, 14848.7, and 21006.6 kJ/mol. Note that the second is less than 2 times larger compared to the first and the fourth is less than 2 times larger compared to the third,



but the third is more than 8 times larger compared to the second. A similar pattern will be observed for all members of group IIA; this explains why naturally occurring ions from this group have a charge of +2. Similarly, atoms of group IA tend to form ions with a +1 charge. *In general, atoms in groups IA and IIA form cations that are isoelectronic with the noble gas in the preceding row.*

► Example

Explain why naturally-occurring monatomic ions of fluorine (the fluoride ions) have a -1 charge.

Answer:

A fluorine atom, with an electron configuration of $[\text{He}]2s^2 2p^5$, has two ways of achieving a noble-gas-like configuration:

- losing 7 electrons (which requires a great deal of energy; does not happen; we do not find F^{7+} ions in nature).
- gaining one electron, forming fluoride ion (F^-) which is isoelectronic with a neon atom. The electron configuration of F^- is $[\text{He}]2s^2 2p^6$, just like Ne.

Why is F^{2-} not observed in nature? If it were formed, its electron configuration would be $[\text{Ne}]3s^1$ and the valence electron is not likely to stay long enough for us to observe it. *In general atoms of nonmetallic elements tend to gain enough electrons to become isoelectronic with the noble gas in the same row.*

We can also explain why the most commonly observed charge of transition metal ions is +2, and why transition metal ions with charges other than +2 are observed. Most transition metal atoms have two electrons in the valence shell; in general, these electrons are easier to remove than the d electrons in an inner shell.

► Example

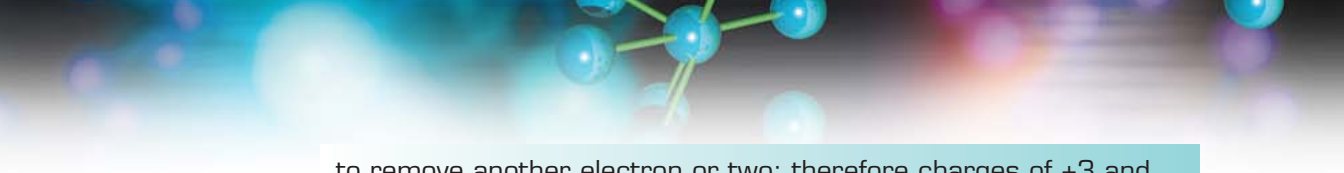
Explain the formation of Fe^{2+} and Fe^{3+} .

Answer:

Fe has an electron configuration of $[\text{Ar}] 4s^2 3d^6$. The valence shell is the 4th shell; the two valence electrons are in the 4s orbital. These electrons are easier to remove compared to the 3d electrons.

The electron configuration of Fe^{2+} is $[\text{Ar}] 3d^6$, not $[\text{Ar}] 4s^2 3d^4$.

Because the electron configuration of transition metal ions with a charge of +2 is not noble-gas-like, it is not drastically more difficult



to remove another electron or two; therefore charges of +3 and +4 could also be observed.

The electron configuration of Fe^{3+} is $[\text{Ar}] 3d^5$.

13.5 Sizes and Ionization Energies of Ions vs. Atoms

Cations are smaller than the atoms that they came from; their ionization energy is higher. Fewer electrons in the valence shell, but the same number of protons in the nucleus, means lower electron-electron repulsion, and a higher effective nuclear charge. The naturally-occurring cations of the main group elements have lost all electrons in the valence shell of the original atom, leaving behind the core, which is obviously smaller and has an extremely high ionization energy.

► Example

Compare size and ionization energy of the following: Mg , Mg^+ , Mg^{2+} ?

Answer: Mg has the largest size; Mg^{2+} has the smallest size.

Mg has the lowest ionization energy; Mg^{2+} has the highest ionization energy.

Anions are larger than the atom that they come from; their ionization energy is lower. More electrons in the valence shell, but the same number of protons in the nucleus, means more electron-electron repulsion, and a smaller effective nuclear charge. Once the valence shell is filled, additional electrons will need to go to an even larger shell.

► Example

Which has the largest size: F , F^- , F^{2-} ?


Answer: F^{2-}

► Example

Which has a higher ionization energy: F^{2-} or Na ?

Answer: Na

It would be harder to remove an electron from Na . Both F^{2-} and Na have the same electron configuration. But Na has a higher



nuclear charge (+11 due to 11 protons in the nucleus) compared to F^{2-} (+9 due to 9 protons in the nucleus). Since the electron configurations are the same; the screening of the valence electron is the same. Therefore, the effective nuclear charge felt by the valence electron of Na would be higher than that of F^{2-} . This explains why F^{2-} is not found in nature; it cannot hold on to its valence electron. Even Na has a hard time holding on to its electron; it is highly reactive.

► Example

Compare the size and ionization energy of Mg^{2+} and Ne.

Answer: Mg^{2+} has a higher ionization energy and is smaller in size. Mg^{2+} is isoelectronic with Neon. So the screening of the valence electrons is the same. However, Mg^{2+} has more protons compared to Ne (12 vs. 10). Therefore, the effective nuclear charge is higher for Mg^{2+} . It would be harder to remove an electron from Mg^{2+} .

13.6 Electronegativity

Electronegativity refers to the ability of an atom to attract electrons that it is sharing with another atom. The trend in electronegativity generally follows that of ionization energy and the reason for the trend is pretty much the same. Across a period (horizontal row), electronegativity increases from left to right, and within a group (vertical column), electronegativity decreases. We can also say that the trend in electronegativity is increasing towards the upper right-hand corner of the periodic table. Thus, fluorine (F) is the most electronegative element. Note that, based on the trend, Ne and He would be expected to be more electronegative than F. However, in nature, He, Ne and the other noble gases are not found sharing electrons with other atoms; they are usually ignored when discussing electronegativities.

► Example

Which is more electronegative: Na or N?

Answer: N

Nonmetals are more electronegative than metals. Nonmetals are found on the upper right-hand corner of the periodic table.



TEST YOURSELF

For answers and other study resources, see:

<http://i-assign.com/ebook/answers/chapter13.htm>.

- The ionization energy of bromine atoms is the energy associated with which of the following?
 - $\text{Br(g)} \rightarrow \text{Br}^+(\text{g}) + \text{e}^-$
 - $\text{Br}_2(\text{l}) \rightarrow 2 \text{Br}^+(\text{g}) + 2\text{e}^-$
 - $\text{Br(g)} + \text{e}^- \rightarrow \text{Br}^-(\text{g})$
 - $\text{Br}_2(\text{l}) + 2\text{e}^- \rightarrow 2 \text{Br}^-(\text{aq})$
- Which of the following has the highest ionization energy in the period where it belongs?
 - Ne
 - Na
 - Br
 - Mn
- Which of the following has the highest ionization energy?
 - Na
 - Rb
 - N
- Which of the following has the smallest atomic radius?
 - O
 - S
 - Li
- The increasing trend in ionization energy across a period, from left to right, is due to...
 - Increasing repulsions among electrons in the valence shell
 - Increasing effective nuclear charge
 - Increasing number of core electrons
 - Increasing size of the valence shell
- The decreasing trend in ionization energy going down a group is, is due to...
 - Increasing repulsions among electrons in the valence shell
 - Increasing effective nuclear charge
 - Decreasing number of core electrons
 - Increasing size of valence shell

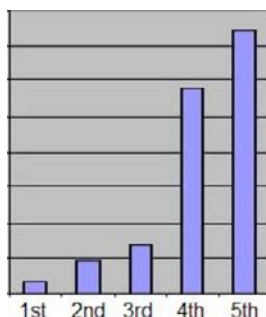
7. Which atom's first five ionization energies best resembles the pattern shown in the graph?

A. Na

B. Mg

C. Al

D. K



8. What is the electron configuration of naturally occurring aluminum ion?

A. $[\text{Ne}] 3s^2 3p^1$

B. $[\text{Ne}] 3s^2$

C. $[\text{Ne}] 3s^1$

D. $[\text{Ne}]$

9. All of the following have the same electron configuration except...?

A. Ne

B. Na^+

C. O^-

D. O^{2-}

10. What is the electron configuration of Fe^{3+} ?

A. $[\text{Ar}] 4s^2 3d^6$

B. $[\text{Ar}] 4s^2 3d^3$

C. $[\text{Ar}] 4s^1 3d^4$

D. $[\text{Ar}] 3d^5$

11. Which of the following has the largest size?

A. K

B. K^+

C. Se

D. Li

12. Which of the following has the largest size?

A. Cl

B. Cl^-

C. F

D. F^-

13. Which of the following has the highest ionization energy?

A. Ne

B. Mg^{2+}

C. Mg

D. F

14. Which of the following has the highest electronegativity?

A. Na

B. Br

C. F

15. Which type of element has the lowest electronegativity?

A. a metal

B. a nonmetal

C. a metalloid

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Molecular Structure

14.1 The Octet/Duet Rule

The chemical properties of atoms primarily depend on their valence configuration. When we talk about chemical properties of atoms, we are referring to their tendency to lose, gain or share electrons. The pattern that emerges when one examines the chemical properties of atoms in the main groups is that they seem to have a tendency to be noble-gas-like; this means losing, gaining, or sharing electrons so that they end up being surrounded by the same number of valence electrons as noble gas atoms. Noble gas atoms, except helium, have 8 valence electrons; a helium atom has two valence electrons. Thus, this tendency to noble-gas-like is referred to as the *octet/duet rule*.

Atoms belonging to the same family or group (vertical column) have similar chemical properties because they have the same valence configuration. Columns in the traditional periodic table are numbered such that the number corresponds to the number of valence electrons.

► Example

C belongs to group IVA (column 14). How many valence electrons does a carbon atom have?

Answer: C has four valence electrons.

IV is the Roman numeral for four. The electron configuration of a carbon atom is $1s^2 2s^2 2p^2$. The valence electrons are the electrons in the 2s and 2p subshells, which are in the 2nd or $n = 2$ shell.

► Example

Which of the following has the same number of valence electrons as a C atom: N or Si?

Answer: Si.

C and Si belong to the same group (IVA). N and C belong to the same period (horizontal row 2). It is atoms in the same group that have the same number of valence electrons.

14.2 Lewis Symbols

A *Lewis symbol* is a visual representation of the valence configuration of a main group atom or monatomic ion. Main group elements or representative elements belong to the “A groups” in the traditional periodic table (columns 1, 2, and 13–18). Dots are drawn around the symbol for the atom; each dot represents a valence electron.

▶ Example

Draw the Lewis symbol for a carbon atom.

Answer: since C has four valence electrons, we draw four dots around the symbol for carbon.

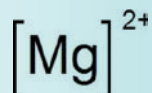


For ions, dots are added or taken away depending on the charge, square brackets are drawn, and the charge is indicated in the upper right hand corner.

▶ Example

Draw the Lewis symbols for magnesium ion.


Answer: Magnesium belongs to group IIA. Therefore, a Mg atom has two valence electrons; its Lewis symbol has two dots. But naturally-occurring magnesium ion has a charge of +2; this means two fewer electrons compared to a magnesium atom. The Lewis symbol for magnesium ion has no dots.



▶ Example

Draw the Lewis symbols for fluoride ion.

Answer: Fluorine belongs to group VIIA. Therefore, a fluorine atom has 7 valence electrons and its Lewis symbol has seven dots. Naturally-occurring fluoride ion has a charge of -1 ; this means one



additional electron compared to a fluorine atom. Therefore, the Lewis symbol for fluoride ion has 8 dots.



By following the octet/duet rule, we can say that the atoms end up as ions with a *noble-gas-like* configuration, or as being *isoelectronic with a noble gas*.

► Example

What is the electron configuration of magnesium ion?

Answer: $1s^2 2s^2 2p^6$

- The electron configuration of Mg atom is $1s^2 2s^2 2p^6 3s^2$ or [Ne] $3s^2$
- For Mg^{2+} ion, the electron configuration is like that of a Neon atom: $1s^2 2s^2 2p^6$
- The valence shell of the magnesium ion is the second shell, and there are **eight** electrons in that shell. We say that by losing two electrons, a magnesium atom acquires an *octet* for its valence configuration.

► Example

What is the electron configuration of hydride ion?

Answer: $1s^2$

- The **hydride** ion is the **negative** ion derived from a hydrogen atom.
- The electron configuration of H is $1s^1$
- The noble gas closest to H in the periodic table is He, which has two electrons and an electron configuration of $1s^2$
- We predict the hydride ion to be isoelectronic with He; we say that when a hydrogen atom becomes a hydride ion, it acquires a *duet* for its valence configuration.

14.3 Lewis Structures

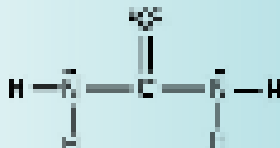
A *Lewis structure* is a visual representation of how the atoms in a molecule or polyatomic ion are sharing valence electrons. In a Lewis structure,

- each atom is represented by its symbol.
- all valence electrons must be represented by dots or lines.
- each dot represents one valence electron.
- a line is equivalent to two dots.
- lines or dots drawn between symbols of two atoms represent valence electrons shared by the two atoms.

For polyatomic ions, the Lewis structure must be enclosed in square brackets and the charge of the ion must be indicated as a superscript in the upper right-hand corner.

► Example

How many valence electrons are shared in the Lewis structure shown below? How many are not shared?



Answer: 16 shared, 8 not shared

The total number of valence electrons shown in the structure above is 24 (16 shared; 8 unshared). There are 8 lines drawn between symbols; each of these 8 lines represents 2 shared electrons; $8 \times 2 = 16$. The total number of valence electrons shown (24) should be equal to the total number of valence electrons from the individual atoms that make up the structure. Note that Nitrogen belongs to group VA; a nitrogen atom has 5 valence electrons. Each H atom has only one electron. Carbon belongs to group IVA; each C atom has 4 valence electrons. Oxygen belongs to group VIA; each O atom has 6 valence electrons.

- From N: $2 \times 5 = 10$
- From H: $4 \times 1 = 4$
- From C: $1 \times 4 = 4$
- From O: $1 \times 6 = 6$

$$10 + 4 + 4 + 6 = 24$$

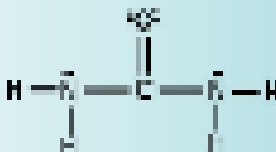
In a Lewis structure, each line or pair of dots shared between two atoms is called a *bonding pair*. A pair of atoms can have up to three bonding pairs between them.

- If only one bonding pair is shown between two atoms, we say that the atoms have a *single bond* between them.
- If there are two bonding pairs between these two atoms, we say that they have a *double bond*.
- If there are three bonding pairs between these two atoms, we say that they have a *triple bond*.

Each pair of *unshared* electrons is called a *lone pair*.

► Example

How many single bonds, double bonds, triple bonds, and lone pairs are shown in the structure below.



Answer:

- Single bonds: 6 (four N-H and two C-N)
- Double bonds: 1 (between C and O)
- Lone pairs: 4 (two on the O, one on each of the N)

► Example

How many valence electrons should be shown in the Lewis structure for SO_4^{2-} ?

Answer: 32 electrons

- The S atom contributes 6 valence electrons since S belongs to group VIA.
- Each of the four O atoms also contributes 6 valence electrons since O belongs to group VIA.
- Total number of valence electrons from one S and four O atoms is:
 $(1)(6) + (4)(6) = 30$.
- To this, we need to add two more electrons since the ion has a charge of -2 .
 $30 + 2 = 32$.

► Example

How many valence electrons should be shown in the Lewis structure for NH_4^+ ?

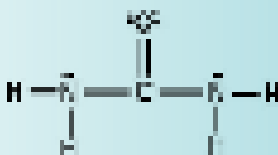
Answer: 8 electrons

- The N atom contributes 5 electrons since N belongs to group VA.
- Each H atom contributes one electron.
- Total number of valence electrons from one N and 4 H:
 $(5) + (4)(1) = 9$.
- We need to subtract one electron because the ion has a charge of +1
 $9 - 1 = 8$.

When atoms share electrons, they also appear to have a tendency to acquire a noble-gas-like configuration. Atoms tend to share electrons such that each one appears to be surrounded by an octet (or a duet in the case of hydrogen).

► Example

Describe how the octet/duet rule is illustrated in the Lewis structure below.



Answer:

- The O atom is surrounded an octet (8 valence electrons): four electrons in the two lone pairs and four electrons in the double bond.
- The C atom is also surrounded by an octet: four electrons in the double bond, and two electrons in each of the two single bonds.
- Each N atom is surrounded by an octet: six in the three single bonds and two in the lone pair.
- Each H atom has a duet: two electrons in each of the single bonds. H cannot exceed a duet, it can bond to only one atom. We say that hydrogen is always a *terminal* atom in a molecule or polyatomic ion; we only find H atoms at the edges of a molecule or polyatomic ion.

14.4 Strategies for Drawing Lewis Structures

Here is a systematic procedure for drawing a structure that follows the octet/duet rule.

Step 1. Start by connecting all the atoms with single bonds. Attach the H atoms last since they should be terminal atoms; H atoms can only be involved in one single bond. Add lone pairs to complete the octet.

Step 2. Count all the valence electrons in the structure; compare with the expected (correct) total number of valence electrons.

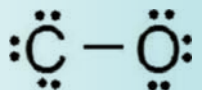
- If the number of valence electrons shown in the structure is correct, you are done.
- If the number of valence electrons shown in the structure is larger than the correct number: remove one lone pair each from neighboring atoms and add a bonding pair between the two atoms.
- Repeat until you get the correct number of valence electrons.

► Example

Draw the Lewis structure for the carbon monoxide molecule, CO.

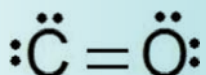
Answer:

Step 1. Start by drawing a tentative structure with the two atoms connected by a single bond; then draw lone pairs in order to have an octet around each atom. In order for both atoms to have an octet, we need three lone pairs on each one.

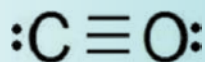


Step 2. Count the number of valence electrons and compare with the correct number.

- The structure as drawn shows 14 valence electrons.
- The correct number should be 10. C belongs to group IVA; C will contribute 4 valence electrons. O belongs to group VIA; O will contribute 6 valence electrons.
- We have only 10 valence electrons to distribute between the two atoms, but we are showing 14 in the tentative structure. Therefore, we remove a lone pair each from the neighboring atoms and add a bonding pair between the two atoms. If we do this, we get:

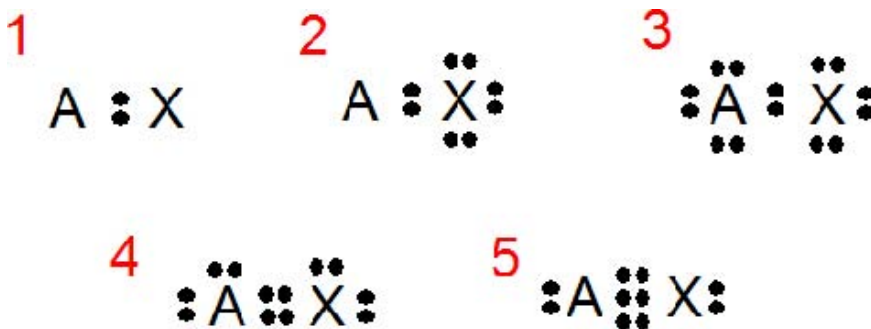


- We now have 12 valence electrons. Again, we know this structure is incorrect because CO only has 10. So, we take out two more lone pairs (one each from neighboring atoms) and add another bonding pair between them.



If we were to explore all the possible ways of drawing a valid Lewis structure for diatomic molecules or ions, we find that there are only five unique ways that it can be done. These five ways are shown in Figure 1.

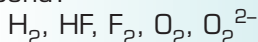
Figure 1. Lewis Structures for Diatomic Species



Note that each way has a unique number of valence electrons: 2, 8, 14, 12, and 10 for structures 1 through 5, respectively.

► Example

Which of the following diatomic species does not have a single bond?



Answer: O_2 ; it has a double bond

- O_2 has 12 valence electrons; each O atom in O_2 has 6 valence electrons: $6 \times 2 = 12$. Therefore, the Lewis structure of O_2 should resemble Structure 4 in Figure 1, which has a double bond.
- H can only form a single bond. Therefore, H_2 and HF are expected to have a single bond. We expect H_2 , with only two

valence electrons, to look like structure 1 in Figure 1. We expect HF to look like structure 2 in Figure 1. H contributes one valence electron and F contributes 7; only structure 2 above has 8 valence electrons.

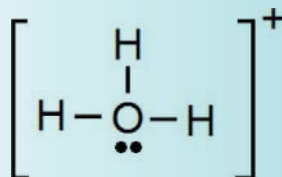
- The F atoms in F_2 also have a single bond between them; each F atom in F_2 contributes 7 valence electrons; $2 \times 7 = 14$; only structure 3 in Figure 1 shows 14 valence electrons.
- The O atoms in peroxide ion, O_2^{2-} , also have a single bond between them; each O atom contributes 6 electrons and the -2 charge means two additional electrons: $2 \times 6 + 2 = 14$.

► Example

Draw the Lewis structure for hydronium ion (H_3O^+).

Answer: +1

Since each H can only have a single bond, the Lewis structure must be one where each H is sharing a pair of electrons with O. In order for the O atom to have an octet, we should draw one lone pair on it.



We then verify if we have the correct number of valence electrons shown. The three single bonds and one lone pair account for 8 valence electrons. H_3O^+ should have 8; one from each of the H atoms, 6 from the O atom, minus one because the + charge indicates one electron lost: $3(1) + 6 - 1 = 8$. Finally, we draw square brackets around the structure and indicate the + charge as a superscript.

14.5 Isomeric Structures

When we have more than two atoms in a molecule or polyatomic ion, there is usually more than one way of connecting the atoms. Each of the unique ways is called an *isomer*; each one represents a different molecule.

► Example

Draw the two possible isomers of a molecule made up of one H, one N, and one C atom.

Answer:

The atoms can be connected as H-C-N or C-N-H. Since H cannot have more than one single bond, C-H-N is not allowed.



It should be easy to verify that both structures satisfy the octet/duet rule and have the correct number of valence electrons. These structures represent two different molecules, two different compounds. The first one is called hydrogen cyanide, the other is called hydrogen isocyanide. These two molecules are called isomers. Note that connecting the atoms as H-N-C is the same as C-N-H; similarly the H-C-N connectivity is the same as N-C-H.

14.6 Resonance Structures

It is possible to have more than one way of distributing valence electrons for a given molecule or ion. Each of these unique ways is called a resonance structure. Unlike isomers, the connectivity in resonance structures is the same; resonance structures represent the same molecule. The existence of two or more resonance structures generally indicates that none of the structures adequately represents reality. Reality is probably a hybrid of the resonance structures, although some structures may be considered “more significant” (that is, resemble reality better than the others). When drawing resonance structures, we draw double-headed arrows between them to indicate resonance.

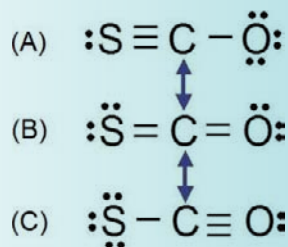
► Example

Draw resonance structures for a OCS, assuming that the C is between O and S.

Answer:

The total number of valence electrons in OCS is 16: 6 from O, 4 from C, and 6 from S. If we explore all the possibilities, we find that any triatomic molecule or ion with 16 valence

electrons will have the resonance structures similar to the ones shown below:



14.7 Formal Charges

Not every possible isomeric structure is stable enough to be observed in nature. We can use formal charges to determine which isomeric structures are more likely to be observed. If more than one resonance structure can be drawn for a given molecule, we can also use formal charges to determine which structure is more significant. In general,

- structures with small formal charges (0, +1, -1) are more likely to be stable isomers or are more significant resonance structures than those that have larger formal charges (such as +2, -2).
- structures where neighboring atoms have formal charges of the same sign are less likely to be stable or significant.
- if neighboring atoms have opposite formal charges, we would expect the more electronegative atom to have the negative formal charge and the less electronegative atom to have the positive formal charge.

To calculate the formal charge of an atom in a structure, use the formula:

$$\text{F.C.} = F - A,$$

where

- F is the number of valence electrons in the Free atom (neutral, not bonded to another atom), and
- A is the apparent number of valence electrons that the atom owns in the structure. To determine A, assume the atom owns half of electrons shared with other atoms and all of the electrons in its lone pairs. In other words,

$$A = B + 2L,$$

where B is the number of bonding pairs and L is the number of lone pairs.

► Example

Determine the formal charges of S in the structure below.



Answer:

- S belongs to group VIA, so a free sulfur atom has 6 valence electrons. $F = 6$
- In the structure, S appears to own 5 electrons. It has three bonding pairs (in the triple bond) and one lone pair. $B + 2L = 5$. Put another way, it appears to own 2 in the lone pair, plus half of the six electrons in the triple bond (3). Therefore:
 $A = 2 + 3 = 5$.
- The formal charge of S is:
 $F.C. = F - A = 6 - 5 = +1$
Compared to a free S atom, the S atom in the structure appears to have lost one electron.

How do we come up with structures that have low formal charges? In general, if a free atom has x valence electrons, it would have a formal charge of zero if it has $(8-x)$ bonding pairs.

► Example

In what ways can a C atom have a formal charge of zero?

Answer:

A carbon atom has 4 valence electrons. It needs 4 more to acquire an octet: $8 - 4 = 4$. Therefore, a C atom gets a formal charge of zero when it has four bonding pairs, as in

- four single bonds.
- two single bonds and one double bond.
- one single bond and one triple bond, or
- two double bonds.

Because of this, carbon is said to be *tetravalent*; the Greek prefix *tetra* means four. A carbon atom by itself, has 4 valence electrons (it belongs to group IVA); it just needs four more electrons to achieve an octet and be noble-gas-like. Carbon atoms are found in molecules of organic compounds. The study of organic compounds is very important. Living things are primarily made of organic compounds.

► Example

In what ways can an O atom have a formal charge of zero?

Answer:

An O atom has 6 valence electrons. It needs two more to acquire an octet: $8 - 6 = 2$. Therefore, a O atom gets a formal charge of zero when it has two bonding pairs (*and* two lone pairs), as in

- two single bonds and two lone pairs.
- one double bond and two lone pairs.

As illustrated in the preceding examples, C has a formal charge of zero in structures where it is involved in four bonding pairs, while O has a formal charge of zero in structures where it is involved in two bonding pairs. For nitrogen atoms, the typical pattern is three bonding pairs (three single bonds as in NH_3 , a double bond and a single bond as in HONO, or a triple bond as in HCN); in these cases, the formal charge of N is zero. Halogens (F, Cl, Br, and I) tend to form just one single bond. The free halogen atoms have 7 valence electrons; by forming one single bond, they achieve an octet and have a formal charge of zero.

Another good strategy for coming up with structures with reasonable formal charges is to surround a less electronegative atom with more electronegative atoms. In these structures, the more electronegative atoms are more likely to get a negative formal charge (as they should) and the less electronegative atom is more likely to get a positive formal charge.

14.8 Exceptions to the Octet/Duet Rule

The octet/duet rule is not a strict rule.

Atoms can have less than an octet. Notable examples B and Be. Experimental evidence suggests that the B atom in BCl_3 is best represented by a structure where the B is surrounded by only six valence electrons (three bonding pairs). Similarly, Be in BeH_2 is best represented by a structure where Be is surrounded by only four electrons (two bonding pairs). One characteristic of these molecules is that they tend to react so that the central atom, which does not have an octet, ends up with an octet by bonding with a molecule or ion with a lone pair.

There are molecules that have an odd number of electrons. Notable examples are NO and NO_2 . In these cases, it is impossible to have all electrons paired and it would not be possible to follow the octet rule. Molecules with unpaired electrons are called radicals and are experimentally detectable using techniques that take advantage of the fact that these molecules are paramagnetic.

Atoms in period 2 cannot have more than an octet, but atoms beyond period 2 can have more than an octet (“expanded octets”). Recall that s, p, and d subshells can accommodate 2, 6, and 10 electrons. The valence shell of atoms in period 2 cannot accommodate more than an octet because they only have s and p subshells. However, beyond period 2, the valence shell can accommodate more than 8 electrons due to the availability of d subshells.

► Example

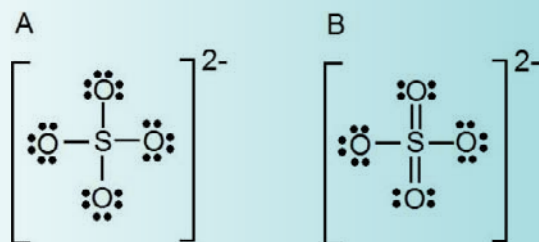
Which atom cannot have more than an octet: C or Si?

Answer: C. Carbon belongs to period 2. Si belongs to period 3 and has d subshells in its valence shell that allows it to accommodate more than an octet.

The use of expanded octets allows us to avoid large formal charges.

► Example

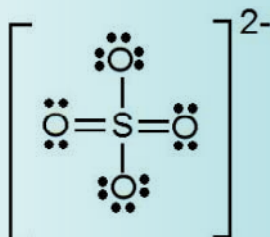
Which of the two resonance structures shown below for sulfate, SO_4^{2-} , is less significant?



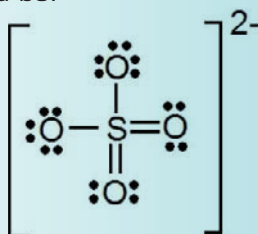
Answer: structure A

The formal charge of S in structure A is +2 (not good); in structure B, its formal charge is zero.

It should be noted that structure B is one of six equally significant Lewis structures; another one would be:



and another one would be:



Reality would best be represented by a hybrid of all six structures; a single bond between S and O is generally found to be longer than a double bond. In sulfate, we would expect each of the S-to-O bonds to be of the same length; we also expect each one to be longer than a typical S-to-O single bond but shorter than a typical S-to-O double bond.

14.9 Molecular Geometry

The subject of molecular geometry deals with shapes of molecules. A Lewis structure is a two-dimensional representation of a molecule or ion; its intent is to show how the valence electrons of atoms are distributed in the molecule. A Lewis structure does not necessarily have to depict the actual shape of the molecule or ion. But we can use it to deduce what the actual shape is.

Since atoms are always in motion, when we talk about shapes of molecules or polyatomic ions, we mean the shape based on the average location of the atoms.

14.9.1 VSEPR Theory

To determine the shape, we use a simple theory called *VSEPR*, which stands for *Valence Shell Electron Pair Repulsion*. The basic idea behind VSEPR is that regions of high electron density around each atom in the molecule tend to be oriented as far away from one another as possible. These regions of high electron density are often referred to as *electron domains* or *electron groups*. The justification for the idea is simple: electrons repel each other. Once we know how the electron domains around an atom are oriented, it becomes easy to imagine the shape of the molecule.

The first step in figuring out the shape of a molecule is to determine the steric numbers of atoms that are bonded to at least two other atoms.

14.9.2 Steric Number

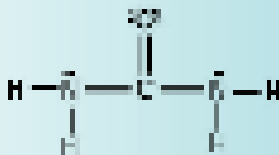
The term *steric number* refers to the number of electron groups around an atom. Once we have determined the steric number, we can imagine how these groups are oriented relative to each other.

To determine steric number,

- a single bond is counted as one group.
- a double bond is counted as one group.
- a triple bond is counted as one group, and
- a lone pair is counted as one group.

► Example

What are the steric numbers of C and N in the structure below?



Answer: The steric number of C is 3; for each of the two N atoms the steric number is 4.

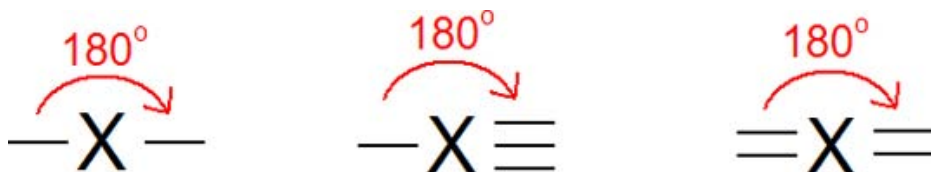
- There are 3 groups of electrons “sticking out” of the carbon atom: two single bonds and one double bond.
- There are four groups of electrons sticking out of each of the nitrogen atoms: 3 single bonds and 1 lone pair.

14.9.3 Predicting Bond Angles and Shapes Based on Steric Number

Once we have determined the steric number of an atom, we can predict the measure of angle formed by the electron groups sticking out of that atom.

Steric Number = 2. If there are only two groups of electrons sticking out of an atom, the two groups will be as far away from each other by being oriented 180° apart. The three bonding patterns where this occurs are illustrated in Figure 2. Since the two electron groups form a straight angle with the atom at the vertex, we say that the electron domain geometry around the atom is *linear*, or that the atom is a *linear center*.

Figure 2. Bonding Patterns for Steric Number=2



The shape of a triatomic molecule or ion is described as linear if the (nuclei of the) three atoms fall on a straight line; this happens if the steric number of the central atom is 2.

► Example

Based on the Lewis structures of H_2O and CO_2 , which molecule is linear: H_2O or CO_2 ?

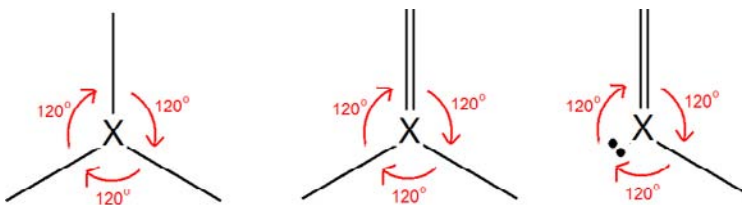


Answer: CO_2

- The steric number for C is 2, the two double bonds will be oriented 180° apart. Therefore, the three atoms CO_2 will be on a straight line.
- In the case of H_2O , the steric number of O is 4. There are four groups of electrons sticking out of the O atom: two single bonds and two lone pairs. The single bonds will not be oriented 180° apart.

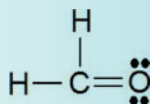
Steric Number = 3. Three groups of electrons will be as far from each other as possible if they are oriented 120° apart. Typical bonding patterns are shown in Figure 3. Since the three groups sticking out of the atom are on the same plane and are pointing towards the corners of a triangle, we say that the electron domain geometry around the atom is *trigonal planar*. Or we say that the atom is a *trigonal planar center*. Strictly speaking, the angles differ slightly from 120° when the groups are not identical. Lone pairs repel other groups more strongly than a single bond. A double bond repels other groups more strongly than a lone pair. Therefore, except for the case where all three groups are single bonds, the angles indicated in Figure 3 are approximate.

Figure 3. Bonding Patterns for Steric Number = 3



► Example

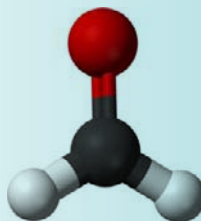
Consider the Lewis structure for formaldehyde.



Which angle would be larger: HCO or HCH?

Answer: The HCO angle will be larger.

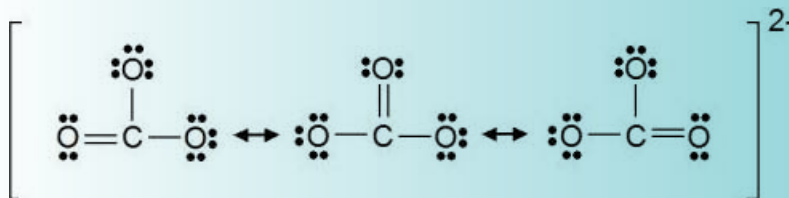
- The C atom is a trigonal planar center; its steric number is 3
- Because the steric number of C is 3, the groups will be oriented about 120° apart.
- Because the C=O bond is a double bond, it is “bulkier” and will “push” the single bonds closer to each other. The actual angles are: 121.27° for HCO and 117.46° for HCH. The 3-D model shown below resembles reality better than the Lewis structure above.



from <http://commons.wikimedia.org/wiki/File:Formaldehyde-3D-balls-A.png> [public domain]

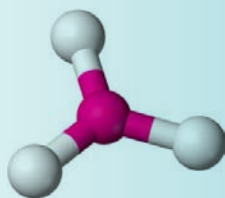
► Example

Describe the OCO bond angles in carbonate ion based on the Lewis structure shown below.



Answer: all OCO angles are exactly 120° .

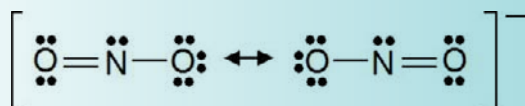
- The C atom is a trigonal planar center
- All three resonance structures have one C=O double bond and two C-O single bonds, suggesting that they are all equally significant. All three C-to-O bonds are, therefore, equivalent.
- The geometry of this ion is said to be of the type AX₃. The A stands for the central atom and the X₃ stands for three atoms bonded to A.
- The model below better resembles reality than the Lewis structure.



from <http://en.wikibooks.org/w/index.php?title=File:Trigonal-3D-balls.png&filetimestamp=20061212171212> (public domain)

► Example

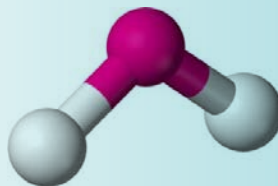
Describe the geometry of nitrite ion based on the Lewis structure shown below.



Answer:

- The N atom is a trigonal planar center since its steric number is 3; there are 3 groups of electrons sticking out of the N. The ONO bond angle is, therefore, expected to be very close to 120°.
- The ion can be described as bent. Any time there are only three atoms in a molecule or ion, the shape is either linear or bent. It is linear if the bond angle is 180°; otherwise, it is bent.
- The geometry of this ion is said to be of the type AX₂E. The A stands for the central atom, the X₂ stands for the two atoms bonded to A, and E stands for one lone pair.

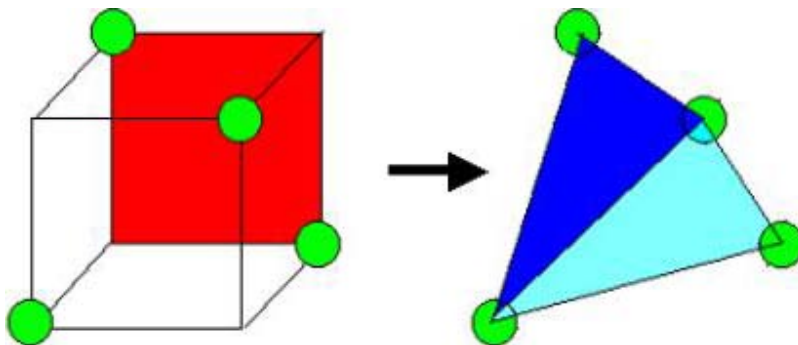
- The model below better resembles reality than the Lewis structure:



from <http://en.wikibooks.org/w/index.php?title=File:Bent-3D-balls.png&filetimestamp=20061212175343> (public domain)

Steric Number = 4. Four groups of electrons sticking out of an atom will be as far from each other as possible if they are oriented such that each one is pointing towards the corners of a regular *tetrahedron*. A regular tetrahedron is a perfectly symmetrical four-sided solid (tetra = four, hedron = side). To visualize a regular tetrahedron, imagine carving it out of a cube as shown in Figure 4. The corners indicated by the green circles are the corners of a tetrahedron; the solid carved out, which can be described as four equilateral triangles forming the sides of a pyramid, is a regular tetrahedron.

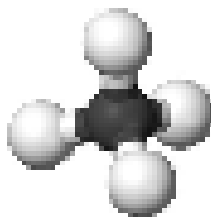
Figure 4. Carving Out A Regular Tetrahedron From A Cube



Another way to imagine a tetrahedron is to imagine three oranges forming a triangle on a table; put a fourth orange on top of the center of the three oranges; the four oranges would be the corners of a tetrahedron.

To imagine an atom with a steric number of 4, imagine it in the middle of the cube in Figure 4; the four groups of electrons will be directed towards the green circles. If there is an atom at the other end of each group, the molecule would look like Figure 5. The shape of the molecule is said to be *tetrahedral* and type AX_4 .

Figure 5. Model Of A Tetrahedral Molecule; Type AX_4

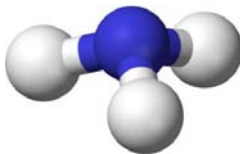


from <http://upload.wikimedia.org/wikipedia/commons/5/58/Methane-3D-balls.png> (public domain)

The angle between any pair of electron groups sticking out of a tetrahedral center is very close to 109.5° . There may be slight distortions if the groups are not all equivalent.

If one of the groups sticking out of a tetrahedral center happens to be a lone pair, as in Figure 6, the shape of the molecule or ion is called *triangular pyramidal* or *trigonal pyramidal*. The bond angles are close to, but slightly less than 109.5° , because the lone pair will repel the single bonds more strongly and push them a little closer together. The geometry of the molecule is said to be AX_3E : three atoms are bonded to the central atom, which has one lone pair.

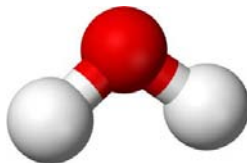
Figure 6. Triangular Pyramid; type AX_3E



from <http://en.wikibooks.org/w/index.php?title=File:Ammonia-3D-balls.png&filetimestamp=20070515220035> (public domain)

If two of the groups sticking out of a tetrahedral center happens to be lone pairs, as in Figure 7, then the shape of the molecule is called bent; there are only three atoms and they are not on a straight line. The bond angle is close to, but slightly less than, 109.5° because of the lone pair. The geometry of the molecule is said to be of type AX_2E_2 . Two atoms are bonded to the central atom, which has two lone pairs.

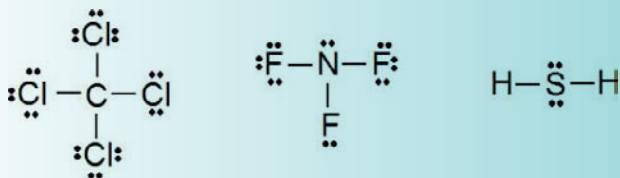
Figure 7. Bent Molecule; Type AX_2E_2



from <http://en.wikibooks.org/w/index.php?title=File:Water-3D-balls.png&filetimestamp=20070425083824> (public domain)

► Example

Describe the molecular geometry of H_2S , NF_3 , and CCl_4 based on their Lewis structures.

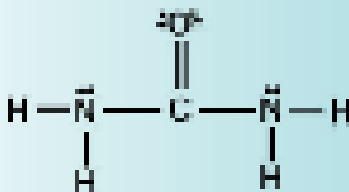


Answer:

- The central atom (S, N, and C) has a steric number of 4 and is a tetrahedral center in all three cases. The bond angles are expected to be close to 109.5° .
- Due to the lone pair, the shape of NF_3 is called trigonal pyramidal or triangular pyramidal.
- Due to the two lone pairs, the shape of H_2S is called bent.

► Example

Consider the Lewis structure shown below. Which bond angles are closest to 109.5° ?

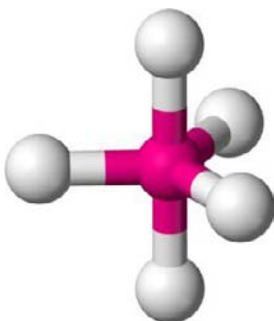


Answer: The angles that have N at the vertex, HNH and HNC.

- The steric number of both N atoms in this molecule is 4. There are four groups of electrons sticking out of each N atom. Therefore, these groups will be oriented about 109.5° apart.
- The steric number of C is 3; it is a trigonal planar center.

Steric Number = 5. If there are five groups of electrons sticking out of an atom, as illustrated in Figure 8, we say that the atom is a trigonal bipyramidal center. If there is an atom at the other end of each of these five groups, the shape of the molecule or ion itself is called trigonal bipyramidal; the geometry is said to be type AX_5 .

Figure 8. Trigonal Bipyramidal Geometry; Type AX_5

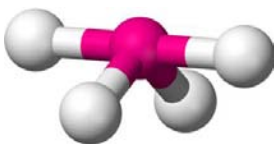


from <http://en.wikibooks.org/w/index.php?title=File:Trigonal-bipyramidal-3D-balls.png&filetimestamp=20061212170609> (public domain)

To visualize this geometry, imagine the central atom in the middle of the earth. Three of the groups will be sticking out towards corners of an equilateral triangle along the equator; hence these three groups, which would be 120° apart are called the equatorial groups. The two other groups are called the axial groups; imagine one is sticking up towards the north pole and the other group sticking out towards the south pole. Each axial group is perpendicular to each of the equatorial groups.

If one or more of the groups sticking out of trigonal bipyramidal center is a lone pair, they take up equatorial positions because these positions are, on average, farther from the other groups than the axial positions. The shapes of the molecules for types AX_4E , AX_3E_2 , and AX_2E_2 are shown in Figure 9.

Figure 9. Trigonal Bipyramidal Geometries, With Lone Pairs



AX_4E ; “see-saw” shape

from <http://en.wikibooks.org/w/index.php?title=File:Seesaw-3D-balls.png&filetimestamp=20070430211139> (public domain)



AX_3E_2 ; “T-shape”

from <http://en.wikibooks.org/w/index.php?title=File:T-shaped-3D-balls.png&filetimestamp=20070430211156> (public domain)



AX_2E_3 ; shape is linear

from <http://en.wikibooks.org/w/index.php?title=File:Linear-3D-balls.png&filetimestamp=20061212175353> (public domain)

► **Example**

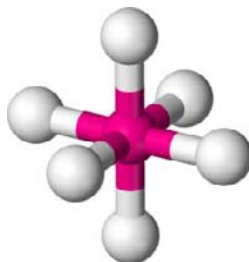
What is the shape of the SF_4 molecule?

Answer: see-saw

- The molecule has 34 valence electrons (6 from S; 7 from each of the four F atoms).
- The S atom is surrounded by four F atoms; each F atom is surrounded by an octet; this accounts for only 32 valence electrons ($4 \times 8 = 32$).
- The remaining two electrons are assigned to the S as a lone pair.
- Therefore, the molecular geometry is type AX_4E . The molecule has 4 S-F bonds and one lone pair on the central atom.

Steric Number = 6. Six groups of electrons sticking out of an atom stay as far apart as possible by taking mutually perpendicular orientations, as illustrated in Figure 10. If there is an atom at the end of each group, the shape of the molecule resembles an 8-sided solid with an equilateral triangle on each side. Thus, the shape is called octahedral (octa = 8, hedron = side). An atom with a steric number of 6 is called an octahedral center.

Figure 10. Octahedral Geometry; Type AX_6

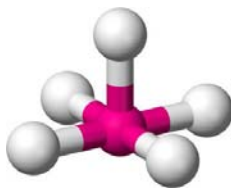


from <http://en.wikibooks.org/w/index.php?title=File:Octahedral-3D-balls.png&filetimestamp=20061212175404> (public domain)

For an octahedral center, as illustrated in Figure 11

- if one of the six groups happens to be a lone pair (type AX_5E), the shape of the molecule is called square pyramidal.
- if two of the six groups are lone pairs (type AX_4E_2), the shape of the molecule is square planar.
- if three of the six groups are lone pairs (type AX_3E_3), the shape of the molecule is T-shape.
- if four of the six groups are lone pairs (type AX_2E_4), the shape of the molecule is linear.

Figure 11. Octahedral Geometries With Lone Pairs



AX_5E ; square pyramidal

from <http://en.wikibooks.org/w/index.php?title=File:Square-pyramidal-3D-balls.png&filetimestamp=20070430211148> (public domain)



AX_4E_2 ; square planar

from <http://en.wikibooks.org/w/index.php?title=File:Square-planar-3D-balls.png&filetimestamp=20061212170229> (public domain)



AX_3E_3 ; “T-shape”

from <http://en.wikibooks.org/w/index.php?title=File:T-shaped-3D-balls.png&filetimestamp=20070430211156> (public domain)



AX_2E_4 ; linear

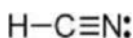
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TEST YOURSELF

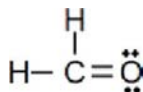
For answers and other study resources, see:

<http://i-assign.com/ebook/answers/chapter14.htm>.

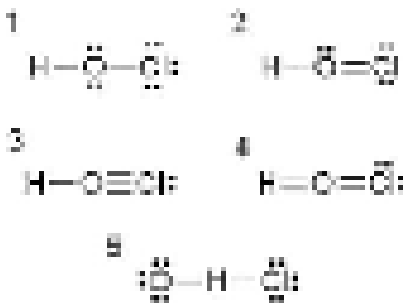
- How many electrons are shown in the Lewis symbol for a nitrogen atom?
A. 5 B. 7 C. 8 D. 14
- How many dots are shown in the Lewis symbol for a nitride ion?
A. 5 B. 7 C. 8 D. 14
- How many electrons are shared between C and N in the Lewis structure shown below?
A. 3 B. 4 C. 6 D. 8



- How many electrons are shared in the structure of formaldehyde shown below?
A. 4 B. 6 C. 8 D. 12



- Which of the structures shown is valid for HOCl?



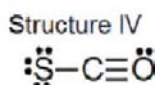
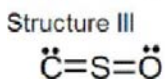
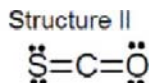
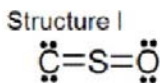
- Which of the following has a double bond?
A. HCl B. O_2^{2-} C. N_2 D. PF
- Which of the following acquires an octet by bonding with three hydrogen atoms?
A. Cl B. O C. C D. N

8. Consider the following partially-drawn structure of 2-butene (C_4H_8) where only the C atoms are shown:



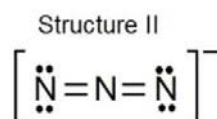
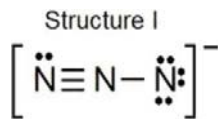
When this structure is completed following the octet/duet rule, how many hydrogen atoms are bonded to the first carbon?

- A. 1 B. 2 C. 3 D. 4
9. Which of the structures shown below are resonance structures?



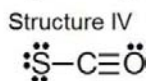
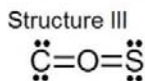
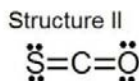
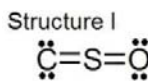
- A. Structures I and II B. Structures II and IV
 C. Structures I and III D. Structures II and III

10. Which of the Lewis structures shown below for azide ion (N_3^-) has a nitrogen atom with a formal charge of -2 ?

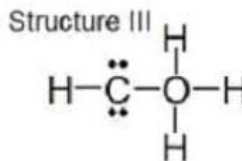
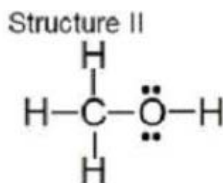
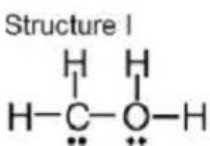


- A. Structure I only B. Structure II only C. Both structures D. neither structure

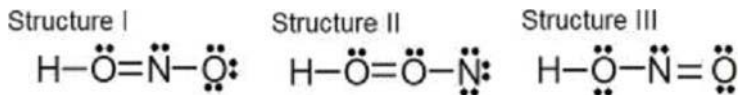
11. Which of the Lewis structures shown below has zero formal charges for *all* the atoms?



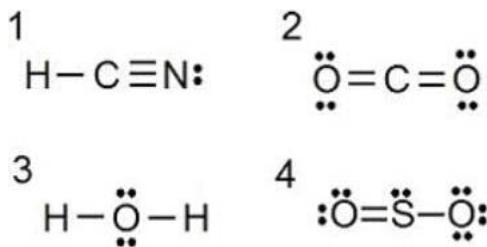
12. Based on formal charges, which of the Lewis structures shown below is the most likely structure of CH_4O ?



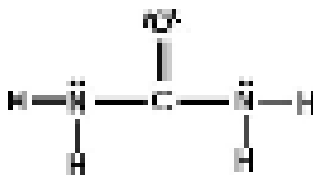
13. Based on formal charges, which of the Lewis structures shown below is the most likely structure of HNO_2 ?



14. Which of the following atoms must have an octet when sharing electrons with other atoms?
- A. N B. B C. P D. none of these
15. Which of the following atoms can have more than an octet of valence electrons when it shares electrons with other atoms?
- A. S B. N C. C D. H
16. Which of the structures below represent a linear molecule?



- A. 1 and 2 B. 2 and 3 C. 3 and 4 D. 1 and 4
17. Which molecule has the smallest bond angles?
- A. CH_4 B. NH_3 C. H_2O
18. For the molecule represented by the Lewis structure below,



the $\text{N}-\text{C}-\text{N}$ bond angle is closest to...

- A. 180° B. 109.5° C. 120°

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Quantum Mechanical Description of Molecules

Quantum mechanics can be applied to molecules in much the same way it is applied to atoms. The wavefunctions that describe electrons in a molecule are called *molecular orbitals*.

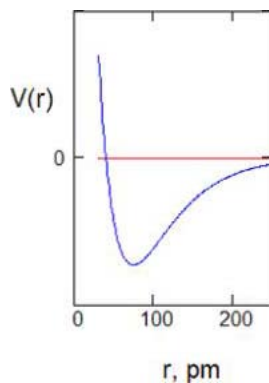
15.1 The Born Oppenheimer Approximation

In determining molecular wavefunctions, we use the Born-Oppenheimer approximation. In this approximation, the geometry of the molecule is first defined; the locations of the nuclei are fixed. Then, we solve the Schrodinger equation with this restriction (that the locations of the nuclei are fixed, not moving). The energies we get are called the *electronic energies*. For each possible geometry, we get a set of molecular orbitals and electronic energies. By examining the set of molecular orbitals for the most stable geometry (the *equilibrium geometry*), we can explain and/or predict properties of the molecule.

How is the equilibrium geometry determined? Consider a diatomic molecule. The geometry of a diatomic molecule is defined by specifying the internuclear distance (r), the distance between the nuclei. At a series of r values, we solve the Schrodinger equation; we get the allowed electronic energies for each r value. By adding the electronic energy to the potential energy of repulsion between the nuclei, we get a *molecular potential energy* function. Since we get a set of allowed energies for each r , we get a set of molecular potential energy functions for the molecule; of these, the one with lowest values corresponds to what is called the *ground electronic state* of the molecule. For diatomic molecules, the molecular potential energy for the ground electronic state resembles the blue curve in Figure 1. The equilibrium geometry corresponds to the distance where the molecular potential energy is at a minimum.

The potential energy curve in Figure 1 can be interpreted as follows. Imagine two positively charged nuclei (initially at infinite distance from each other) approaching each other. Since like charges repel, we would expect them to slow down, which means a decrease in kinetic energy and an increase in potential energy as they approach each

Figure 1. Molecular Potential Energy for a Diatomic Molecule



other. However, this is not what happens because the repulsions are alleviated by the presence of electrons between the nuclei. Electrons are negatively charged and exert attractive forces on the positively charged nuclei. As illustrated in Figure 1; the potential energy typically drops first, then increases once the nuclei get too close to each other. At very short distances, the repulsions between the nuclei can no longer be alleviated by the presence of the electrons and we see a sharp increase in potential energy. A balance between repulsive and attractive forces occurs at the equilibrium geometry.

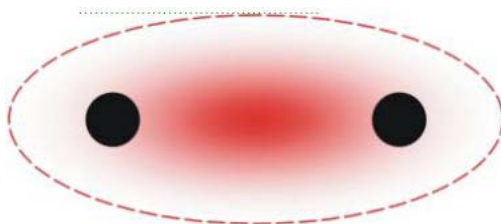
To facilitate interpretation of molecular orbitals, they are calculated in terms of the atomic orbitals (of the atoms in the molecule). Two popular ways of doing this are the LCAO-MO (linear combination of atomic orbitals - molecular orbital) and VB (valence bond) methods.

15.2 Valence Bond Method

The valence bond (VB) method accounts for bonding between two atoms in terms of overlapping atomic orbitals. What this means is that the functions associated with the atomic orbitals of bonded atoms are combined so that the resulting function (the molecular orbital) predicts a high probability of finding the electron between the two atoms. For two atoms linked by a single bond, valence bond theory proposes a “head on” overlap, called a *sigma bond*. Figure 2 illustrates what happens when 1s orbitals of two H atoms overlap. The red shading in Figure 2 is represents electron density; the probability of finding an electron is highest in areas where the shading is thickest.

For double bonds, the VB method proposes a sigma bond and a *pi bond*, which is illustrated in Figure 3. A pi bond is the result of the overlapping p orbitals on neighboring atoms. In a pi bond, there are two regions of high electron density: one on each side of the internuclear axis. The internuclear axis refers to the line that goes through both nuclei. For

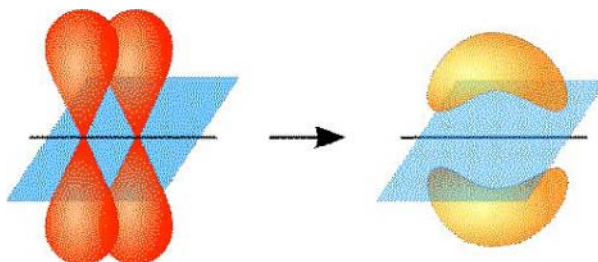
Figure 2. Sigma Bond



<http://en.wikibooks.org/wiki/File:Ligatio-covalens.jpg>

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Figure 3. Pi Bond



<http://en.wikipedia.org/wiki/File:Pi-Bond.svg>

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triple bonds, the VB method proposes a sigma bond and two pi bonds. In Figure 3, the pi bond is shown as having high electron densities above and below the internuclear axis; a second pi bond would have high electron densities in front of and behind the internuclear axis.

► Example

How many sigma and pi bonds are there between C and N in the HCN?



Answer: one sigma and two pi bonds.

15.2.1 Explaining Bond Angles

In polyatomic molecules, the concept of hybridization is invoked in order to make the idea of overlapping orbitals consistent with the observed molecular geometry.

Consider the acetylene molecule:



In this molecule, the H-C-C angle is 180° . This is explained by assuming that in the molecule, the C atom no longer has one 2s and three 2p orbitals. Instead, the 2s and one of the 2p orbitals are said to hybridize. It is now said to have two (2sp) hybrid orbitals and two 2p orbitals. In other words,

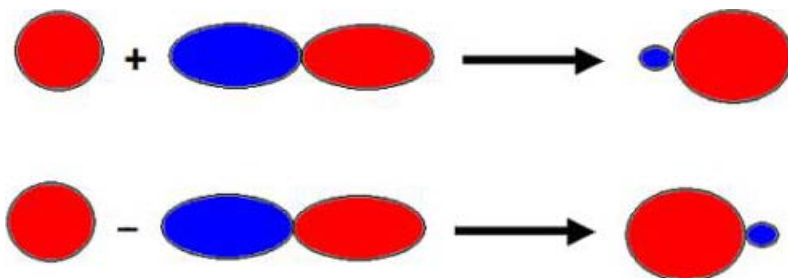
(2s, 2p, 2p, 2p) in free C atom
becomes

(2sp, 2sp, 2p, 2p) in the molecule

Remember that orbitals are mathematical functions that give us information about regions where electrons are likely to be found. For the two sp hybrids, the regions of high electron density are directed 180° apart, as illustrated in Figure 4. In Figure 4, the s orbital is represented by the red sphere and the p orbital is represented by the two lobes. The algebraic sign of the wavefunctions are color-coded (+ for red, - for blue). By adding the s and p orbitals together, we get constructive interference (the big red region) on one side of the nucleus and destructive interference (the small blue region) on the other side. The big red region corresponds to a region of high electron density. A similar result is obtained by subtraction, except that the region of high electron density is on the other side, 180° away.

In acetylene, one of the sp hybrid orbitals of C overlaps with the s orbital of H; we say that the H-to-C bond is an s-to-sp overlap. The other sp hybrid overlaps with an orbital from the other C. Since the other C is also a linear center, we expect it to also have a similar hybridization. Therefore, we expect one of the three C-to-C bonding pairs to be due to an sp-to-sp overlap. The s-to-sp and sp-to-sp overlaps are classified as sigma bonds. Since the C-to-C bond is a triple bond; the two other bonding pairs are said to be due to pi bonds, sideways overlap of p orbitals.

Figure 4. Construction of sp Hybrids

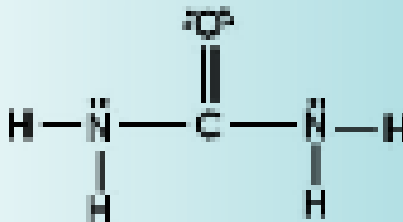


In general, we can correlate the steric number to the hybridization of the atom.

- If the steric number is 2 (linear center), the hybridization is sp .
- If the steric number is 3 (trigonal planar center), the hybridization is sp^2 .
- If the steric number is 4 (tetrahedral center), the hybridization is sp^3 .
- If the steric number is 5 (trigonal planar center), the hybridization is dsp^3 (or sp^3d).
- If the steric number is 6 (octahedral center), the hybridization is d^2sp^3 (or sp^3d^2).

► Example

According to the valence bond method, what hybrid orbitals overlap in the C-to-N bond in the urea? See structure below.



Answer: sp^2 -to- sp^3

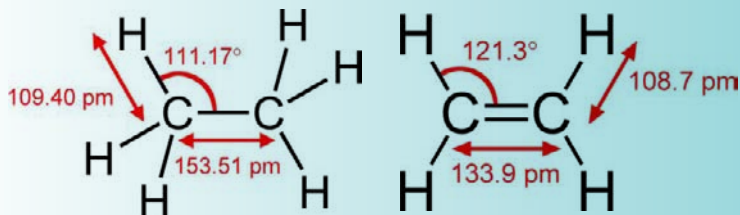
- The steric number of C is 3; therefore, the hybrid orbital it is using for each of its three sigma bonds is sp^2 .
- The steric number of N is 4; therefore, the four groups of electrons “sticking out” of it are in sp^3 hybrid orbitals.

15.2.2 Explaining Bond Lengths

Hybridization can be used to explain the effect of multiple bonding on bond lengths. For a hybrid orbital with a greater “p character,” the region of high electron density stretches out farther from the nucleus; sp^3 hybrids have higher p character than sp^2 hybrids; more p orbitals are used to construct the sp^3 hybrid orbital. This means that the greater the p character of the orbitals used for bonding, the longer the bond.

► Example

Explain why the C-to-C bond in H_3C-CH_3 is longer than that in $H_2C=CH_2$. Explain why the C-to-H bond is shorter than the C-to-C bond in both molecules.



Figures from <http://en.wikipedia.org/wiki/File:Ethane-staggered-CRC-MW-dimensions-2D.png> and <http://en.wikipedia.org/wiki/File:Ethylene-CRC-MW-dimensions-2D.png> (both public domain)

Answer:

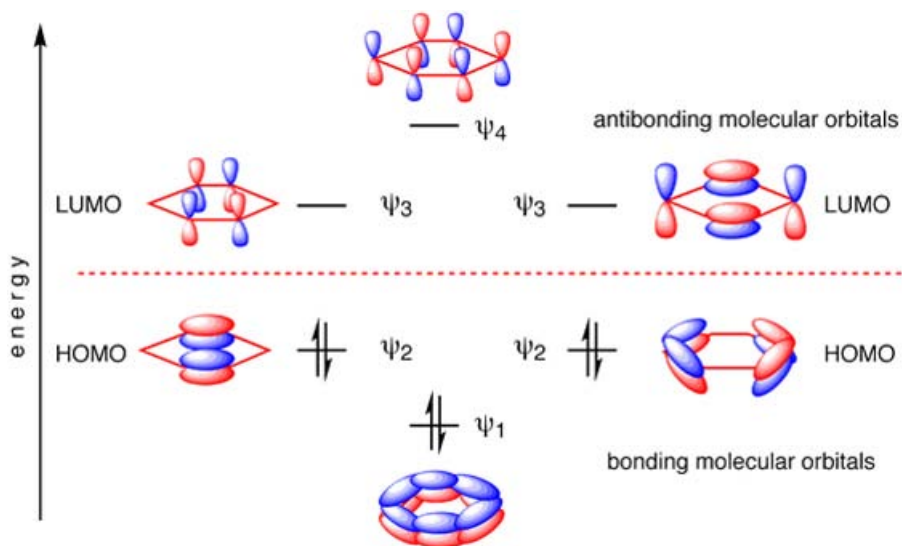
- Both C atoms in $\text{H}_3\text{C}-\text{CH}_3$ are sp^3 hybridized; the C-to-C bond in this molecule is due to an sp^3 -to- sp^3 overlap.
- Both C atoms in $\text{H}_2\text{C}=\text{CH}_2$ are sp^2 hybridized. The C-to-C sigma bond in this molecule is an sp^2 -to- sp^2 overlap.
- The C-to-C bond is longer for the sp^3 -to- sp^3 overlap compared to an sp^2 -to- sp^2 overlap. An sp^3 orbital has greater p character than an sp^2 orbital; the region of high electron density stretches out farther from the nucleus.
- The C-to-H bond is shorter than the C-to-C bond in $\text{H}_3\text{C}-\text{CH}_3$ because the H atom uses a 1s orbital to bond with C. An electron in a 1s orbital is closer to the nucleus than an electron in a 2s or 2p (or 2sp) orbital. Thus, the s-to- sp^3 overlap in the C-to-H bond is expected to be shorter than the sp^3 -to- sp^3 overlap in the C-to-C bond. A similar explanation applies to the bonds in $\text{H}_2\text{C}=\text{CH}_2$.

15.3 LCAO-MO Method

In the valence bond method, each molecular orbital is said to be localized; each molecular orbital describes a distribution of electron density that is significant only between a pair of atoms. In the VB method, the calculation is restricted so that each molecular orbital is constructed only from atomic orbitals of two neighboring atoms.

In the LCAO-MO method, the molecular orbitals can be *delocalized*. A molecular orbital in the LCAO-MO method can describe an electron distribution that is spread out over the entire molecule. Each molecular orbital is expressed in terms of the atomic orbitals of all the atoms in the molecule. Whether or not a particular atomic orbital

Figure 5. Molecular Orbitals of Benzene



<http://www.chemtube3d.com/BenzeneMOs.html>

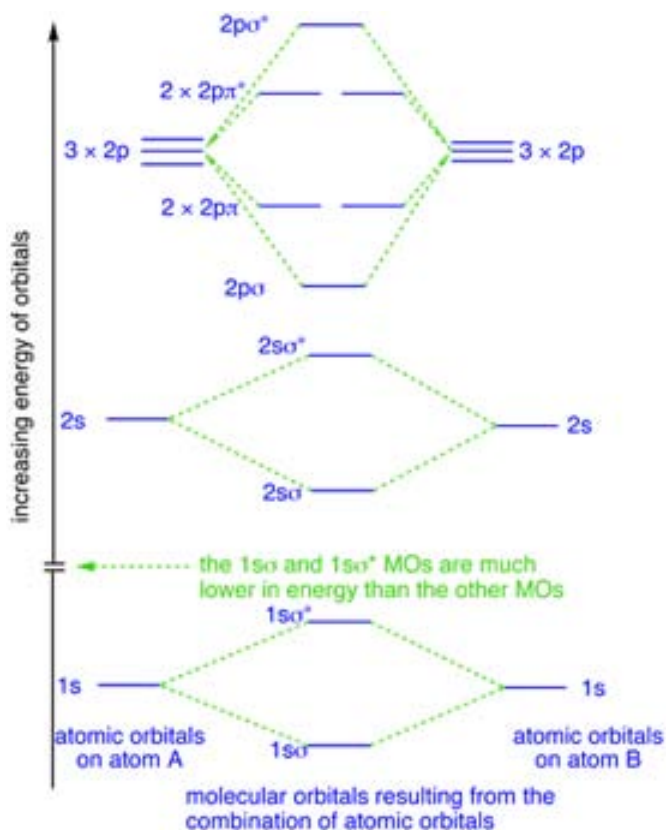
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“contributes” significantly to a molecular orbital depends on the symmetry properties of the molecule. Figure 5 illustrates six of the molecular orbitals of benzene (C_6H_6); the orbitals illustrated in the Figure are constructed from the six $2p_z$ orbitals (one from each of the C atoms in the molecule).

A *molecular orbital diagram* is used to summarize how molecular orbitals are related to the atomic orbitals. Such a diagram for F_2 is shown in Figure 6. The horizontal lines in middle of the diagram represent the energies of (an electron described by) the molecular orbitals; they are labeled with the names of the orbitals ($1s\sigma$, $1s\sigma^*$, etc). The horizontal lines on the sides represent the energies of atomic orbitals of the two atoms used to construct the molecular orbitals. The green dashed lines indicate which atomic orbitals have significant contributions to the construction of the pertinent molecular orbitals.

If the energy of a molecular orbital is less than that of the atomic orbitals from which it is constructed, it is said to be a bonding orbital; otherwise it is called an antibonding orbital. An asterisk (*) in the name of the orbital is used to indicate that

Figure 6. Molecular Orbitals of F_2



from <http://www.chemtube3d.com/orbitalsfluorine.htm>

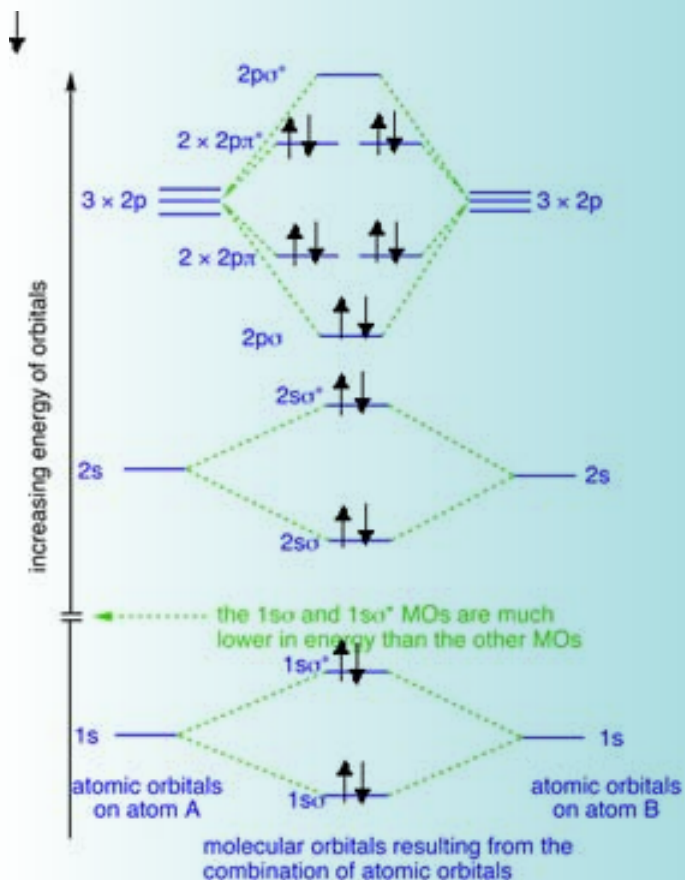
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the orbital is antibonding. Antibonding orbitals are associated with low electron densities between the nuclei. We assign electrons to molecular orbitals just like we do for atomic orbitals. We follow the Aufbau principle, Pauli's Exclusion principle, and Hund's rule to determine the ground state of the molecule. If more electrons are assigned to bonding orbitals, we expect the atoms to form a covalent bond. The bond order is calculated by taking the difference between the number of electrons in bonding orbitals and antibonding orbitals, then dividing the result by 2. A larger bond order implies a stronger bond.

► Example

Draw arrows to represent electrons on the molecular orbital diagram for F_2 . Determine the bond order.

Answer: We need to draw 18 arrows since each F atom has 9 electrons. From the diagram, we can see that we have 10 electrons in bonding orbitals and 8 in antibonding orbitals. The bond order is $(10-8)/2$, or 1.

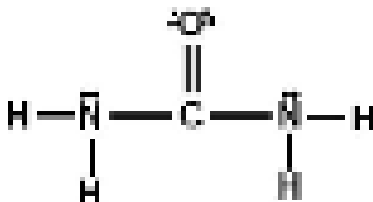


TEST YOURSELF

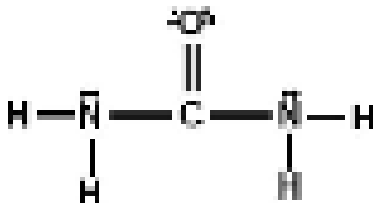
For answers and other study resources, see:

<http://i-assign.com/ebook/answers/chapter15.htm>.

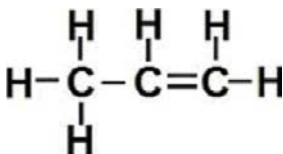
1. What type of orbital hybridization explains the linear electronic geometry around an atom with a steric number of 2?
A. sp B. sp^2 C. sp^3 D. sp^3d E. sp^3d^2
2. What is the hybridization of the valence orbitals of the carbon atom in the structure below?



- A. sp B. sp^2 C. sp^3 D. sp^3d
3. In the structure below, the sigma bond between which two atoms is due to an sp^2 -to- sp^2 overlap?



- A. C and O B. C and N C. N and H
4. In the structure below, which of these bonds is the longest?



- A. the C—C bond B. the C=C bond C. the C—H bond
5. Using Figure 6, explain why O_2 is paramagnetic. Determine the bond order.

Intermolecular Forces

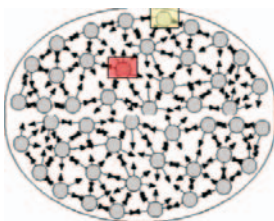
Properties of substances depend on how molecules interact. In this chapter, we examine the types of intermolecular forces and how they are manifested in properties of substances.


16.1 Explaining Properties of Substances

In general, properties like boiling point, melting point, viscosity, and surface tension depend on the strength of the attractive forces among the molecules. The stronger the attractive forces, the higher the boiling point, viscosity and surface tension of a liquid, and the higher the melting point of a solid.

Molecules gain more freedom of movement as a solid melts or as a liquid vaporizes. The amount of energy that they need to overcome the forces of attraction among them increases the stronger the forces are. Thus, they need to be heated to a higher temperature before they melt or boil. A higher temperature is indicative of higher molecular kinetic energies. *Viscosity* refers to the resistance of gases and liquids to flow. The stronger the attractive forces among the molecules of the gas or liquid, the more resistant they would be to flow. Surface tension refers to the energy needed to increase the surface area of a liquid. Molecules in the bulk are completely surrounded by other molecules and, therefore, experience stronger attractions compared to molecules on the surface. This is illustrated in Figure 1, where a molecule in the bulk is highlighted in red and a molecule on the surface is highlighted in yellow.

Figure 1. Representation of Liquid Droplet Molecules





To increase the surface area of a liquid requires movement of molecules from the bulk, where they experience stronger attractions, to the surface. This requires energy. The stronger the attractive forces, the more energy would be required, the higher the surface tension.

► Example

What can be said about attractive forces among water molecules compared to attractive forces among O_2 molecules based on the fact that water is a liquid at room temperature while O_2 is a gas?

Answer:

The fact that O_2 is a gas at room temperature means its boiling point is below room temperature. In fact, we can look it up and find it to be -183°C . This means O_2 is a liquid below -183°C and a gas above -183°C .

The fact that water is a liquid at room temperature means that its boiling point is above room temperature. In fact, we know that water boils at 100°C . It is a liquid below 100°C and is a gas above 100°C .

Since H_2O boils at a higher temperature than O_2 , we conclude that attractive forces among H_2O molecules must be stronger than attractive forces among O_2 molecules.

How two different substances interact can be explained by comparing:

- the strength of attraction among molecules of the same kind,
- and the strength of attraction among molecules of one substance with molecules of the other substance.

► Example

How do we explain why ethyl alcohol is soluble in water, but vegetable oil is not?

Answer:

When a substance is dissolved in another liquid, the particles that make up the substance (which is called the solute) disperse throughout the other liquid (which is called the solvent) and each one is surrounded by solvent molecules (“solvated”). The extent to which this happens depends on three factors:

1. strength of *solute-solute interaction*. The stronger the attraction among the particles that make up the solute, the less likely the solute particles will disperse.

2. strength of *solvent-solvent interaction*. The stronger the attraction among the particles that make up the solvent, the less likely that the solute particles can disperse among the solvent molecules.
3. strength of *solute-solvent interaction*. The stronger the attraction between a solute particle and a solvent particle, the more likely the solute will be solvated.

To explain the solubility of ethyl alcohol and vegetable oil in water, we compare 1 and 3 since our solvent is the same (water) in both cases. We can surmise that solute-solute interactions are stronger among vegetable oil molecules or that solute-solvent interactions are stronger between water molecules and ethyl alcohol molecules. These are, in fact, the conclusions we will reach if we examine the structures of ethyl alcohol, vegetable oil, and water.

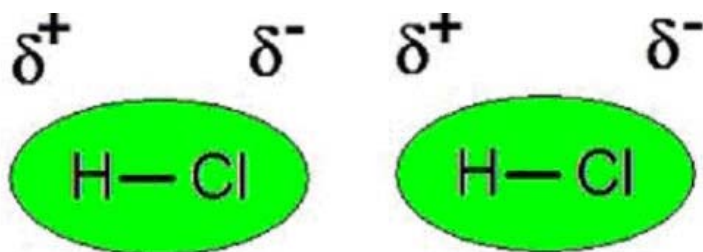
16.2 Types of Intermolecular Forces

The attractive forces between two molecules can be classified into two major types: *van der Waals forces* and *hydrogen bonding interactions*. Van der Waals forces can be further classified into: *dipole-dipole interaction*, *dipole - induced dipole interaction*, and *London dispersion forces*

16.2.1 Dipole-Dipole Interaction

Dipole-dipole interaction refers to the attractive force that is due to molecular polarity. It exists only between two polar molecules, as illustrated in Figure 2. The bond between H and Cl in HCl is polar. There is a higher electron density in the Cl end of the molecule; this end, we say, is partially negative. The H end of the molecule is partially positive and it is attracted to the partially negative end of a neighboring HCl molecule. The partial charges are indicated by the lower case delta (δ), followed by a + or - sign.

Figure 2. Dipole-dipole Interaction



How can we tell if a molecular is polar? A molecule is polar if:

- it has at least one polar bond,
- and if it has more than one polar bond, the polarities of the bonds do not cancel out due to symmetry.

How can we tell if a bond is polar? If the electronegativities of two atoms are different, then any sharing of electrons between the two atoms would be unequal. Shared electrons would spend more time closer to the more electronegative atom. We say that the bond is *polarized* towards the more electronegative atom. We could also say that the bond is *polar covalent*. We can refer to a table of electronegativities (as defined by Linus Pauling); see Table 1. On the Pauling scale, atoms are assigned electronegativities ranging from 0.7 for the least electronegative atom (Francium) to 4.0 for the most electronegative atom (Fluorine); on this scale, hydrogen has an electronegativity of 2.2. Note that electronegativity increases towards F. Metals have electronegativities **less than 1.9** and nonmetals have electronegativities larger than 2.1.

With the electronegativity difference between F and the least electronegative nonmetals being around 1.8 or 1.9, we can pretty much consider any pair of atoms that differ in electronegativity by 2.0 or higher as being in an *ionic bond*. Pauling defined the percent ionic character of a bond using the equation:

$$\% \text{ionic character} = 1 - \exp(-x^2/4),$$

where x is the electronegativity difference between the two atoms. Plugging in a value of 2.0 for x gives us:

$$\% \text{ionic character} = 1 - \exp(-2.0^2/4) = 0.63, \text{ or } 63\%$$

If we try to calculate the electronegativity difference between pairs of atoms, we will find that some pairs of atoms that we would normally consider as forming ionic bonds (metal + nonmetal) actually have an electronegativity difference less than 2.0. The bonds between these atoms should be considered as polar covalent bonds, not ionic.

Table 1. Electronegativities

H: 2.2							
Li: 1.0	Be: 1.6		B: 2.0	C: 2.5	N: 3.0	O: 3.5	F: 4.0
Na: 0.9	Mg: 1.3		Al: 1.6	Si: 1.9	P: 2.2	S: 2.6	Cl: 3.0
K: 0.8	Ca: 1.0		Ga: 1.8	Ge: 2.0	As: 2.2	Se: 2.6	Br: 2.8

*Data from A.L. Allred, *J. Inorg. Nucl. Chem.*, 17, 215 (1961).

The “metal + nonmetal = ionic bond” rule is just a rule of thumb. There are numerous exceptions. Indeed, an entire field of study (coordination chemistry) deals with covalently bonded transition metal atoms.

If the electronegativity difference between two atoms is larger than zero but less than 0.5, the polarization is negligible; the bond between them is classified as *polar covalent*, but *essentially nonpolar*.

► Example

Classify the bond between C and H, Li and I, Na and Cl, Na and Na.

Answer:

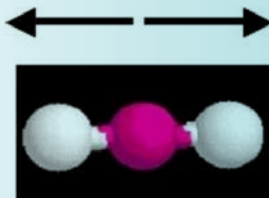
- For C and H: electronegativities of C and H are 2.5 and 2.2; difference = 0.3. The bond is polar covalent, but essentially nonpolar.
- For Li and I: electronegativities of Li and I are 1.0 and 2.7; difference = 1.7. The bond is polar covalent.
- For Na and Cl: electronegativities of Na and Cl are 0.9 and 3.0; difference = 2.1. The bond is ionic.
- For Na and Na: the electronegativity difference is obviously zero; bond is pure covalent. [Note: *metallic bonding* refers to bonding among atoms in a metallic solid; but the bond between just two atoms of a metallic element is pure covalent].

► Example

Explain why CO_2 is nonpolar.

Answer:

In CO_2 , the C-to-O bonds are both polar, but because the two C=O bonds are 180° apart, the polarities cancel out as shown below.



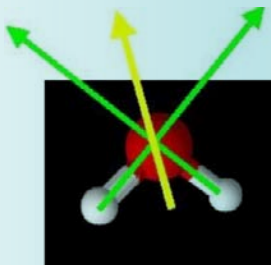
This is true for any molecule where all bonds are *identical* and have a perfectly symmetrical orientation (2 around a linear center, 3 around a trigonal planar, 4 around a tetrahedral center, 5 around a trigonal bipyramidal center, or 6 around an octahedral center). The molecule is nonpolar regardless of whether the bonds are polar or nonpolar.

► Example

Explain why a water molecule is polar.

Answer:

In water molecules, the polarities (shown in green in the figure below) do not cancel out. There is a net polarity towards the oxygen atom as indicated by the yellow arrow in the figure.



► Example

For which pair of molecules does dipole-dipole interaction exist: CO_2 and CO_2 , H_2O and H_2O ?

Answer: H_2O and H_2O .

Water molecules are polar molecules. CO_2 molecules, on the other hand, are nonpolar molecules.

16.2.2 London Dispersion Forces


London dispersion refers to the force of attraction that exists between *any* pair of molecules. It is due to temporary molecular polarizations, which occur because electrons are always moving. The larger the molecule, the more frequently the polarizations occur. Therefore, we expect attractions to be stronger among larger molecules.

► Example

For which of the following pairs of molecules are attractions due London dispersion forces strongest: CH_4 and CH_4 , C_2H_6 and C_2H_6 .

Answer: C_2H_6 and C_2H_6

We expect London dispersion forces to be stronger between larger molecules.



London dispersion is the *predominant* van der Waals interaction among most molecules. It is tempting to think that London dispersion would be weaker than dipole-dipole interaction since it is due to temporary polarizations, while dipole-dipole interactions are due to permanent polarization. However, calculations indicate that dispersion forces are just as strong among small polar molecules (like HCl) as dipole-dipole interaction. The apparent inconsistency is due to quantum effects.

16.2.3 Dipole - induced Dipole Interaction

Dipole - induced dipole interaction occurs between a polar molecule and a nonpolar molecule. When a nonpolar molecule comes close to the positive end of polar molecule, its electrons would be attracted toward the polar molecule causing temporary (or induced) polarization. Similarly, when a nonpolar molecule comes close to the negative end of a polar molecule, its electrons would be repelled, again causing temporary (or induced) polarization.

► Example

For which of the following pairs do we expect dipole - induced dipole interaction?

- A. H_2O and H_2O
- B. CO_2 and CO_2
- C. H_2O and CO_2

Answer: C

H_2O is a polar molecule. We expect two water molecules to have dipole-dipole as well as London dispersion forces between them. CO_2 is nonpolar; we expect the only interaction between two CO_2 molecules to be London dispersion. We expect dipole - induced dipole interaction to occur between H_2O (which is polar) and CO_2 (which is nonpolar).

16.2.4 Hydrogen Bonding Interaction

In a molecule, a hydrogen atom covalently bonded to a highly electronegative atom (F, O, or N) is almost stripped bare of electrons. This makes it strongly attracted to a *lone pair* of a highly electronegative atom (F, O, or N) in a neighboring molecule. The interaction is called hydrogen bonding.

Figure 3 illustrates hydrogen bonding interaction between two water molecules. The H atoms in water (like the H highlighted in green) are bonded to a highly electronegative atom (oxygen). Because it is almost stripped bare of electrons, it is strongly attracted to the lone pair of the oxygen atom (highlighted in purple) in the neighboring water molecule.

Figure 3. Hydrogen Bonding Interaction Between Two Water Molecules

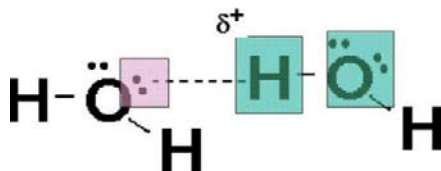
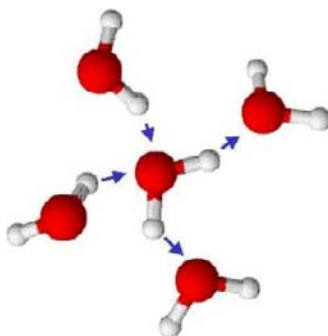


Figure 4. Extensive Hydrogen Bonding Interactions in Water



Hydrogen bonding interaction is much stronger than dipole-dipole interaction. For small molecules it is also stronger than London dispersion forces. Hydrogen bonding accounts for the unusually high boiling point of water. Water molecules are small; substances made of molecules of comparable size are gaseous at room temperature. For example, O₂ is a gas at room temperature, while water is a liquid even though H₂O molecules are smaller than O₂ molecules. One would expect London dispersion forces to be stronger among O₂ molecules. The “anomaly” is explained when one takes into account that water molecules are polar and capable of extensive hydrogen bonding as illustrated in Figure 4.

16.3 Ion-Molecule Interactions

Interaction of ions with molecules can be classified as *ion-dipole* interaction or *ion-induced dipole* interaction. Ion-induced dipole interaction involves ions and nonpolar molecules.

► Example

What type of interaction is involved between Na^+ ions and H_2O molecules when NaCl is dissolved in water?

Answer: Ion - dipole interaction

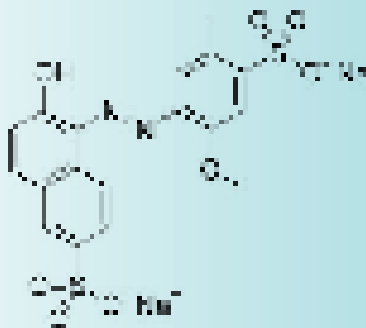
Na^+ is an ion and H_2O is a polar molecule. The oxygen end of the H_2O molecules will be attracted to the positively charged Na^+ ion.

16.4 Hydrophobicity and Hydrophilicity

Among large molecules (4 or more atoms besides hydrogen), London dispersion is the predominant type of interaction. However, if these molecules have N or O atoms, these atoms will typically have a lone pair that would be capable of hydrogen-bonding interaction with water molecules. Parts of the molecule near or at the N and O atoms are said to be hydrophilic (water-loving) and the rest of the molecule is said to be hydrophobic. The strong London dispersion forces between large molecules are mainly due to the hydrophobic parts and are, therefore, referred to as hydrophobic interactions. We see major applications of these ideas in biological sciences (lipid bilayers, hydrogen bonding in DNA molecules, enzyme-substrate interaction, etc.).

► Example

Consider the structure shown below for the molecule found in the food dye known as FD&C Red 40. Each unlabeled corner in the structure represents a C atom with enough H around it so that each C atom has an octet. Is this dye likely to be soluble or insoluble in water?



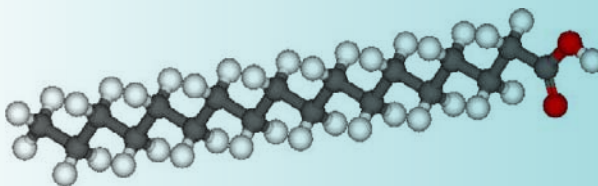
from http://en.wikipedia.org/wiki/File:Allura_Red_AC.png
(public domain)

Answer: Soluble

This molecule has numerous hydrophilic parts (O and N atoms) capable of hydrogen bonding with water molecules. This is a commonly used food dye; we find it in drink mixes like Kool-Aid™.

► Example

Consider the model shown below for a molecule of stearic acid, $C_{18}H_{36}O_2$. Based on this information, is stearic acid likely to be soluble or insoluble in water?



from [http://en.wikipedia.org/wiki/File:Octadecanoic_acid_\(stearic\).png](http://en.wikipedia.org/wiki/File:Octadecanoic_acid_(stearic).png)

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Answer: Insoluble

Most of the molecule is hydrophobic. The only hydrophilic part is shown in red (the oxygen atoms). Stearic acid is an example of a fatty acid and is found in animal fats and vegetable oils.



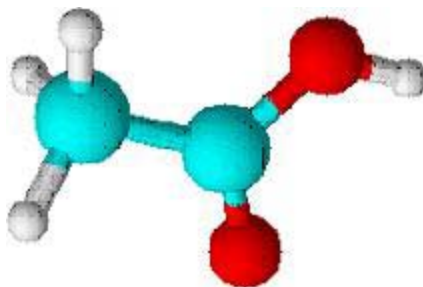
TEST YOURSELF

For answers and other study resources, see:

<http://i-assign.com/ebook/answers/chapter16.htm>.

- Which of the following has the highest electronegativity?
A. Na B. Br C. F
- Which type of element has the lowest electronegativity?
A. a metal B. a nonmetal C. a metalloid
- Which pair of atoms would form a bond where the polarity is directed towards the first atom?
A. C and C B. H and F C. O and C D. I and Cl
- Which pair of atoms would form a polar covalent but essentially nonpolar bond?
A. N and N B. H and C C. Na and Cl D. Be and I
- Which of the following is/are true?
1) A nonpolar molecule can have polar bonds.
2) A molecule with no polar bonds is nonpolar.
A. 1 only B. 2 only C. both D. neither
- Which of the following molecules is polar?
A. H_2O B. BF_3 C. CH_4 D. PF_5
- For which pair of molecules does dipole-dipole interaction occur?
A. H_2O and CO_2 B. H_2O and HF C. CO_2 and CO_2 D. CH_4 and CO_2
- For which pair of molecules is London Dispersion strongest?
A. H_2O and H_2O B. H_2O and H_2S C. H_2S and H_2S
- Which of the following has the lowest boiling point?
A. O_2 B. F_2 C. Cl_2

10. Which of the following explains why the melting point of iodine is higher than that of iodine chloride?
- A. London dispersion forces are stronger among I_2 molecules, which are larger and more polarizable
 - B. ICl molecules are capable of dipole-dipole interaction, whereas I_2 molecules are not
 - C. Both
 - D. Neither
11. How many atoms in the acetic acid molecule (CH_3COOH) are capable of hydrogen bonding interaction with water molecules?
- A. 1
 - B. 2
 - C. 3
 - D. 4



12. Which type of intermolecular forces is present between any pair of molecules?
- A. London dispersion forces
 - B. dipole-dipole interaction
 - C. hydrogen bonding interaction
13. Which of the following is least soluble in water?
- A. NH_3
 - B. HF
 - C. CH_4

The Mole Concept

Because atoms, ions, and molecules are very, very small, it is convenient to count them in groups called *moles*.

17.1 Counting by Moles

A mole (officially abbreviated **mol**) is a *group count*, just like a dozen. While a dozen count is exactly equal to twelve, a mole count is exactly equal to *Avogadro's number*. Avogadro's number, N_A , is a 24-digit exact, whole number. We do not yet know all 24 digits. The first six digits are known to be 6, 0, 2, 2, 1, and 3; these are followed by 18 more digits. For most purposes, it is sufficient to express Avogadro's number to three significant digits; it is approximately equal to 6.02×10^{23} , or about 602 billion trillion.

► Example

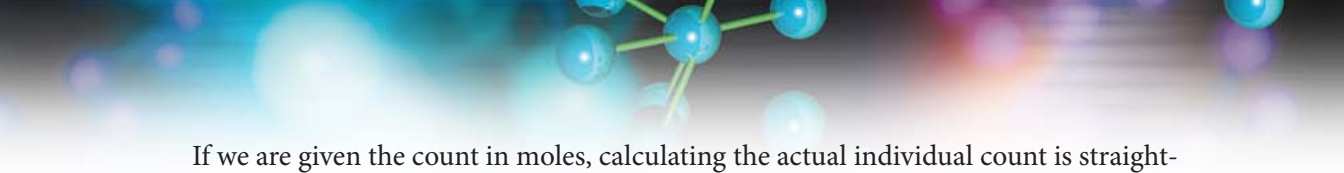
Which has more atoms: 1 mol ^{12}C or 1 mol ^{13}C ?

Answer:

neither, the number of atoms in either case is the same.

This is like asking “which has more people: 1 dozen children or 1 dozen adults?” We expect 1 mol of C-13 to weigh more than 1 mol C-12, just as we expect 1 dozen adults to weigh more than 1 dozen children. But as long as the question involves *counting*, they are the same.

The definition of Avogadro's number. Avogadro's number is equal to the number of atoms in exactly 12 grams of carbon-12. Imagine we have a sample that is exactly 12 grams, and each and every atom in the sample is C-12. If we could count all the atoms in that sample, the number we get is defined as Avogadro's number. We could also say that one mole of carbon-12 is defined to have a mass of exactly 12 grams. The unit for Avogadro's number is mol^{-1} (which is read as “per mole”). For clarity, it is often useful to explicitly specify what is being counted, as in *atoms mol⁻¹*, or *ions mol⁻¹*, or *molecules mol⁻¹*.



If we are given the count in moles, calculating the actual individual count is straightforward. Essentially, we multiply the mole count by Avogadro's number to get the individual count. If n is the mole count and N is the individual count, we multiply n by Avogadro's number (N_A) to get N :

$$N = n N_A$$

The same basic idea is involved when we convert dozens to an individual count. If we have 2 dozen eggs, we multiply 2 by 12 to get the individual count of 24 eggs.

$$2.0 \cancel{\text{ doz}} \left(\frac{12 \text{ eggs}}{1 \cancel{\text{ doz}}} \right) = 24 \text{ eggs}$$

► Example

Consider a sample containing 2.0 moles of CO_2 molecules. How many CO_2 molecules are there in this sample?

Answer: 1.2×10^{24} molecules

$$\begin{aligned} N &= n N_A = (2.0 \times 10^{23} \cancel{\text{ mol}}) (6.02 \times 10^{23} \text{ molecules } \cancel{\text{ mol}^{-1}}) \\ &= 1.2 \times 10^{24} \text{ molecules} \end{aligned}$$

We can also treat this question as a unit conversion problem; we can set up the calculation as follows:

$$2.0 \cancel{\text{ mol}} \times \left(\frac{6.02 \times 10^{23} \text{ molecules}}{1 \cancel{\text{ mol}}} \right) = 1.2 \times 10^{24} \text{ molecules}$$

Note that we rounded off Avogadro's number to only 3 significant digits since the amount to be converted (2.0 mol) is only given to two significant digits.

What if we want to convert individual count to group count? All we have to do is divide the number of eggs by 12 to get the dozen count. Similarly, if we know the individual count (N), we just divide it by the Avogadro's number (N_A) to get the mole count (n).

$$n = \frac{N}{N_A}$$

► Example

How many moles of Mg atoms are there in a sample containing 3.00×10^{23} atoms of Mg.

Answer:

$$n = \frac{N}{N_A} = \frac{3.00 \times 10^{23} \text{ atoms}}{6.022 \times 10^{23} \text{ atoms mol}^{-1}} = 0.498 \text{ mol}$$

Note that we used 4 significant digits for Avogadro's number here since the amount that needs to be converted has 3 significant digits. We can also treat this as a conversion problem and set up the calculation as follows:

$$3.00 \times 10^{23} \text{ atoms} \times \left(\frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} \right) = 0.498 \text{ mol}$$

17.2 Counting Atoms in Molecules

To count atoms of an element in a molecule, we make use of the fact that subscripts in a formula are counting numbers; they tell us how many atoms of a given element are present in one formula unit. Therefore, they also tell us how many moles of atoms of a given element are present in a mole of formula units.

► Example


How many O atoms are in 2.0 mol CO_2 ?

Answer: 4.0 mol

The subscripts in the formula tell us that there are **2 atoms of O** in one molecule of CO_2 . Therefore, there are 2 moles of O in 1 mole of CO_2 and we can treat this as a simple conversion problem. We set up the solution as follows:

$$2.0 \text{ mol CO}_2 \times \left(\frac{2 \text{ mol O}}{1 \text{ mol CO}_2} \right) = 4.0 \text{ mol O}$$

We multiply the number of molecules, 2.0 moles of CO_2 , by a conversion factor that relates moles of O to moles of CO_2 .



Essentially, what we are doing is multiplying the moles of molecules by the subscript of the atom we are interested in. If we need the individual count, we simply multiply the mole count by Avogadro's number.

► Example

How many atoms are in 2.0 mol CO₂?

Answer:

A molecule of CO₂ consists of three atoms — one C atom and two O atoms. Since a mole is just a group count, we can say that a mole of CO₂ molecules consists of three moles of atoms — one mole of C and two moles of O. In other words: there are 6.0 moles of atoms in 2.0 moles of CO₂ molecules.

$$2.0 \text{ mol CO}_2 \times \left(\frac{3 \text{ mol atoms}}{1 \text{ mol CO}_2} \right) = 6.0 \text{ mol atoms}$$

17.3 Counting Ions in Ionic Compounds

To count ions in a sample of an ionic compound, we make use of the fact that the subscript of the ion in the formula tells us how many ions are in one formula unit of the compound. Therefore, the subscript also tells us how many moles of ions are in one mole of formula units.

► Example

How many cations are in 3.0 moles of ammonium sulfate?

Answer. 6.0 mol

The formula of ammonium sulfate is (NH₄)₂SO₄. This means that one formula unit of the compound consists of **two** cations (the subscript for ammonium in the formula is **2**) and one anion (the implied subscript for sulfate in the formula is 1). This also means that one mole of ammonium sulfate is made up of 2 moles of ammonium ions and 1 mole of sulfate ions. Therefore:

$$3.0 \text{ mol (NH}_4)_2\text{SO}_4 \times \left(\frac{2 \text{ mol NH}_4^+}{1 \text{ mol (NH}_4)_2\text{SO}_4} \right) = 6.0 \text{ mol NH}_4^+$$



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<http://i-assign.com/ebook/answers/chapter17.htm>.

- Which of these is false?
 - A mole of atoms contains exactly 6.02×10^{23} atoms
 - The exact number of molecules in one mole of molecules is equal to Avogadro's number
 - The exact number of ions in one mole of ions is equal to Avogadro's number
 - None of the above
- Which has more atoms?
 - 1 mole of Mg-24
 - 1 mole of Mg-26
 - neither
- Which has more molecules?
 - 1 mole of SO_2
 - 1 mole of SO_3
 - neither
- How many atoms of carbon are in a 2.50 mol sample of carbon?
 - 1.51×10^{24}
 - 30.0
 - 4.15×10^{-22}
- How many moles of O_2 molecules are in a sample containing 3.0×10^{22} O_2 molecules?
 - 2.0 mol
 - 1.06×10^{-21} mol
 - 0.050 mol
- How many atoms of oxygen are in 1.50 mol CO_2 ?
 - 1.50 mol
 - 0.300 mol
 - 3.00 mol
 - 0.750 mol
- Which has more atoms?
 - 3.0 mol SO_2
 - 2.0 mol SO_3
 - neither
- Which has more O atoms?
 - 3.0 mol SO_2
 - 2.0 mol SO_3
 - neither
- How many cations are in 2.00 mol Na_3PO_4 ?
 - 0.667 mol
 - 6.00 mol
 - 0.500 mol
 - 1.00 mol
- How many moles of nitrate ions are in a mixture of 2.00 mol calcium nitrate and 1.50 mol aluminum nitrate?

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Molar Mass

Since atoms, molecules and ions are too small and too numerous for us to actually count one by one, we count them in groups called moles. To do this, we need to know the mass of a mole of atoms (or ions or molecules); if we do, then all we would have to do is weigh a sample and do a simple calculation to determine the number of moles.

18.1 Determining Molar Mass

The term *molar mass* refers to the mass per mole. The unit for molar mass is g/mol or g mol^{-1} . By definition:

- one atom of carbon-12 has a mass of exactly 12 u.
- one mole of carbon-12 atoms has a mass of exactly 12 grams.

A consequence of these two definitions is that:

if something has a mass of X atomic mass units, then a mole of that something has a mass of X grams.

This also means that an Avogadro number of atomic mass units is equivalent to one gram; to three significant digits:

$$6.02 \times 10^{23} \text{ u} = 1.00 \text{ g}$$

or, dividing both sides by 6.02×10^{23} , we can show that:

$$1.00 \text{ u} = 1.66 \times 10^{-24} \text{ g}$$

► Example

The mass of one proton is 1.00 u. What is the mass of one mole of protons?

Answer: 6.02×10^{23} u, or 1.00 g

► Example

Calculate the mass of one C-12 atom in g.

Answer: 1.99×10^{-23} g

Since the mass of one C-12 atom is exactly 12 u, then, to three significant digits, the mass in grams is (using factor label):

$$(12 \cancel{\mu}) \times \left(\frac{1.66 \times 10^{-24} \text{ g}}{1.00 \cancel{\mu}} \right) = 1.99 \times 10^{-23} \text{ g}$$

or (using algebraic substitution):

$$12 \text{ u} = 12 (1.66 \times 10^{-24} \text{ g}) = 1.99 \times 10^{-23} \text{ g}$$

► Example

What is the molar mass of C-12?

Answer: exactly 12/mol or 12 g mol^{-1}

By definition, one mole of C-12 has a mass of exactly 12 g.

► Example

If we look up the mass of a C-13 atom, we find that it is 13.0033548 u. What is the molar mass of C-13?

Answer: 13.0033548 g/mol, or $13.0033548 \text{ g mol}^{-1}$


For most purposes, it is sufficient to round off molar masses to four significant figures; in the case of C-13, the molar mass is 13.00 g/mol. In general, the numerical value of the molar mass of a specific isotope should be close to a whole number (the mass number).

► Example

Which isotope has a molar mass of 34.97 g/mol: Cl-35 or Cl-37?

Answer: Cl-35

To the nearest whole number, 34.97 g/mol is 35 g/mol. Indeed, we can look it up and find it to be so.



Typical periodic tables will not have molar masses listed for specific isotopes. The numerical value of the average mass of the atoms, the *atomic weight*, is typically given in a periodic table. This is also the numerical value of the molar mass of a naturally-occurring sample of the element.

► Example

The atomic weight for Cl is given in a typical periodic table as 35.45. What does this mean?

Answer: This means that the average mass of Cl atoms in a naturally-occurring sample is 35.45 u, and the molar mass of a naturally-occurring sample of Cl atoms is 35.45 g/mol.

► Example

What is the molar mass of C?

Answer: unless otherwise specified, we have to assume that we're dealing with a naturally-occurring sample. We can look up this value from a periodic table and find that it is 12.01 g/mol.

► Example

What is the molar mass of oxide ions (O^{2-})?

Answer: 16.00 g/mol

This is essentially the same as the molar mass of O atoms, which we can look up and find to be 16.00 g/mol. An oxide ion has two more electrons compared to a neutral oxygen atom; we would expect its molar mass to be larger. But electrons hardly contribute to the total mass of an atom, so we can generally ignore charges when calculating molar masses.

► Example

What is the molar mass of H_2O ?

Answer: 18.02 g/mol

A mole of H_2O molecules contains two moles of H and one mole of O atoms. Referring to a periodic table, we find that:

- The mass of 2 moles of H is 2×1.008 g.

- The mass of 1 mole of O is 1×16.00 g. Adding up the masses gives us a total of 18.02 g for one mole of H_2O . Therefore, the molar mass of H_2O is 18.02 g/mol.

NOTE: most modern Chemistry textbooks have standardized on the term “Molar Mass” but other terms are still being used. These other terms include: (average) atomic mass, atomic weight, gram atomic weight, gram atomic mass, formula weight, gram formula weight, molecular mass, molecular weight, gram molecular weight, and gram molecular mass. There are subtle differences in the meanings of these terms, but numerically, they are all the same.

18.2 Counting by Weighing

Knowing the molar mass of a substance allows us to count the atoms, molecules or ions in any sample of that substance by simply weighing the sample. If we know that the mass of one mole of something is MM, then the mass (m) of n moles is:

$$m = n \text{ MM}$$

Dividing both sides of this equation by n, we can show that the number of moles (n) is just equal to the mass divided by the molar mass:

$$n = \frac{m}{\text{MM}}$$

► Example

What is the mass of 2.0 mol H_2O ?

Answer: 36 g

To convert moles to mass, we need to know the molar mass. In an earlier example, we found the molar mass of H_2O to be 18.02 g mol⁻¹. Therefore, the mass of 2.0 mol H_2O is:

$$m = n \text{ MM} = (2.0 \text{ mol}) (18.02 \text{ g mol}^{-1}) = 36 \text{ g}$$

It is often useful to be more descriptive when specifying units. In this case, we can write our units as “g H_2O ” and “mol H_2O .”

$$2.0 \text{ mol H}_2\text{O} \times \left(\frac{18.02 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}} \right) = 36 \text{ g H}_2\text{O}$$

Note that mol^{-1} means mol in the denominator. We can think of molar mass as a conversion factor to change moles to grams. If we want to change grams to moles instead, we can just flip this conversion factor, as in the next example.

► Example

How many molecules are in a 36.04 g sample of water?

Answer: 2.000 mol

Earlier, we found the molar mass of water to be 18.02 g/mol. So:

$$\frac{36.04 \cancel{\text{g}}}{18.02 \cancel{\text{g}} \text{ mol}^{-1}} = 2.000 \text{ mol}$$

or:

$$36.04 \cancel{\text{g H}_2\text{O}} \times \left(\frac{1 \cdot \text{mol H}_2\text{O}}{18.02 \cancel{\text{g H}_2\text{O}}} \right) = 2.000 \text{ mol H}_2\text{O}$$

We can multiply this answer by Avogadro's number if we want an individual count. An answer in moles is a perfectly acceptable way of answering a "how many" question. A mole is a group count, just like a dozen. Saying you have 2 dozen eggs is the same thing as saying you have 24 eggs.

18.3 Counting by Measuring Volume

Substances that exist as liquids under ordinary conditions are not always easy to weigh. This is especially true for liquids that are volatile, toxic, or corrosive. It would be more convenient to measure their volume in the laboratory. If we know the density of a pure liquid, then we can do volume-to-mass conversion so that we figure out the moles of substance in our sample. The density is defined as the ratio of the mass (m) to volume (V).

$$d = \frac{m}{V}$$

► Example

The density of carbon tetrachloride, CCl_4 , is 1.59 g/mL . How many moles CCl_4 are present in a 200.0 mL sample of this liquid?

Answer: 2.07 mol

First, we rearrange the defining equation for density to solve for the mass:

$$m = V d = (200.0 \text{ mL}) (1.59 \text{ g mL}^{-1}) = 318 \text{ g}$$

Then, we convert grams to moles. For this, we need the molar mass of CCl_4 , which is 153.8 g/mol :

$$n = \frac{m}{M} = \frac{318 \text{ g}}{153.8 \text{ g mol}^{-1}} = 2.07 \text{ mol}$$

or:

$$318 \text{ g CCl}_4 \times \left(\frac{1 \text{ mol CCl}_4}{153.8 \text{ g CCl}_4} \right) = 2.07 \text{ mol CCl}_4$$

Ofentimes, we know how many moles of a liquid substance we need. To figure out what volume to dispense, we first convert moles to mass, then figure out the volume from the mass.

► Example

An organic synthesis experiment calls for 0.200 mol of ethanol, $\text{C}_2\text{H}_5\text{OH}$. The density of ethanol is 0.785 g/mL . What volume of ethanol do we need?

Answer: 11.7 mL

First, we figure out the mass of ethanol that we need. For this, we need the molar mass, which is 46.07 g/mol .

$$m = n \text{ MM} = (0.200 \text{ mol}) (46.07 \text{ g mol}^{-1}) = 9.214 \text{ g}$$

Next, we calculate the volume by rearranging the defining equation for density; solving for V , we get:

$$V = \frac{m}{d} = \frac{9.214 \text{ g}}{0.785 \text{ g mL}^{-1}} = 11.7 \text{ mL}$$

There should only be three significant digits in our calculated mass, but we kept an extra digit since we needed to carry it over to another calculation.

18.4 Amount of Element in a Compound

The *percent composition* of a compound refers to a listing of the amounts of all the elements present in the compound, with each amount expressed as percentage of the total mass. The percentage of an element is simply equal to the mass of the element present in a pure sample of the compound, divided by the mass of the sample, multiplied by 100%. Since compounds have definite composition, we should get the same value regardless of the mass of sample, provided the sample is pure. It is convenient to just use the mass of one mole to do these calculations.

▶ Example

Determine the percent composition of NO_2 .

Answer: 30.45% N, 69.55% O

One mole of NO_2 contains:

- one mole of N, or 14.01 g
- two moles of O, or $2 \times 16.00 \text{ g} = 32.00 \text{ g}$

for a total mass of 46.01 g. Therefore:

$$\% \text{N in } \text{NO}_2 = \frac{\text{mass}_\text{N}}{\text{mass}_\text{NO}_2} \cdot 100 \% = \frac{14.01 \cancel{\text{g}}}{46.01 \cancel{\text{g}}} \cdot 100 \% = 30.45 \%$$

$$\% \text{O in } \text{NO}_2 = \frac{\text{mass}_\text{O}}{\text{mass}_\text{NO}_2} \cdot 100 \% = \frac{32.01 \cancel{\text{g}}}{46.01 \cancel{\text{g}}} \cdot 100 \% = 69.55 \%$$

Note that percentages should add up to 100%, so we could have solved for %O by subtracting the % NO_2 from 100%.

To calculate the amount of an element in a sample of a compound, we simply multiply the mass of the compound by the percentage of the element.

▶ Example

How much oxygen can be obtained from 50.0 g of NO_2 ?

Answer: 34.8 g

In the previous example, we saw that the percentage of O in NO_2 is 69.55%. Therefore, the amount of oxygen present in 50.0 g of NO_2 is 69.55% of 50.0 g.

$$50.0 \text{ g} \times 69.55\% = 50.0 \text{ g} \times 0.6955 = 34.8 \text{ g}$$

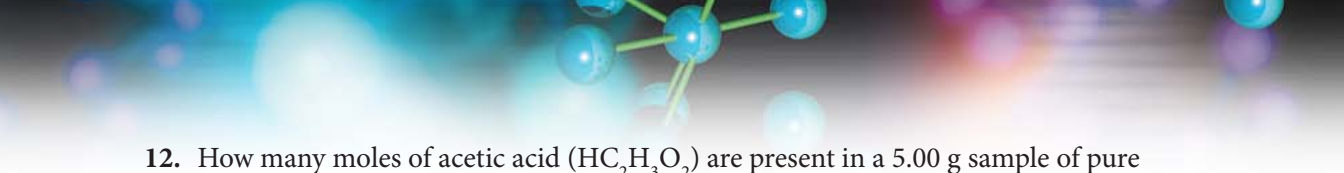


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- To two significant figures, the mass of an electron is 9.1×10^{-31} kg. Convert this to atomic mass units.
- Which of the following is a plausible mass for a diatomic molecule?
A. 5.32×10^{-23} g B. 2.33×10^{-31} kg C. 160 g D. 1.66×10^{-21} g
- Which of the following has a molar mass of 60.06 g/mol?
A. CaCO_3 B. $\text{HC}_2\text{H}_3\text{O}_2$ C. none of these
- What is the molar mass of NH_3 ?
A. 8.00 g/mol B. 10.00 g/mol C. 15.02 g/mol D. 17.03 g/mol
- What is the molar mass of $\text{Ca}(\text{NO}_3)_2$?
A. 70.09 g/mol B. 82 g/mol C. 164.10 g/mol
- What is the molar mass of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$?
A. 160.7 g/mol B. 322.9 g/mol C. 72.05 g/mol
- What is the mass of one mole of CO_2 ?
A. 28.01 g B. 30.01 g C. 44.01 g
- What is the mass of 2.00 mol NH_3 ?
A. 20.0 g B. 34.1 g C. 30.0 g
- If an experiment calls for 0.500 mol calcium carbonate (CaCO_3), how many grams of pure calcium carbonate do we need?
- If an experiment calls for 0.200 mol acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$), how many grams of acetic acid do we need?
- How many moles of CH_4 are in 4.00 g of CH_4 ?
A. 0.249 mol B. 64.0 mol C. 0.307 mol

- 
12. How many moles of acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$) are present in a 5.00 g sample of pure acetic acid?
13. Which sample has more O atoms?
A. 4.00 g O_2 B. 4.00 g O_3 C. neither (equal)
14. Which sample has more anions?
A. 4.00 g calcium carbonate B. 4.00 g calcium nitrate C. neither (equal)
15. Acetone is a liquid with a density of 0.7925 g mL^{-1} and its molar mass is 58.08 g mol^{-1} . What volume of acetone should be dispensed if an experiment calls for 0.500 mol of acetone?
16. Concentrated HCl is an aqueous solution that is 36–38% HCl by mass. Suppose a concentrated HCl solution, with a density of 1.18 g mL^{-1} , is 38% HCl by mass. What volume of this solution contains 0.500 mol HCl?
17. What is the percentage (by mass) of O in CO_2 ?
A. 27.29% B. 66.67% C. 72.71%
18. How many moles of O atoms are present in 50.0 g of NO_2 ?
19. Calculate the mass of O atoms in 2.00 mol NO_2 .
20. Calculate the moles of C in a mixture of 10.0 g calcium carbonate and 15.0 g aluminum carbonate.

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Elemental Analysis

Elemental Analysis is the determination of the elemental composition of a compound. The goal of elemental analysis is the determination of the *empirical formula* of a compound.

19.1 Empirical Formula

The *empirical formula* of a compound is the simplest way of representing the relative abundance of the atoms of the elements that make up a compound. The greatest common factor of the subscripts in an empirical formula is 1. If the greatest common factor of the subscripts of a formula is not 1, then just divide all the subscripts by that factor in order to get the empirical formula.

► Example

What is the empirical formula of glucose ($C_6H_{12}O_6$)?

Answer: The subscripts are 6, 12, and 6. The greatest common factor is 6. Dividing by 6, we get:

- C: $6/6 = 1$
- H: $12/6 = 2$, and
- O: $6/6 = 1$

The subscripts for the empirical formula are 1, 2, and 1. Therefore, the empirical formula is CH_2O .

How can we tell if the greatest common factor is 1? If the smallest number is 1, or if we divide all the numbers by the smallest number and we get at least one non-integer, then the greatest common factor is 1.

► Example

Is $C_3H_6O_2$ an empirical formula?

Answer: Yes, the greatest common factor for the subscripts (3, 6, and 2) is 1. If we were to divide all three numbers by the smallest (which is 2):

- $3/2 = 1.5$
- $6/2 = 3$
- $2/2 = 1$

we find that one of the resulting numbers (1.5) is not an integer.

19.2 Molecular Formula

The subscripts of the (correct) molecular formula of a compound are multiples of the subscripts of the empirical formula.

► Example

If the empirical formula of a compound is CH_2 , what are the possible molecular formulas?

Answer: CH_2 , C_2H_4 , C_3H_6 , C_4H_8 , etc.

The subscripts of the empirical formula are 1 and 2 for C and H, respectively. Remember that unwritten subscripts are implied to be 1. To get the multiples:

- we multiply both numbers by 1; this gives us 1 and 2.
- we multiply both numbers by 2; this gives us 2 and 4.
- we multiply both numbers by 3; this gives us 3 and 6.
- etc.

The *empirical mass* is the molar mass associated with the empirical formula of a compound. The actual molar mass of a compound is a multiple of the empirical mass. If we divide the molar mass by the empirical mass we should get a whole number.

► Example

What are the possible molar masses of a compound with an empirical formula of CH_2 .

Answer: multiples of 14.02 g mol^{-1}

- The molar mass if the molecular formula is CH_2 is $(12.01 + 2 \times 1.008) \text{ g mol}^{-1}$, or 14.02 g mol^{-1} .

- If the molecular formula is CH_2 , then the molar mass is 14.02 g mol^{-1} .
- If the molecular formula is C_2H_4 , then the molar mass is $2 \times 14.02 \text{ g mol}^{-1}$, or 28.04 g mol^{-1} .
- If the molecular formula is C_3H_6 , then the molar mass is $3 \times 14.02 \text{ g mol}^{-1}$, or 42.06 g mol^{-1} .
- etc...

► Example

Which of the following is *least* likely to be obtained as the molar mass of a compound with an empirical formula of CH_2 ?
A. 28.1 g/mol , B. 42.1 g/mol , C. 78.0 g/mol

Answer: C

The empirical mass is $(12.01 + 2 \times 1.008) \text{ g/mol}$, or 14.02 g/mol . Let's examine the choices given for the molar mass. Dividing by the empirical mass, we get

- $28.2/14.02 = 2.01$ (this is close enough to a whole number).
- $42.1/14.02 = 3.00$.
- $78.0/14.02 = 5.56$ (too far from a whole number).

19.3 Determining Empirical Formula

The general strategy for determining the empirical formula of a compound is to:

- break the compound down into its component elements.
- determine the number of atoms of each element obtained (the counts can be individual counts or group counts in moles).
- determine the subscripts of the empirical formula by reducing the count-to-count ratio to the smallest possible set of whole numbers.

► Example

A sample of a compound of carbon and hydrogen is found to contain 2.500×10^{22} C atoms and 7.490×10^{22} H atoms. What is the empirical formula?

Answer: CH_3

The C-to-H count-to-count ratio is 2.500×10^{22} -to- 7.490×10^{22} . We need to reduce this to the smallest whole number ratio. A good strategy is to divide by the smaller number.

$$2.500 \times 10^{22} / 2.500 \times 10^{22} = 1.000$$
$$7.490 \times 10^{22} / 2.500 \times 10^{22} = 2.996$$

When doing this type of calculation, we have to make sure that we follow the rules for rounding involving significant figures. We should not expect to see exact whole numbers, especially from experimental data. Experimental data are subject to random errors. Since 2.996 is very close to 3, the C-to-H count ratio is 1:3. The empirical formula is CH_3 .

► Example

A sample of a compound of nitrogen and oxygen contains 1.90 mol N and 3.80 mol O. What is the empirical formula of the compound?

Answer: NO_2

The N-to-O mole-to-mole ratio is 1.90-to-3.80. Reduce this to the smallest whole number ratio. A good strategy is to divide by the smaller number.

$$1.90 / 1.90 = 1.00$$

$$3.80 / 1.90 = 2.00$$

Therefore, the empirical formula is NO_2 .

In reducing count-to-count or mole-to-mole ratios to whole numbers, we round off only those numbers that are very close to a whole number.

► Example

A sample of a compound of C and H contains 5.00 mol C and 6.65 mol H. What is the empirical formula of the compound?

Answer: C_3H_4

Reduce the mole-to-mole ratio (5.00-to-6.65) to a the smallest whole number ratio. A good starting strategy is to divide by the smaller number.


$$5.00 / 5.00 = 1.00$$

$$6.65 / 5.00 = 1.33$$

Do *not* round off 1.33 to 1. The next thing to do is multiply by 2 to see if we can get all the numbers close to a whole number.

$$1.00 \times 2 = 2.00$$

$$1.33 \times 2 = 2.66$$



The number 2.66 is still far from a whole number. Try multiplying by 3 instead.

$$1.00 \times 3 = 3.00$$

$$1.33 \times 3 = 3.99$$

Now, 3.99 can be rounded off to 4. The empirical formula is C_3H_4 .

Typical laboratory data give us information about masses, not moles. We just need to convert the information to moles to determine the empirical formula.

► Example

A sample of a compound of C and H contains 1.200 g C and 0.4000 g H. What is the empirical formula of the compound?

Answer:

First convert given information to moles:

- 1.200 g C \rightarrow 0.09992 mol C
- 0.4000 g H \rightarrow 0.3968 mol H

Then, reduce the mole-to-mole ratio to a whole number ratio.

Start by dividing with the smaller number:

- C: $0.09992/0.09992 = 1.000$
- H: $0.3968/0.09992 = 3.971$

The number 3.971 is close enough to a whole number, so we can round it off (to 4). The empirical formula is CH_4 .

We do not need to know the actual amount of compound to determine empirical formula. We just need to know the relative amounts of the elements present. Relative amounts are usually given as percentages by mass. If we have the percentages, we can assume any amount of compound and base our calculations on the amount of each element in that sample. A convenient amount to assume is 100 g.

► Example

A compound of K, Cl, and O is found to be 31.9% K and 28.9% Cl. Determine the empirical formula.

Answer: $KClO_3$

Since we are given percentages, we assume we have a 100 g sample of the compound. We calculate the amounts of K, Cl, and O in this sample.

- K: 31.9% of 100 g is 31.9 g

- Cl: 28.9% of 100g is 28.9 g
- O: Remaining percentage = $100\% - (31.9\% + 28.9\%) = 39.2\%$
39.2% of 100 g is 39.2 g

Next, we change mass to moles:

- K: 31.9 g \rightarrow 0.816 mol
- Cl: 28.9 g Cl \rightarrow 0.815 mol
- O: 39.2 g \rightarrow 2.45 mol

Then reduce mole-to-mole ratio to small whole numbers by dividing with the smallest number (0.815):

- K: $0.816/0.815 = 1.00$
- Cl: $0.815/0.815 = 1.00$
- O: $2.45/0.815 = 3.01$ (close enough to a whole number; round off to 3)

Thus, the K:Cl:O ratio is 1:1:3.

19.4 Combustion Analysis

Combustion analysis is a common procedure used to do elemental analysis of organic compounds. In combustion analysis, all the C atoms in the compound end up as CO_2 and all the H atoms in the compound end up as H_2O . In the laboratory, a sample of the compound is burned; in the process the CO_2 and H_2O produced are collected.

► Example

A 2.003 g sample of compound containing C, H, and O is burned, and 4.401 g of CO_2 and 2.703 g of H_2O were collected. What is the empirical formula of the compound?


Answer: $\text{C}_2\text{H}_6\text{O}$

Remember that the goal is to get the mole-to-mole ratio of the elements. So, the first step is to convert the given information to moles:

- 4.401 g $\text{CO}_2 \rightarrow$ 0.1000 mol CO_2
- 2.703 g $\text{H}_2\text{O} \rightarrow$ 0.1500 mol H_2O

From these, we can calculate the moles of C and H that came from the compound:

- C: 0.1000 mol CO_2 has 0.1000 mol C, which came from the compound
- H: 0.1500 mol H_2O has 0.3000 mol H, which came from the compound



Now, we just need to figure out moles of O. First, we subtract the mass of C and H from the total mass to get the mass of O, so that we can calculate moles of O:

- 0.1000 mol C \rightarrow 1.201 g C
- 0.3000 mol H \rightarrow 0.3024 g H
- Therefore:

$$\begin{aligned}\text{mass of O} &= \text{total mass of sample} - (\text{mass of C} + \text{mass of H}) \\ &= 2.003 \text{ g} - (1.201 \text{ g} + 0.3024 \text{ g}) \\ &= 0.800 \text{ g}\end{aligned}$$

We can now calculate moles of O in the compound:
 $0.800 \text{ g O} \rightarrow 0.0500 \text{ mol O}$.

At this point, we have the moles of all the elements in the compound:

- 0.1000 mol of C
- 0.3000 mol H, and
- 0.0500 mol of O

Divide by the smallest number to try to get whole numbers:

- C: $0.1000/0.0500 = 2.00$
- H: $0.3000/0.0500 = 6.00$
- O: $0.0500/0.0500 = 1.00$

The obvious mole-to-mole ratio is 2:6:1. Therefore, the empirical formula of the compound is $\text{C}_2\text{H}_6\text{O}$.



TEST YOURSELF

For answers and other study resources, see:

<http://i-assign.com/ebook/answers/chapter19.htm>.

1. What is the sum of the subscripts in the empirical formula of C_6H_{12} ?
A. 1 B. 2 C. 3 D. 18
2. A compound with an empirical formula of NO_2 has a molar mass between 43 and 47 g/mol. What is the molecular formula of the compound?
A. NO_2 B. N_2O C. N_2O_3 D. N_2O_4
3. A sample of a compound contains 3.581×10^{22} C atoms and 1.436×10^{23} H atoms. What is the empirical formula of the compound?
A. CH B. CH_4 C. C_2H_5 D. C_3H_4
4. A sample of a compound contains 0.5860 moles of P and 1.466 moles of O. What is the empirical formula of the compound?
A. PO B. PO_4 C. P_2O_5 D. P_3O_4
5. A sample of a compound contains 19.27 g Fe and 7.360 g O. What is the empirical formula of the compound?
A. FeO B. FeO_2 C. Fe_2O_3 D. Fe_3O_4
6. Which of the following is an empirical formula of a compound that is 14.37% hydrogen by mass?
A. CH_2 B. CH_3 C. C_2H_4 D. C_3H_6
7. What is the formula for the compound composed of 71.62% gold, 13.10% carbon, and 15.28% nitrogen?
A. AuCN B. $Au(CN)_2$ C. $Au(CN)_3$ D. $ACN)_4$
8. Combustion analysis of a sample of hydrocarbon produced 0.100 mol CO_2 and 0.200 mol H_2O . What is the empirical formula of the compound?
9. Combustion analysis of a 3.003 g sample of a compound containing C, H, and O produced 0.100 mol CO_2 and 0.100 mol H_2O . What is the empirical formula of the compound?

Stoichiometry

Stoichiometry deals with the relationships between amounts of reactants and products involved in a reaction. Its major application is in the field of *analytical chemistry*, which is concerned with the determination of the amounts of substances in real-world material samples.

20.1 Relating Amounts of Reactants and Products

If we know at least two things:

- the chemical equation for a reaction
- and the change in moles of one reactant or product involved in the reaction

then we can calculate the amounts of all other reactants and products that are also involved. This is because the amounts involved are directly proportional and the mole-to-mole ratio is given by the coefficients in the balanced equation. Mathematically, we say that:

$$\frac{n_1}{n_2} = \frac{c_1}{c_2}$$

where n_1 and n_2 are the *changes* in moles of substances “1” and “2” and c_1 and c_2 are their coefficients. We can rearrange this equation to a more ready-to-use form:

$$n_1 = n_2 \cdot \frac{c_1}{c_2}$$

In other words, if we know the change in moles of substance “2” that were involved, we assign it to n_2 , then multiply it by the ratio of coefficients, (c_1/c_2) , to get n_1 , the change in moles of substance “1”. The ratio of coefficients, (c_1/c_2) , essentially serves as a conversion factor.

► Example

Consider the reaction $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{l})$

How many moles of H_2O are produced if 0.20 mol O_2 is consumed during the reaction? How many moles of H_2 are consumed?

Answer: $0.40 \text{ mol H}_2\text{O}$ (produced), 0.40 mol H_2 (consumed)
The coefficients of H_2O and O_2 in the balanced equation are **2** and **1**. Therefore:

$$0.20 \text{ mol } \cancel{\text{O}_2} \times \left(\frac{2 \text{ mol H}_2\text{O}}{1 \text{ mol } \cancel{\text{O}_2}} \right) = 0.40 \text{ mol H}_2\text{O (produced)}$$

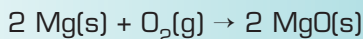
The coefficients of H_2 and O_2 are 2 and 1. Therefore:

$$0.20 \text{ mol } \cancel{\text{O}_2} \times \left(\frac{2 \text{ mol H}_2}{1 \text{ mol } \cancel{\text{O}_2}} \right) = 0.40 \text{ mol H}_2 \text{ (consumed)}$$

It is very important to keep in mind that n_1 and n_2 are changes in amounts (moles). They are not necessarily the amounts that you have at the beginning of the reaction.

► Example

Consider the combustion of Mg:



If 0.500 mol Mg is ignited and 0.100 mol of Mg remains after the reaction, how much MgO was produced?

Answer: 0.400 mol MgO

The amount of Mg consumed is the difference between the starting amount and the remaining amount:

$$(0.500 \text{ mol Mg}) - (0.100 \text{ mol Mg}) = 0.400 \text{ mol Mg (consumed)}$$

The coefficients of Mg and MgO are both 2. Therefore:

$$0.400 \text{ mol } \cancel{\text{Mg}} \times \left(\frac{2 \text{ mol MgO}}{2 \text{ mol } \cancel{\text{Mg}}} \right) = 0.400 \text{ mol MgO}$$

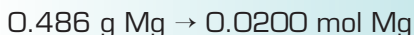
In a typical laboratory setting, we measure amounts in grams, not moles. In these cases, we first convert known amounts in grams to moles. If we are interested in solving for amounts in grams, we just convert any mole amount we calculate to grams.

► Example

Consider the combustion of Mg: $2 \text{Mg(s)} + \text{O}_2\text{(g)} \rightarrow 2 \text{MgO(s)}$
If 0.486 g Mg is burned, how much MgO is obtained?

Answer: 0.0200 mol MgO, or 0.806 g MgO

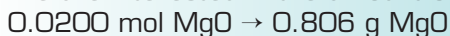
We first convert the given amount in grams to moles:



From this we can calculate moles of MgO obtained:

$$0.0200 \text{ mol Mg} \times \left(\frac{2 \text{ mol MgO}}{2 \text{ mol Mg}} \right) = 0.0200 \text{ mol MgO}$$

If we are interested in the amount of MgO in grams:



20.2 Using Moles of Reaction

An alternative approach to solving stoichiometry problems is to use extent of reaction. One mole of reaction is defined as the extent of reaction where the changes in the moles of reactants of products correspond to their coefficients in the balanced equation. In other words, if x moles of reaction has occurred, the change in moles of any reactant or product is equal to its coefficient times x :

$$n_1 = c_1 x$$

$$n_2 = c_2 x$$

$$n_3 = c_3 x$$

etc.

► Example

Consider the reaction $3\text{H}_2\text{(g)} + \text{N}_2\text{(g)} \rightarrow 2 \text{NH}_3\text{(g)}$

How many moles of the substances are involved if the reaction occurs to the extent of 0.50 mol?

Answer: 1.5 mol H_2 consumed; 0.50 mol N_2 consumed, 1.0 mol NH_3 produced

- Coefficient of H_2 is 3. Therefore, moles of H_2 consumed = $3x = 3(0.50 \text{ mol}) = 1.5 \text{ mol}$
- Coefficient of N_2 is 1. Therefore, moles of N_2 consumed = $x = 0.50 \text{ mol}$
- Coefficient of NH_3 is 2. Therefore, moles of NH_3 produced = $2x = 2(0.50 \text{ mol}) = 1.0 \text{ mol}$

If we want to be more descriptive with our units, here is how we should have done the calculation of moles of H_2 in the preceding example:

$$\left(\frac{3 \text{ mol H}_2}{1 \text{ mol rxn}} \right) (0.50 \text{ mol rxn}) = 1.5 \text{ mol H}_2$$

In other words, the unit for a coefficient is moles of whatever per mole of reaction. Note: “rxn” is a commonly used abbreviation for reaction.

Typically, we have information to determine the change in moles of one of the reactants or products. Dividing this by the appropriate coefficient gives us the value of x . We can then easily solve for change in moles of other reactants or products as shown above.

► Example

Consider the reaction $3\text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$

Use moles of reaction to calculate moles of H_2 and N_2 consumed if 0.60 mol NH_3 are produced?

Answer: 0.90 mol H_2 consumed, 0.30 mol N_2 consumed

When using moles of reaction, it is convenient to set up a table of changes:

	H_2	N_2	NH_3
Changes	$3x$	x	$2x$

Based on the given information:

- Change in $\text{NH}_3 = 2x = 0.60 \text{ mol}$; therefore: $x = 0.30 \text{ mol}$
- Change in $\text{H}_2 = 3x = 3(0.30 \text{ mol}) = 0.90 \text{ mol}$
- Change in $\text{N}_2 = x = 0.30 \text{ mol}$

Moles of reaction are particularly useful where the information available is limited.

► Example

Consider the reaction $3\text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$

Suppose 1.00 mol H_2 and 1.50 mol N_2 were to be allowed to react and, sometime later, a total of 2.30 mol of gas molecules were found in the reaction mixture. How much H_2 , N_2 , and NH_3 are in the final mixture?

Answer: 0.70 mol H_2 , 1.40 mol N_2 , 0.20 mol NH_3

For questions like this, it is convenient to set up an “ICE” table. Tabulate the Initial moles, Change in moles, and Ending moles.

	H ₂	N ₂	NH ₃
Initial moles	1.00 mol	1.50 mol	0 mol
Change in moles	3x mol	x mol	2x mol
Ending moles	(1.00 - 3x) mol	(1.50 - x) mol	(0 + 2x) mol

Based on the given information, total ending moles = 2.30 mol.
Therefore:

$$(1.00 - 3x) + (1.50 - x) + (0 + 2x) = 2.30$$

Solving for x, we get: x = 0.10. Therefore:

- Ending moles of H₂ = (1.00 - 3x) mol = 0.70 mol
- Ending moles of N₂ = (1.50 - x) mol = 1.40 mol
- Ending moles of NH₃ = (0 + 2x) mol = 0.20 mol

20.3 Limiting Reactant Problems

Consider a chemical reaction involving two or more reactants. As soon as one reactant runs out, the reaction would no longer be able to generate additional products. That reactant, the one that would run out first, puts a limit on how much product we can generate. That reactant is, therefore, called the *limiting reactant* or limiting reagent. The amount of product obtained if the limiting reactant were to completely run out is called the reaction's *theoretical yield*.

► Example

A 2.0 g sample of reactant X is completely used up in a reaction with excess Y to yield 18.0 g of product Z. A 4.0 g sample of reactant Y is completely used up in a reaction with excess X to yield 4.5 g of product Z. If 2.0 g X and 4.0 g Y are mixed, what is the limiting reactant? What is the theoretical yield?

Answer: Y is the limiting reactant, 4.5 g Z is the theoretical yield
What this problem is essentially saying is that:

- 2.0 g X can yield up to 18.0 g of Z.
- 4.0 g Y can yield up to 4.5 g of Z.

Therefore, a mixture of 2.0 g X and 4.0 g Y can only yield up to 4.5 g of Z. By the time this much Z has formed, we will have run out of Y. We cannot make any more. Y is the limiting reactant and 4.5 g of Z is the theoretical yield.

► Example

Consider the reaction: $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{l})$
Suppose we have a mixture of 3.0 mol $\text{H}_2(\text{g})$ and 2.0 mol $\text{O}_2(\text{g})$.
Verify that H_2 is the limiting reactant. Calculate how much O_2 would remain unreacted when H_2 runs out. Calculate the theoretical yield.

Answer:

If all of the H_2 were consumed, we can calculate how much O_2 is also consumed by multiplying the amount of H_2 (in moles) by the ratio of coefficients (of O_2 and H_2) in the balanced equation:

$$3.0 \text{ mol } \cancel{\text{H}_2} \times \left(\frac{1 \text{ mol } \text{O}_2}{2 \cancel{\text{ mol } \text{H}_2}} \right) = 1.5 \text{ mol } \text{O}_2 \text{ (consumed)}$$

The amount of O_2 consumed (1.5 mol) is less than what we have to begin with (2.0 mol). So we still have unreacted O_2 while H_2 is completely consumed.

$$2.0 \text{ mol } \text{O}_2 - 1.5 \text{ mol } \text{O}_2 = 0.5 \text{ mol } \text{O}_2, \text{ remaining}$$

We say that O_2 is our excess reactant (or excess reagent).

We can calculate the theoretical yield by calculating the amount of product (H_2O) generated when the limiting reactant runs out. We multiply amount of H_2 (in moles) by the ratio of coefficients (of H_2O and H_2).

$$3.0 \text{ mol } \cancel{\text{H}_2} \times \left(\frac{2 \text{ mol } \text{H}_2\text{O}}{2 \cancel{\text{ mol } \text{H}_2}} \right) = 3.0 \text{ mol } \text{H}_2\text{O}$$

The theoretical yield is 3.0 mol H_2O , or 54 g H_2O .

20.3.1. Strategy for Determining Excess Reactant

The preceding example illustrates a strategy that we can use to determine excess reactant:

- Assume one of the reactants is the limiting reactant and is completely consumed.
- Calculate how many moles of the other reactant would also be consumed.
- Subtract amount of excess reagent consumed from the starting amount of excess reagent to get the remaining amount. If the answer is negative, we made the wrong assumption; start over and assume the other reactant is limiting.

In the preceding example, had we assumed that O_2 is the limiting reactant, we would have gotten a negative remaining amount for H_2 , which would be physically unreasonable.

20.3.2 Strategy for Determining Theoretical Yield

The quickest way to determine the theoretical yield is to do the following:

- For each reactant, calculate how many moles of product would be generated if the reactant were completely consumed.
- The smaller amount of product generated is the theoretical yield. The reactant that would generate the smaller amount of product is the limiting reactant; by the time we generate this much product, one of the reactants would have been completely consumed and it would not be possible to generate any additional product.

In the preceding example, had we assumed that O_2 is the limiting reactant, we would have gotten more than 3.0 mol H_2O , which would be impossible. We have shown that by the time the amount of H_2O produced reaches 3.0 mol, no more H_2 will be left; the reaction cannot proceed further.

20.3.3 Using an ICE Table

An ICE table is a convenient way to organize the information to solve stoichiometry problems. It is especially useful for limiting reactant problems. In this table, we list (below the formulas of reactants and products) the initial (I) moles of reactants and products present, the change (C) in moles, and the ending (E) moles.

► Example

Consider the reaction $3H_2(g) + N_2(g) \rightarrow 2NH_3(g)$
For a mixture of 0.600 mol H_2 and 1.000 mol N_2 , determine the theoretical yield and amount of unreacted excess reactant if the reaction were to go to completion.

Answer: Theoretical yield of 0.400 mol NH_3 , 0.800 mol unreacted N_2

	H_2	N_2	NH_3
Initial moles	0.600 mol	1.000 mol	0 mol
Change in moles	$3x$ mol	x mol	$2x$ mol
Ending moles	$(0.600 - 3x)$ mol	$(1.000 - x)$ mol	$(0 + 2x)$ mol

The reaction is said to go to completion if the limiting reactant is completely consumed. If the reaction were to go to completion, then the ending amount for at least one of the reactants (the limiting reactant) should be zero, and the other should be zero or positive.

Assuming H_2 is the limiting reactant:
Ending moles of $\text{H}_2 = (0.600 - 3x) \text{ mol} = 0$
Solving for x , we get: $x = 0.200 \text{ mol}$
Ending moles of $\text{N}_2 = (1.000 - x) \text{ mol}$
 $= (1.000 - 0.200) \text{ mol}$
 $= 0.800 \text{ mol}$
Ending moles of $\text{NH}_3 = (0 + 2x) \text{ mol}$
 $= 2(0.200) \text{ mol}$
 $= 0.400 \text{ mol}$

Assuming N_2 is the limiting reactant:
Ending moles of $\text{N}_2 = (1.000 - x) \text{ mol} = 0$
Solving for x , we get: $x = 1.000 \text{ mol}$
Ending moles of $\text{H}_2 = (0.600 - 3x) \text{ mol}$
 $= [0.600 - 3(1.000)] \text{ mol}$
 $= -2.400 \text{ mol (NEGATIVE!)}$
Ending moles of $\text{NH}_3 = (0 + 2x) \text{ mol}$
 $= 2(1.000) \text{ mol}$
 $= 2.000 \text{ mol}$

Obviously N_2 cannot be the limiting reactant. If it were consumed completely, we would end up with a negative amount of H_2 , which is physical unreasonable. Therefore, we conclude that H_2 is the limiting reactant, the amount of unreacted N_2 if the reaction went to completion is 0.800 mol , and the theoretical yield is 0.400 mol NH_3 .

20.3.4 Percent Yield

Limiting reactant is defined as the reactant that *would* (not *will*) run out first. Strictly speaking, in reality, no reactant is completely consumed. Reactions are reversible; products can react to re-generate the reactants. When a reaction appears to have stopped, what has actually happened is that the forward and reverse reactions are occurring at the same rate; we have reached what is called a state of (dynamic) *equilibrium*.

There are cases where consumption of the limiting reactant is *essentially* complete; in these cases we say the reaction has *gone to completion*. A commonly used strategy to make reactions go to completion is to use a very large excess of one of the reactants (usually, the less expensive one); the basis for this is a principle known as Le Chatelier's principle.

In practical situations, the amount of product obtained by carrying out a reaction (the *actual yield*) is less than the theoretical yield. Reasons other than reversibility include loss of product during the recovery process as well as side reactions that lead to the formation of other products. The percent yield of a product is defined as:

$$\text{Percent Yield} = \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \times 100 \%$$

► Example

Consider a hypothetical reaction: $2A + B \rightarrow C$

Suppose 0.300 mol A and 0.200 mol B were allowed to react, but only 0.120 mol C was produced. Calculate the percent yield.

Answer: 80.0%

The actual yield is given as 0.120 mol C. To calculate percent yield, we need to know the theoretical yield.

If A were completely consumed, the amount of C expected would be:

$$0.300 \text{ mol A} \times \left(\frac{1 \text{ mol C}}{2 \text{ mol A}} \right) = 0.150 \text{ mol C}$$

If B were completely consumed, the amount of C expected would be:

$$0.200 \text{ mol B} \times \left(\frac{1 \text{ mol C}}{1 \text{ mol B}} \right) = 0.200 \text{ mol C}$$

Therefore, the limiting reactant is A and the theoretical yield is 0.150 mol C. By the time this much C is formed, the reaction has to stop. It is not possible to completely use up B and get 0.200 mol C. To determine percent yield, we simply divide the actual yield by the theoretical yield, then multiply by 100%:

$$\begin{aligned} \text{Percent Yield} &= \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \times 100 \% \\ &= \frac{0.120 \text{ mol}}{0.150 \text{ mol}} \times 100 \% = 80.0 \% \end{aligned}$$



TEST YOURSELF

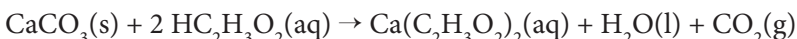
For answers and other study resources, see:

<http://i-assign.com/ebook/answers/chapter20.htm>.



How much NH_3 is produced if 0.200 mol H_2 is consumed?

- A. 0.133 mol B. 0.300 mol C. 2.00 mol



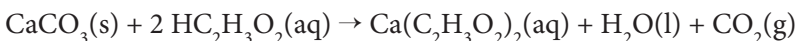
A solution containing acetic acid is mixed with CaCO_3 . How much acetic acid is consumed in a reaction that produces 0.400 mol CO_2 ?

- A. 0.200 mol B. 0.400 mol C. 0.800 mol



Suppose a reaction mixture initially contained 0.800 mol N_2 , and now contains only 0.500 mol N_2 as a result of the reaction, how much H_2 was consumed?

- A. 0.100 mol B. 0.900 mol C. 0.300 mol



A solution containing acetic acid is mixed with 0.600 mol CaCO_3 . Suppose the reaction produces 0.400 mol CO_2 . How much CaCO_3 is left unreacted?

- A. 0.200 mol B. 0.400 mol C. 0.800 mol



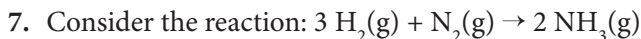
How much hydrogen is needed to produce 25.0 g of NH_3 ?

- A. 2.22 g B. 4.44 g C. 1.97 g

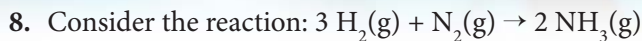


Suppose 0.500 mol of N_2 is used up in this reaction. How much NH_3 is produced?

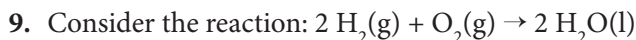
- A. 4.26 g B. 8.50 g C. 17.0 g



For a mixture of 2.00 mol N_2 and 3.00 mol H_2 , how much of the excess reactant would remain if the limiting reactant is consumed?

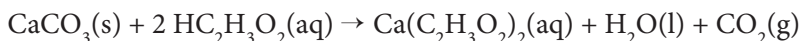


What is the theoretical yield of NH_3 from a mixture of 2.00 mol N_2 and 3.00 mol H_2 ?



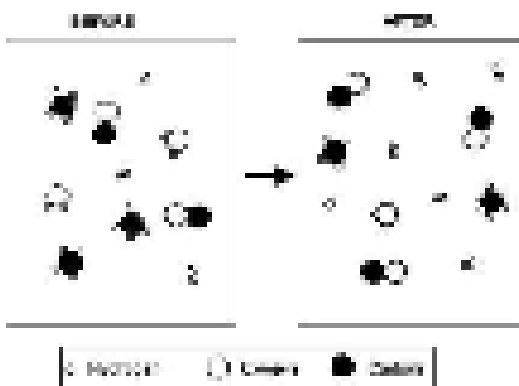
What is the limiting reactant in a mixture containing 1.00 g H_2 and 1.00 g O_2 ? What is the theoretical yield for H_2O in grams? Hint: convert amounts to moles first.

10. Consider a 5.32 g sample of CaCO_3 (99.87% pure) in a flask and a 100.0 mL sample of vinegar (5% acidity) in a graduated cylinder. The combined mass of both reagents and containers is 255.98 g. The vinegar is poured into the flask with the calcium carbonate and the following reaction occurs:

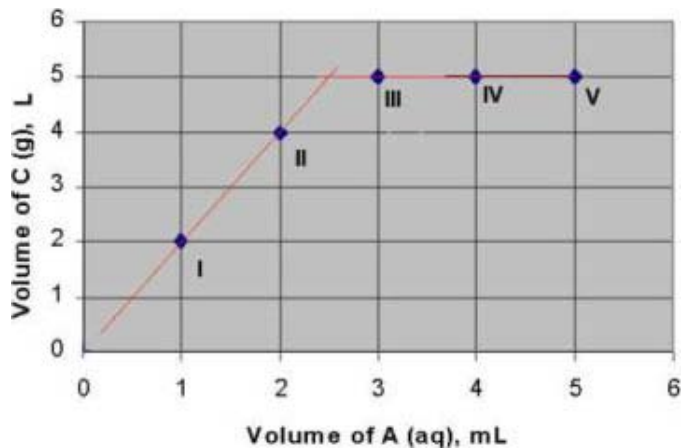


After swirling the reaction mixture for about twenty minutes, the combined mass of the reaction mixture and containers is found to be 254.46 g. What is the percent yield of carbon dioxide in this experiment?

11. Consider a reaction between substances A and B. Suppose 0.200 mol A and 0.100 mol B are mixed and, a few minutes later, the amounts remaining are 0.160 mol A and 0.090 mol B. Which substance is the limiting reactant? How much of the excess reactant would be left unreacted if the reaction went to completion?
12. Consider a reaction between substances X and Y, to yield product Z. Suppose 0.400 g of X and 3.600 g of Y are mixed and 0.100 g of X and 1.200 g of Y are found unreacted when the reaction stops. What is the limiting reactant? Calculate the theoretical yield. Calculate the percent yield, assuming no side reactions and no product lost during the experiment.
13. Consider the reaction illustrated in the figure below. What is the limiting reactant?



14. A series of experiments (I, II, III, IV, and V) reacted different amounts of solution A(aq) with 1.00 mL of solution B(aq). The reaction goes to completion and a gaseous product, C(g) is obtained in each case. Suppose the experimental results are as shown below:



What is the limiting reactant in experiment I? II? III? IV? V?

Reactions in Aqueous Solutions

A very large number of important reactions occur in aqueous solution. A solution is a homogeneous mixture; an aqueous solution is one where the predominant component (the solvent) is water.

21.1 The Solution Process

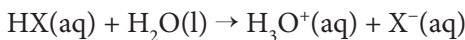
To understand aqueous reactions, we need to first understand what happens to compounds when they are mixed with water. When a compound dissolves in water, the ions or molecules that make up the compound are evenly dispersed in the water; each ion or molecule is surrounded by water molecules (“solvated” or “hydrated”). These ions or molecules may also react with water molecules.

The dispersal of the ions allows aqueous solutions of ionic compounds to conduct electricity (note: pure water is a poor electrical conductor). Thus, ionic compounds are called *strong electrolytes*.


If a compound dissolves in water but the resulting solution does not conduct electricity, then we conclude that the compound is made up of molecules that do not yield ions; we call the compound a *nonelectrolyte*.

There are molecular compounds that react with water molecules and yield ions when dissolved in water. Those that yield hydronium ions (H_3O^+) are called *acids*; those that yield hydroxide (OH^-) ions are called *bases*. The reaction of these compounds with water is called *ionization*.

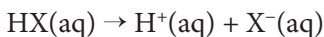
Acid molecules *dissociate* (“break up”) into H^+ and anions; the resulting H^+ ions are transferred to H_2O molecules to form hydronium ions (H_3O^+). If we represent an acid by “HX”, then we can represent the ionization of HX in water by:



We could say that the acid (HX) “donates” a proton (H^+) to a water molecule, leading to the formation of hydronium ion (H_3O^+) and an anion (X^-). We could also say that a water



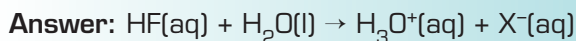
molecule causes an HX molecule to dissociate by “pulling” a proton away from the HX molecule. It is customary to use $\text{H}^+(\text{aq})$ to represent hydronium ions, to abbreviate the ionization reaction to:



and to refer to the reaction as a *dissociation* reaction.

► Example

Write the chemical equation that for the reaction of HF molecules with water molecules.



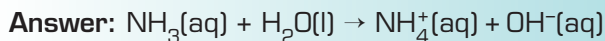
Base molecules, such as NH_3 , cause H_2O molecules to dissociate by “pulling” protons away from water molecules. If we represent a base molecule by “B”, then the ionization is represented by:



We could say that the base molecule (B) “accepts” a proton (H^+) from a water molecule.

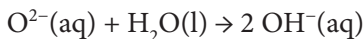
► Example

Write the chemical equation that for the reaction of NH_3 molecules with water molecules.



Most molecular acids and bases are only partially ionized; they are, therefore, called *weak electrolytes*. By partial ionization, we mean that only a small fraction of the molecules are ionized at any given time. There are, in fact, only six known molecular compounds that completely ionize in water; these are the *strong acids*, (HCl , HBr , HI , H_2SO_4 , HNO_3 , HClO_4); strong acids are strong electrolytes.

Ionic compounds whose anions are oxide or hydroxide yield hydroxide ions when dissolved in water and are, therefore, considered as *strong bases*. Any oxide ion that makes it into water immediately gains a proton (H^+) from a water molecule, forming two hydroxide ions.



21.2 Chemical Equations for Dissolution

To represent the dissolution of a substance in water, we write:

- the formula of the compound on the reactant side, with the (s), (l), or (g) label to indicate whether the physical state of the substance is solid, liquid, or gas, and
- the same formula on the product side, with the (aq) label.

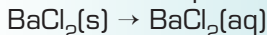
A chemical equation written this way is called a *molecular equation* (or complete formula equation). However, when dealing with *strong electrolytes*, it is best to write an *ionic equation* to reflect the fact that the ions are not paired up or “stuck” together in solution. In an ionic equation, formulas of strong electrolytes in aqueous solution are written as separate ions.

► Example

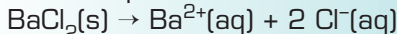
Write the chemical equation for the dissolution of barium chloride (a solid) in water.

Answer:

The molecular equation is



The ionic equation is



The term molecular equation is really a poor choice of words in this case, since no molecules are actually involved. However, we need to be familiar with it since it is the commonly used terminology.

► Example

Write the chemical equation for the dissolution of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$, a solid) in water.

Answer: $\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(\text{aq})$

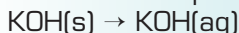
There is no ionic equation associated with this process since glucose is not a strong electrolyte. How do we know? It is not an ionic compound, and it is not one of the six molecular compounds known to completely ionize in water.

► Example

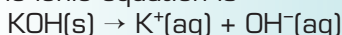
Write the chemical equation for the dissolution of potassium hydroxide (a solid) in water.

Answer:

The molecular equation is



The ionic equation is



KOH is an example of a base. Bases are substances that yield OH^- when dissolved in water. Metal hydroxides like KOH are classified as *strong* bases because, like any ionic compound, they are completely dissociated into ions when dissolved in water.

▶ Example

Calcium carbonate is insoluble in water. Write the ionic equation for the dissolution process.

Answer:

Molecular equation: $\text{CaCO}_3(s) \rightleftharpoons \text{CaCO}_3(aq)$

Ionic equation: $\text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq)$

If a solid compound is insoluble* in water, it is customary to draw a double arrow to represent its “dissolution” in water. This indicates that if the compound is mixed with water, most of the ions will be in the solid, not in solution. However, CaCO_3 , like any ionic compound, is completely ionized in water. Therefore, it is best to write $\text{CaCO}_3(aq)$ as separate ions.

*Note: the term “insoluble” does not mean zero solubility; it actually means very low solubility.

▶ Example

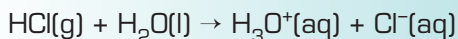
Write the chemical equation for the dissolution of hydrogen chloride (HCl, a gas) in water.

Answer:

The molecular equation for the dissolution is: $\text{HCl}(g) \rightarrow \text{HCl}(aq)$

The ionic equation is: $\text{HCl}(g) \rightarrow \text{H}^+(aq) + \text{Cl}^-(aq)$

HCl is a strong electrolyte. It is one of the six known strong acids. The proton (H^+) is actually transferred to a water molecule, so we can also represent the overall process by



► Example

Write the chemical equation for the dissolution of acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$, a liquid) in water.

Answer: $\text{HC}_2\text{H}_3\text{O}_2(\text{l}) \rightarrow \text{HC}_2\text{H}_3\text{O}_2(\text{aq})$

$\text{HC}_2\text{H}_3\text{O}_2$ is a weak electrolyte; it is not one of the six strong acids. Majority of the acetic acid molecules are un-ionized in water; only a small fraction are ionized at any given time.

► Example

Write the chemical equation for the dissolution of ammonia (NH_3 , a gas) in water. NH_3 is a weak base.

Answer: $\text{NH}_3(\text{g}) \rightarrow \text{NH}_3(\text{aq})$

Most of the NH_3 molecules remain un-ionized in water.

21.3 Solubility Rules

Imagine a sample (of a compound) comparable in size to a grain of rice. If you can get this sample to dissolve in about a teaspoon (5 mL) of water, the compound is said to be *soluble* in water; otherwise, the compound is said to be *insoluble* in water. A soluble compound mixed with water gives a clear (transparent) solution; an insoluble compound mixed with water gives a cloudy mixture. Note that *insoluble* does not mean zero solubility; it actually means *very, very, very low solubility*; a better term for *insoluble* is *slightly soluble*.

We can predict the solubility of common ionic compounds in water by applying a few simple rules. You are likely to see different versions of these rules in different textbooks. They are essentially the same, except that some textbooks include more ions than others. It depends on what the authors consider as “common.” In general, the rules tell us:

- which compounds are always soluble (rule 1),
- which compounds are generally soluble and what the exceptions are (rule 2), and
- that most everything else is insoluble and what the exceptions are (rule 3).

These rules are empirical; they are based on experimental observations. We apply them in the order listed; once we find a rule that applies, we ignore the rest.

- Rule 1. Compounds of the following are always soluble: sodium, potassium, ammonium, nitrate, nitrite, perchlorate, acetate.

- Rule 2. Compounds of the following are generally soluble:
 - chloride, bromide, iodide — except with Ag^+ , Pb^{2+} , Hg_2^{2+} , and Cu^+ .
 - sulfate — except with lead(II), barium, strontium, calcium, and mercury(I).
 - fluoride — except with lead(II) and group II(A).
- Rule 3. The rest are generally insoluble. Exceptions: sulfides of group II(A) are soluble, hydroxides of calcium, strontium and barium are moderately soluble.

► Example

Classify the following as soluble or insoluble in water:

$\text{NaC}_2\text{H}_3\text{O}_2$, K_2CO_3 , CaCO_3 , MgCl_2 , ZnSO_4 ,
 PbSO_4 , AgBr , MgS , CuI , AgF , CuS , Ag_3PO_4

Answer:

$\text{NaC}_2\text{H}_3\text{O}_2$ is soluble (rule 1), K_2CO_3 is soluble (rule 1), CaCO_3 is insoluble (rule 3), MgCl_2 is soluble (rule 2), ZnSO_4 is soluble (rule 2), PbSO_4 is insoluble (rule 2), AgBr is insoluble (rule 2), MgS is soluble (rule 3), CuI is insoluble (rule 2), AgF is soluble (rule 2), CuS is insoluble (rule 3), Ag_3PO_4 is insoluble (rule 3).

21.4 Precipitation Reactions

When aqueous solutions containing ions are mixed, a precipitation reaction may occur. Precipitation occurs when it is possible to form an insoluble compound. We would expect the mixture to suddenly turn cloudy as a result of the formation of insoluble compound, which eventually settles to the bottom of the container.

► Example

Write the chemical equation for the precipitation reaction that occurs when solutions of $\text{KI}(\text{aq})$ and $\text{Pb}(\text{NO}_3)_2(\text{aq})$ are mixed.

Answer: $\text{Pb}(\text{NO}_3)_2(\text{aq}) + 2 \text{KI}(\text{aq}) \rightarrow \text{PbI}_2(\text{s}) + 2 \text{KNO}_3(\text{aq})$

If we mix $\text{KI}(\text{aq})$ and $\text{Pb}(\text{NO}_3)_2(\text{aq})$, we would end up with a solution that contains the following ions:

K^+ , I^- , Pb^{2+} , and NO_3^-

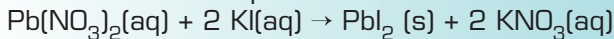
Using the solubility rules, we predict that PbI_2 is insoluble in water (rule 2). Therefore, we write PbI_2 with (s) in the chemical equation; we expect it to *precipitate*. We expect the other product (KNO_3) of this double replacement reaction to remain in solution; KNO_3 is soluble in water (rule 1). Thus, we put an (aq) label next to KNO_3 when we write the chemical equation.

21.5 Ionic Equations

When strong electrolytes (ionic compounds and strong acids) are dissolved in water, we know that the ions are individually hydrated. Therefore, when writing chemical equations for aqueous reactions, it is better to write the ions of strong electrolytes (in solution) separately. When we do this, we may find that some ions are not actually involved in the reaction; these are called *spectator* ions. In these cases, we can write a simpler, more accurate representation of the reaction by writing a net ionic equation. The *net ionic equation* shows only the ions and molecules that are actually involved in the reaction; spectator ions are excluded.

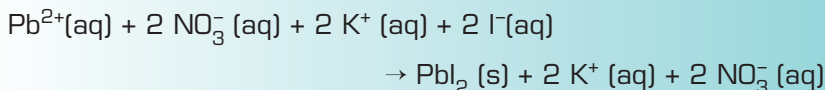
► Example

Write the net ionic equation for the reaction:



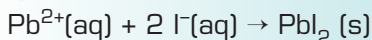
Answer: $\text{Pb}^{2+}(\text{aq}) + 2 \text{I}^{-}(\text{aq}) \rightarrow \text{PbI}_2(\text{s})$

A more accurate way of representing the reaction is to write formulas for strong electrolytes in aqueous solution as separate ions:



This is called a *full or complete ionic equation*. The ions are not written separately for PbI_2 since most of them will be in the solid (precipitate), not in the solution.

If we look carefully at the full ionic equation, we can see that nothing really happened to the K^{+} and NO_3^{-} ions. So, an even better representation for the reaction is:

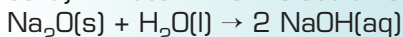


This called the *net ionic equation*. We could say that since K^{+} and NO_3^{-} appear on both sides of the full ionic equation, they cancel out; they are not involved and are called *spectator ions*.

When writing ionic equations, the formula of a solid reactant should not be written as separate ions even if it is a strong electrolyte.

► Example

Write the ionic equation for the “dissolution” of sodium oxide (a solid) in water. The molecular equation is:



Answer:

The ionic equation is: $\text{Na}_2\text{O}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2 \text{Na}^+(\text{aq}) + 2 \text{OH}^-(\text{aq})$
 Na_2O is the oxide of a metal (Na). Oxides of metallic elements react with water to yield metal hydroxides; they are also known as base anhydrides.

21.6 Reactions of Acids

An acid is a molecular compound that yields H^+ in aqueous solutions. Therefore, reactions common to acids in aqueous solution involve interactions of H^+ with other ions or molecules present in the solution.

21.6.1 Reactions with Metal Oxides and Metal Hydroxides

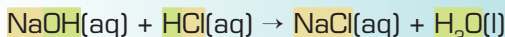
The reaction of an acid with a metal oxide or metal hydroxide leads to the formation of salt and water. The H^+ ions from the acid combine with O^{2-} or OH^- ions to form H_2O . The salt consists of cations from the metal oxide (or metal hydroxide) and anions from the acid.

► Example

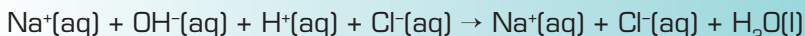
Write the net ionic equation for the reaction of $\text{NaOH}(\text{aq})$ and $\text{HCl}(\text{aq})$.

Answer: $\text{OH}^-(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$

The molecular equation is:

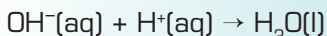


The products are H_2O and a salt (NaCl). Based on empirical solubility rules, we expect the NaCl product to be in aqueous solution; NaCl is soluble in water. To write the full ionic equation, we write the formulas of strong electrolytes, substances that are completely dissociated into ions, as separate ions. HCl is a strong electrolyte; it is one of the six known strong acids. Ionic compounds in aqueous solutions, such as NaOH and NaCl, are completely dissociated and should be written as separate ions. Therefore, the full ionic equation is:

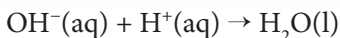


The net ionic equation is obtained by removing the spectator ions (Na^+ and Cl^-) which appear on both sides of the full ionic equation.

The net ionic equation is:



In general, the equation:



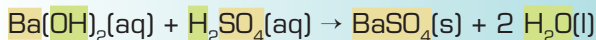
is the net ionic equation whenever aqueous solutions of a metal hydroxide and a strong acid are mixed. Exceptions would be cases where an insoluble product is formed.

► Example

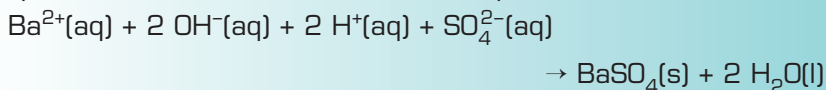
Write the net ionic equation for the reaction of $\text{Ba}(\text{OH})_2(\text{aq})$ with $\text{H}_2\text{SO}_4(\text{aq})$.

Answer:

The molecular equation is:



The products are H_2O and a salt, BaSO_4 . The salt is made up of Ba^{2+} from $\text{Ba}(\text{OH})_2$ and SO_4^{2-} from H_2SO_4 . Since H_2SO_4 is a strong acid, it is completely dissociated in aqueous solution and should be written as separate ions. An aqueous solution of $\text{Ba}(\text{OH})_2$ is specified in the question and we expect ionic compounds like $\text{Ba}(\text{OH})_2$ to be completely dissociated in aqueous solution. Therefore, $\text{Ba}(\text{OH})_2$ should be written as separate ions. Based on empirical solubility rules, we expect BaSO_4 to be insoluble in water; we expect it to be a precipitate and we do *not* write it as separate ions. Therefore, the full ionic equation is:



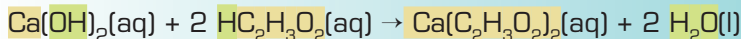
This is also the net ionic equation since no ion appears by itself on both sides of the equation; there are no spectator ions.

► Example

Write the net ionic equation for the reaction of $\text{Ca}(\text{OH})_2(\text{aq})$ with $\text{HC}_2\text{H}_3\text{O}_2(\text{aq})$.

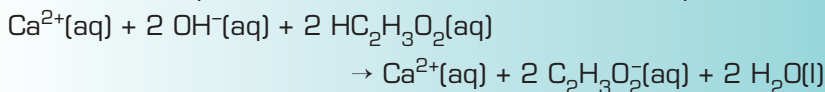


The molecular equation is:

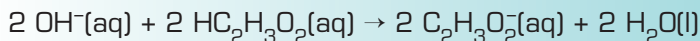


The products are H_2O and a salt, $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$. Based on empirical solubility rules, we expect calcium acetate to be soluble in water; since it is a strong electrolyte, we need to write it as separate ions. Calcium hydroxide is also a strong electrolyte and should be written as separate ions. Acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, is not

one of the six strong acids; it is a weak electrolyte and should not be written as separate ions. Therefore, the full ionic equation is:



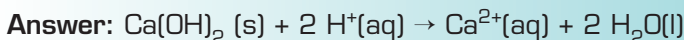
To get the net ionic equation, we omit the spectator ion, $\text{Ca}^{2+}(\text{aq})$:



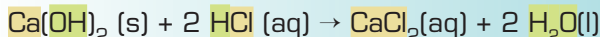
We can simplify the net ionic equation by dividing all the coefficients by their greatest common factor (which is 2).

► Example

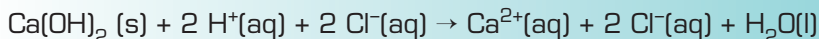
Write the net ionic equation for the reaction of $\text{Ca}(\text{OH})_2(\text{s})$ and $\text{HCl}(\text{aq})$.



The molecular equation is:



The products are H_2O and a salt (CaCl_2). The salt's cation is Ca^{2+} , from $\text{Ca}(\text{OH})_2$, and its anion is Cl^{-} , from HCl . Since HCl is a strong acid, it is completely dissociated in aqueous solution and should be written as separate ions. Based on empirical solubility rules, we expect the salt to be in aqueous solution; we expect it to be completely dissociated and write it as separate ions. Therefore, the full ionic equation is



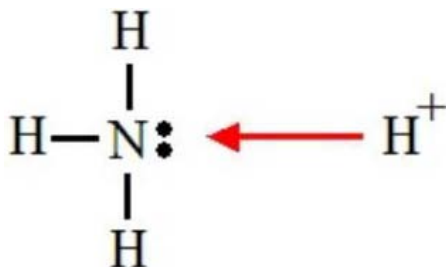
The net ionic equation is obtained by omitting the spectator ions (Cl^{-}), which appear on both sides of the full ionic equation.

21.6.2 Reactions with Ammonia and Amines

Ammonia and amines are compounds made up of nitrogen containing molecules and are called *bases*. The N atom in these molecules have an unshared pair of electrons that attracts the H^{+} ion, as illustrated in Figure 1 for NH_3 . This results in a covalent bond being formed between N and H. Unlike acids, which release H^{+} ions in water, base molecules attract H^{+} ions instead. Since H^{+} (a hydrogen atom without its electron) is just a proton, we say that a base molecule has a tendency to be *protonated*. Thus, the N-containing molecule is converted into a polyatomic cation; in the case of NH_3 , the cation formed is ammonium (NH_4^{+}).

The reaction of an acid with these compounds can be classified as a combination reaction; one product is formed, a salt; in the case of ammonia, the salt formed is an ammonium salt.

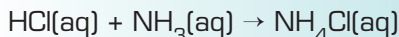
Figure 1. Protonation of Ammonia



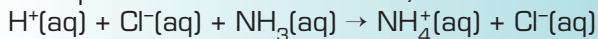
► Example

Write the chemical equation for the reaction of $\text{HCl}(\text{aq})$ and $\text{NH}_3(\text{aq})$.

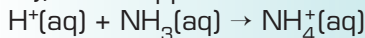
Answer: The H^+ from HCl combines with NH_3 to form ammonium ions (NH_4^+). The product of the reaction is a salt called ammonium chloride. The chloride ion (Cl^-) is the anion formed when an HCl molecule dissociates in water. So, the molecular equation is:



To write the full ionic equation, we write the formulas of the strong electrolytes as separate ions. The strong electrolytes in this chemical equation are HCl , which is one of the six known strong acids, and NH_4Cl . Both of these are completely dissociated in aqueous solution. Therefore, the full ionic equation is:



The net ionic equation is obtained by taking out the spectator ion (Cl^-), which appears on both sides of the full ionic equation.



21.6.3 Reactions with Salts

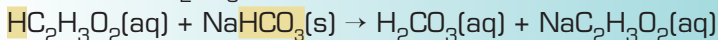
Salts are ionic compounds for which the anion is neither oxide nor hydroxide. The common feature of the reaction of acids with salts is the interaction of H^+ ions with the anion of the salt, to yield another acid as a product. The remaining ions combine to form another salt. We need to examine the net ionic equation to reasonably predict if there will be a reaction.

► Example

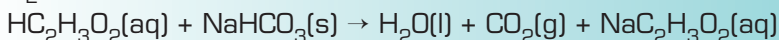
Predict what happens when vinegar, $\text{HC}_2\text{H}_3\text{O}_2(\text{aq})$, is mixed with baking soda (sodium bicarbonate), $\text{NaHCO}_3(\text{s})$.

Answer:

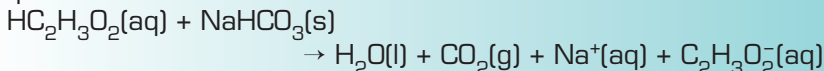
The H^+ from the acid combines with the anion from the salt to yield another acid, H_2CO_3 (carbonic acid).



However, H_2CO_3 is known to readily decompose to $\text{H}_2\text{O}(\text{l})$ and $\text{CO}_2(\text{g})$. CO_2 is a gas under ordinary conditions and it has a low solubility in water, about 0.15 g per 100 g of water. Therefore, we would typically expect the bulk of the CO_2 produced to be in the gas phase. In fact, when if we carry out this reaction, we will likely observe the CO_2 as bubbles (“fizz”). Therefore, the overall reaction is:



To write the full ionic equation, we write $\text{NaC}_2\text{H}_3\text{O}_2(\text{aq})$ as separate ions; it is the only strong electrolyte in aqueous solution (for this reaction). $\text{HC}_2\text{H}_3\text{O}_2$ is a weak acid; NaHCO_3 would completely dissociate in aqueous solution but, in baking soda, the ions are held together by ionic bonds in the solid. Thus, the full ionic equation is:



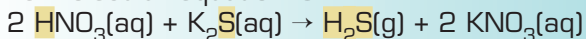
If we examine the full ionic equation, we can see that there are no spectator ions. Therefore, it is also the net ionic equation.

► Example


Predict what happens when $\text{HNO}_3(\text{aq})$ is mixed with $\text{K}_2\text{S}(\text{aq})$.

Answer:

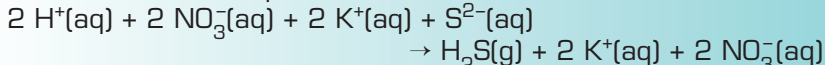
The H^+ from the acid combines with the anion from the salt to yield another acid (H_2S); the remaining ions (K^+ and NO_3^-) combine to form the salt. It is very likely that, if we carry out this reaction in the laboratory, we will observe the odor of rotten eggs due to $\text{H}_2\text{S}(\text{g})$. At room temperature, the solubility of H_2S in water is only 0.35 g per 100 g of water. Typically, this concentration is significantly exceeded. Thus, we specify $\text{H}_2\text{S}(\text{g})$ rather than $\text{H}_2\text{S}(\text{aq})$. The molecular equation is:



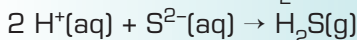
Based on the empirical solubility rules, we predict KNO_3 to remain in aqueous solution. $\text{KNO}_3(\text{aq})$, $\text{HNO}_3(\text{aq})$ and $\text{K}_2\text{S}(\text{aq})$ are strong



electrolytes in aqueous solution and should be written as separate ions in the full ionic equation.



We can see that K^+ and NO_3^- are spectator ions; they appear on both sides of the equation. The net ionic equation is simply the combination of H^+ from the acid and the anion from the salt (S^{2-}) to form a weak acid (H_2S):



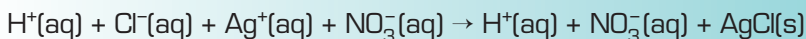
Note: This is not the only reaction that can occur. This is what we predict would happen based on the expected behavior of acids in general. HNO_3 is known to react with sulfides in what is called a redox reaction; redox reactions are covered in another lesson.

► Example

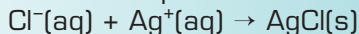
Predict what happens when $\text{HCl}(\text{aq})$ is mixed with $\text{AgNO}_3(\text{aq})$.

Answer:

We can imagine that the H^+ from the acid combines with the anion from the salt (NO_3^-) to yield another acid (HNO_3); the remaining ions (Ag^+ and Cl^-) combine to form another salt (AgCl). Based on the empirical solubility rules, we predict AgCl to be insoluble; we expect it to precipitate. All the other substances in the molecular equation are strong electrolytes in aqueous solution. Therefore, to write the ionic equation, they should be written as separate ions:



We can see that H^+ and NO_3^- are spectator ions; they appear on both sides of the equation. The net ionic equation,



has nothing to do with the H^+ from the acid.

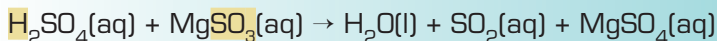
► Example

Predict what happens when sulfuric acid, $\text{H}_2\text{SO}_4(\text{aq})$, is mixed with $\text{MgSO}_3(\text{aq})$.

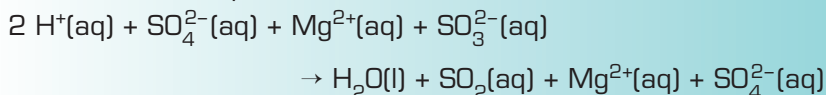
Answer:

The H^+ from the acid combines with the anion from the salt to yield another acid, H_2SO_3 (sulfurous acid). However, H_2SO_3 is

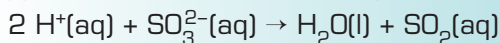
known to readily decompose to $\text{H}_2\text{O}(\text{l})$ and $\text{SO}_2(\text{aq})$. The overall molecular equation is:



and the full ionic equation is:



since sulfuric acid, $\text{MgSO}_3(\text{aq})$, and $\text{MgSO}_4(\text{aq})$ are all strong electrolytes in aqueous solution. The net ionic equation is obtained by canceling out the spectator ions, $\text{Mg}^{2+}(\text{aq})$ and $\text{SO}_4^{2-}(\text{aq})$, which appear on both sides of the equation. The net ionic equation is:



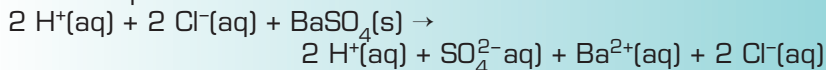
At room temperature, if the amount of SO_2 produced exceeds 10 g per 100 g of water, we may observe bubbles and a sharp odor due to $\text{SO}_2(\text{g})$.

▶ Example

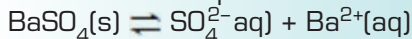
Predict what would happen when hydrochloric acid, $\text{HCl}(\text{aq})$, is mixed with barium sulfate $\text{BaSO}_4(\text{s})$.

Answer:

We can imagine that the H^+ from the acid combines with the anion from the salt (SO_4^{2-}) to yield another acid, H_2SO_4 (sulfuric acid) and a salt that is soluble in water (BaCl_2). To write the full ionic equation, we write $\text{BaCl}_2(\text{aq})$ and $\text{H}_2\text{SO}_4(\text{aq})$ as separate ions; they are both strong electrolytes in aqueous solution. The full ionic equation is:




If we get rid of the spectator ions, $\text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$, we are left with a net ionic equation of:



which just describes the “dissolution” of BaSO_4 in water.

This is just what would happen if we added water to solid barium sulfate, even without the acid. We replaced the single arrow with double-headed arrow since we know from our empirical solubility rules that BaSO_4 is insoluble in water. This means that the reaction, as written, will occur to a very, very small extent. For practical purposes, we could say that there really is no reaction when we mix $\text{HCl}(\text{aq})$ and $\text{BaSO}_4(\text{s})$. It is probably



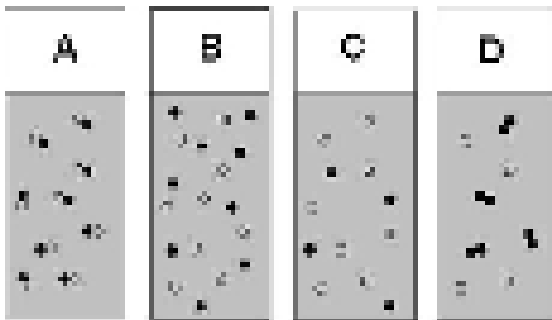
just as well since this is what happens when a person about to have a gastric x-ray is given a “barium cocktail.” If the barium sulfate were to react with HCl in the stomach and release a significant amount of toxic Ba^{2+} ions in solution, the patient could die.

TEST YOURSELF

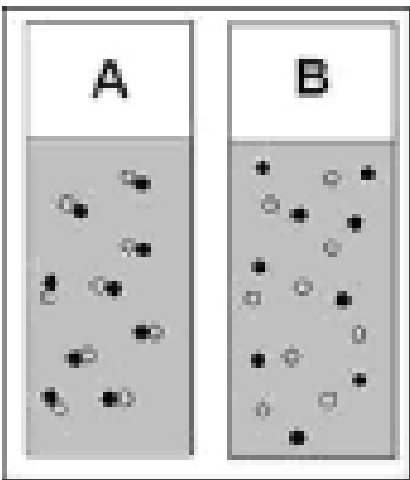
For answers and other study resources, see:

<http://i-assign.com/ebook/answers/chapter21.htm>.

1. Which figure below best represents an aqueous solution of CaCl_2 ?




2. Which figures below best represent aqueous solutions of HF and HCl?




- A. A for both B. B for both C. HF-B, HCl-A D. HF-A, HCl-B

3. Which of the following best represents the dissolution of $\text{CaCl}_2(\text{s})$ in water?

- A. $\text{CaCl}_2(\text{s}) \rightarrow \text{Ca}^{2+}(\text{aq}) + 2 \text{Cl}^{-}(\text{aq})$
B. $\text{CaCl}_2(\text{s}) \rightarrow \text{CaCl}_2(\text{aq})$
C. $\text{CaCl}_2(\text{s}) \rightarrow \text{Ca}^{2+}(\text{aq}) + \text{Cl}_2^{-}(\text{aq})$

- 
4. Which of the following best represents the dissolution of methanol, $\text{CH}_3\text{OH}(\text{l})$, in water?
- A. $\text{CH}_3\text{OH}(\text{l}) \rightarrow \text{CH}_3\text{OH}(\text{aq})$
B. $\text{CH}_3\text{OH}(\text{l}) \rightarrow \text{CH}_3^+(\text{aq}) + \text{OH}^-(\text{aq})$
C. $\text{CH}_3\text{OH}(\text{l}) \rightarrow \text{CH}_3\text{O}^-(\text{aq}) + \text{H}^+(\text{aq})$
D. $\text{CH}_3\text{OH}(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{CH}_3\text{OH}_2^+(\text{aq}) + \text{OH}^-(\text{aq})$
5. Which of the following best represents the ionization of nitric acid in water?
- A. $\text{HNO}_3(\text{aq}) \rightarrow \text{H}(\text{aq}) + \text{NO}_3(\text{aq})$
B. $\text{HNO}_3(\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$
C. $\text{HNO}_3(\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{N}^{3-}(\text{aq}) + 3 \text{O}^{2-}(\text{aq})$
D. $\text{HNO}_3(\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{N}^{3-}(\text{aq}) + \text{O}_3^-(\text{aq})$
6. Which of the following best represents the dissolution of gaseous ammonia (NH_3) in water?
- A. $\text{NH}_3(\text{g}) \rightarrow \text{NH}_3(\text{aq})$
B. $\text{NH}_3(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$
C. $\text{NH}_3(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{NH}_4\text{OH}(\text{aq})$
D. $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$
7. Which of the following is a weak base?
- A. NaOH B. $\text{Mg}(\text{OH})_2$ C. K_2O D. NH_3
8. Which of the following is insoluble in water?
- A. Na_2CO_3 B. MgSO_4 C. PbCl_2 D. CaS
9. Which of the following is insoluble in water?
- A. CuCl_2 B. Hg_2Cl_2 C. HgBr_2 D. $\text{Ca}(\text{NO}_3)_2$
10. Which of the following is soluble in water?
- A. MgCO_3 B. MgF_2 C. $\text{Mg}(\text{OH})_2$ D. MgSO_4
11. Precipitation is expected from which mixture?
- A. $\text{Na}_2\text{CO}_3(\text{aq}) + \text{KNO}_3(\text{aq})$ B. $\text{AgNO}_3(\text{aq}) + \text{CaCl}_2(\text{aq})$
C. Neither D. Both

12. A student is given two test tubes and is told that one contains NaCl(aq) , while the other test tube contains $\text{Ba(NO}_3)_2\text{(aq)}$. Which precipitating reagent, if added to both test tubes would allow the student to determine their contents?
 A. $\text{AgNO}_3\text{(aq)}$ B. $\text{K}_2\text{SO}_4\text{(aq)}$ C. neither D. both
13. What is the net ionic equation for the precipitation reaction that occurs when $\text{K}_2\text{SO}_4\text{(aq)}$ and $\text{Pb(NO}_3)_2$ are mixed?
 A. $\text{K}^+\text{(aq)} + \text{NO}_3^-\text{(aq)} \rightarrow \text{KNO}_3\text{(s)}$ B. $\text{Pb}^+\text{(aq)} + \text{SO}_4^-\text{(aq)} \rightarrow \text{PbSO}_4\text{(s)}$
 C. $\text{Pb}^{2+}\text{(aq)} + \text{SO}_4^{2-}\text{(aq)} \rightarrow \text{PbSO}_4\text{(s)}$
14. What is the net ionic equation for the precipitation reaction that occurs when $\text{Na}_2\text{CO}_3\text{(aq)}$ and AgNO_3 are mixed?
 A. $\text{Na}^+\text{(aq)} + \text{NO}_3^-\text{(aq)} \rightarrow \text{NaNO}_3\text{(s)}$ B. $\text{Ag}^+\text{(aq)} + \text{CO}_3^{2-}\text{(aq)} \rightarrow \text{Ag}_2\text{CO}_3\text{(s)}$
 C. $\text{Ag}^{2+}\text{(aq)} + \text{CO}_3^{2-}\text{(aq)} \rightarrow \text{AgCO}_3\text{(s)}$ D. $2 \text{Ag}^+\text{(aq)} + \text{CO}_3^{2-}\text{(aq)} \rightarrow \text{Ag}_2\text{CO}_3\text{(s)}$
15. For which of the following mixtures is the net ionic equation for neutralization given by:
 $\text{H}^+\text{(aq)} + \text{OH}^-\text{(aq)} \rightarrow \text{H}_2\text{O(l)}$
 A. $\text{HBr(aq)} + \text{KOH(aq)}$ B. $\text{HCl(aq)} + \text{NaOH(s)}$
 C. $\text{HC}_2\text{H}_3\text{O}_2\text{(aq)} + \text{Ba(OH)}_2\text{(aq)}$ D. $\text{HI(aq)} + \text{NH}_3\text{(aq)}$
16. What is the net ionic equation for the reaction between HF(aq) and $\text{Ca(OH)}_2\text{(aq)}$?
 A. $2 \text{HF(aq)} + \text{Ca(OH)}_2\text{(aq)} \rightarrow 2 \text{H}_2\text{O(l)} + \text{CaF}_2\text{(s)}$
 B. $2 \text{H}^+\text{(aq)} + 2 \text{F}^-\text{(aq)} + \text{Ca}^{2+}\text{(aq)} + 2 \text{OH}^-\text{(aq)} \rightarrow 2 \text{H}_2\text{O(l)} + 2 \text{F}^-\text{(aq)} + \text{Ca}^{2+}\text{(aq)}$
 C. $2 \text{HF(aq)} + \text{Ca}^{2+}\text{(aq)} + 2 \text{OH}^-\text{(aq)} \rightarrow 2 \text{H}_2\text{O(l)} + 2 \text{F}^-\text{(aq)} + \text{Ca}^{2+}\text{(aq)}$
 D. $2 \text{HF(aq)} + \text{Ca}^{2+}\text{(aq)} + 2 \text{OH}^-\text{(aq)} \rightarrow 2 \text{H}_2\text{O(l)} + \text{CaF}_2\text{(s)}$
17. What is the net ionic equation for the reaction between Mg(OH)_2 in milk of magnesia with HCl (in stomach acid)? The complete formula equation is:
 $\text{Mg(OH)}_2 + 2 \text{HCl} \rightarrow \text{MgCl}_2 + 2 \text{H}_2\text{O}$
 A. $\text{Mg}^{2+} + 2 \text{OH}^- + 2 \text{H}^+ + 2 \text{Cl}^- \rightarrow \text{Mg}^{2+} + 2 \text{Cl}^- + 2 \text{H}_2\text{O}$
 B. $\text{Mg(OH)}_2 + 2 \text{H}^+ + 2 \text{Cl}^- \rightarrow \text{Mg}^{2+} + 2 \text{Cl}^- + 2 \text{H}_2\text{O}$
 C. $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$
 D. $\text{Mg(OH)}_2 + 2 \text{H}^+ \rightarrow \text{Mg}^{2+} + 2 \text{H}_2\text{O}$

- 
18. What is the net ionic equation for the reaction between $\text{HNO}_3(\text{aq})$ and $\text{NH}_3(\text{aq})$?
- A. $\text{HNO}_3(\text{aq}) + \text{NH}_3(\text{aq}) \rightarrow \text{NH}_4\text{NO}_3(\text{aq})$
B. $\text{H}^+(\text{aq}) + \text{NO}_3^-(\text{aq}) + \text{NH}_3(\text{aq}) \rightarrow \text{NH}_4^+(\text{aq}) + \text{NO}_3^-(\text{aq})$
C. $\text{H}^+(\text{aq}) + \text{NH}_3(\text{aq}) \rightarrow \text{NH}_4^+(\text{aq})$
19. Which of the following appears in the net ionic equation for the reaction of $\text{HNO}_2(\text{aq})$ and $\text{Na}_2\text{CO}_3(\text{aq})$?
- A. $\text{HNO}_2(\text{aq})$ B. $\text{H}^+(\text{aq})$ C. $\text{Na}^+(\text{aq})$
20. Which of the following does not appear in the net ionic equation for the reaction of $\text{Ca}_3(\text{PO}_4)_2(\text{s})$ and $\text{HCl}(\text{aq})$?
- A. $\text{Ca}^{2+}(\text{aq})$ B. $\text{PO}_4^{3-}(\text{aq})$ C. $\text{H}^+(\text{aq})$ D. $\text{H}_3\text{PO}_4(\text{aq})$
21. Which of the following does not appear in the net ionic equation for the reaction $\text{BaCO}_3(\text{s})$ and $\text{H}_2\text{SO}_4(\text{aq})$?
- A. Ba^{2+} B. $\text{CO}_2(\text{g})$ C. $\text{H}_2\text{O}(\text{l})$ D. $\text{BaSO}_4(\text{s})$

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Molarity and Solution Stoichiometry

Since a large number of important reactions occur in aqueous solution, we need to learn how to count atoms, molecules, and ions present in aqueous solutions.

22.1 Molarity

The predominant component of a solution is called the *solvent*; all the other components are called *solutes*. When the solvent is water, we say that the solution is an *aqueous solution*. Unless otherwise specified, it is customary to assume that a solution is aqueous.

▶ Example

Imagine a solution prepared stirring a pinch of sugar into a glass of water. Identify the solute and solvent.

Answer: the solvent is water; the solute is sugar.

The *concentration* of a solute in a solution refers to the ratio of the amount of solute to either the amount of solvent or the amount of solution. Think of a concentration as a measure of how crowded the solute particles are; the higher the concentration, the more crowded.

Since there are many ways of expressing amounts, there are many ways of expressing concentration. The most commonly used way in Chemistry is *molarity* (or *molar concentration*). Aqueous solutions in the laboratory are typically labeled with the molar concentration of the solutes. Molarity is defined the moles of solute that would be present in a liter of solution. If M is the molarity, n is the moles of solute, and V is the volume of solution in liters, then:

$$M = \frac{n}{V}$$

Since one millimole is 1/1000 of a mole and one milliliter is 1/1000 of a liter, molarity can also be defined as the millimoles of solute per milliliter of solution.

The unit for molarity is *moles per liter*, which can be written as mol/L, mol L⁻¹, or M. It can also be written as mmol/mL or mmol mL⁻¹. If the solution contains only one solute, it is customary to refer to molar concentration of that solute as the *molarity of the solution*. If there is more than one solute, the molar concentration of a solute can also be referred to as the *molarity of the solution with respect to that solute*.

► Example

Describe the solution in the bottle illustrated below.



Answer:

NaCl is a solute in this solution. If we have a one-liter sample of this solution, that sample would contain 0.1 moles of NaCl. If we have a one-milliliter sample of this solution, that sample would contain 0.1 millimoles of NaCl. The label is read as “0.1 molar sodium chloride.” We can say that the solution is “0.1 molar in NaCl” or “0.1 molar with respect to NaCl.”

22.1.1 Calculating Amount of Solutes

We are frequently interested in determining the amount of solute present in a given sample of solution. This is easily done by solving for n in the defining equation for molarity:

$$M = \frac{n}{V}$$

Multiplying both sides by V , we get:

$$n = VM$$

► Example

How much Na_2CO_3 is in a 2.00 L sample of 0.200M Na_2CO_3 ?

Answer: 0.400 mol or 42.4 g

Based on the definition of molarity, we conclude that one liter of this solution would contain 0.200 moles of Na_2CO_3 . Common sense tells us that two liters should contain twice as much Na_2CO_3 , and that is what we get when we do the calculation:

$$n = VM = (2.00 \text{ L})(0.200 \text{ mol L}^{-1}) = 0.400 \text{ mol}$$

Two liters, times 0.200 moles for each liter, equals 0.400 moles. In cases where we have to deal with more than one solute, we can avoid ambiguity by being more descriptive with our units. For example, we use “mol Na_2CO_3 ” instead of just “mol.” We can also put L in the denominator instead of writing L^{-1} .

$$2.00 \text{ L} \times \left(\frac{0.200 \text{ mol Na}_2\text{CO}_3}{1 \text{ L}} \right) = 0.400 \text{ mol Na}_2\text{CO}_3$$

Note that the ratio of (moles of solute) and (Liters of solution) implied by the molarity is essentially a conversion factor, to change liters of solution to moles of solute.

If we are interested in the amount in grams, all we need to do is convert from moles to grams. We would need the molar mass of Na_2CO_3 , which is 105.99 g/mol.

$$0.400 \text{ mol Na}_2\text{CO}_3 \times \left(\frac{105.99 \text{ g Na}_2\text{CO}_3}{1 \text{ mol Na}_2\text{CO}_3} \right) = 42.4 \text{ g Na}_2\text{CO}_3$$

► Example

How would you prepare a 2.00 L solution of 0.200M Na_2CO_3 ?

Answer: Based on the preceding example, we know that this solution should contain 42.4 grams of sodium carbonate. So, we go to the laboratory, weigh out 42.4 grams of sodium carbonate, then add enough water to make a solution with a total volume of 2.00 liters.

► Example

How many moles of sucrose ($C_{12}H_{22}O_{11}$) does a 25.0 mL sample of 0.500 M $C_{12}H_{22}O_{11}$ contain?

Answer:

Since we're given the volume in mL, we can first get the amount of solute in millimoles.

$$n = VM = (25.0 \text{ mL})(0.500 \text{ mmol mL}^{-1}) = 12.5 \text{ mmol}$$

Then, we change millimoles to moles:

$$12.5 \text{ mmol} = 12.5 (10^{-3} \text{ mol}) = 0.0125 \text{ mol}$$

Alternatively, we can first convert mL to L,

$$25.0 \text{ mL} = 25.0 (10^{-3} \text{ L}) = 0.0250 \text{ L},$$

then multiply the volume in liters by the molarity:

$$n = VM = (0.0250 \text{ L})(0.500 \text{ mol L}^{-1}) = 0.0125 \text{ mol}$$

22.1.2 Counting Ions in Solution

When dealing with aqueous solutions of electrolytes, we are often interested in the amount of specific ions. In these cases, we just multiply moles of compound with the subscript of the ion in one formula unit.

► Example

How many moles of chloride ions are there in 2.00 L of 0.300 M $BaCl_2$?

Answer: First, we find the moles of $BaCl_2$:

$$2.00 \text{ L} \times \left(\frac{0.300 \text{ mol } BaCl_2}{1 \text{ L}} \right) = 0.600 \text{ mol } BaCl_2$$

The subscript of chloride in $BaCl_2$ is 2; this means that there are 2 moles of chloride ions for every mole of $BaCl_2$. Therefore, the number of moles of chloride ions is two times 0.600 moles, or 1.20 moles:

$$0.600 \text{ mol } BaCl_2 \times \left(\frac{2 \text{ mol } Cl^-}{1 \text{ mol } BaCl_2} \right) = 1.20 \text{ mol } Cl^-$$

22.1.3 Calculating Molarity

To calculate the molarity of a compound in solution, all we have to do is figure out how many moles of the compound is present (in a given volume of solution), then divide that by the volume of solution in liters.

► Example

Suppose a 2.00 L solution contains 0.400 mol NaOH. What is the molar concentration of NaOH in this solution?

Answer:

$$M = \frac{n}{V} = \frac{0.400 \text{ mol}}{2.00 \text{ L}} = 0.200 \text{ mol L}^{-1}$$

If we are given the amount of solute in grams, we just need to convert it to moles first.

22.1.4 Molar Concentration of Ions

When dealing with strong electrolytes, we are usually interested in the molar concentration of specific ions. If we know the molarity of the compound, all we have to do is multiply it by the appropriate subscript to get the molarity of the ion we're interested in.

► Example

What is the molar concentration of sulfate ions in 0.500 M Na_2SO_4 ?

Answer: The coefficient of sulfate in Na_2SO_4 is 1. Therefore,

$$\frac{0.500 \text{ mol } \cancel{\text{Na}_2\text{SO}_4}}{\text{L}} \times \frac{1 \text{ mol } \text{SO}_4^{2-}}{1 \cancel{\text{ mol } \text{Na}_2\text{SO}_4}} = 0.500 \cdot \frac{\text{mol } \text{SO}_4^{2-}}{\text{L}}$$

The molar concentration of a specific ion or molecule is denoted by putting the formula of the ion or molecule inside square brackets. In the preceding example, we say that the molar concentration of sulfate ions is 0.500 mol L^{-1} by writing:

$$[\text{SO}_4^{2-}] = 0.500$$

or:

$$[\text{SO}_4^{2-}] = 0.500 \text{ mol L}^{-1}$$

The unit (mol L^{-1}) is implied but some teachers prefer that the unit be explicitly indicated.

If more than one strong electrolyte is present in solution, then the molar concentration of an ion is calculated by adding up contributions from all sources.

► Example

What is the molar concentration of chloride ions in a solution that is 0.10M with respect to NaCl and 0.20M with respect to BaCl₂?

Answer: 0.50 mol L⁻¹

The contribution from NaCl is:

$$\frac{0.10 \text{ mol NaCl}}{\text{L}} \times \frac{1 \text{ mol Cl}^-}{1 \text{ mol NaCl}} = 0.10 \cdot \frac{\text{mol Cl}^-}{\text{L}}$$

and the contribution from BaCl₂ is:

$$\frac{0.20 \text{ mol BaCl}_2}{\text{L}} \times \frac{2 \text{ mol Cl}^-}{1 \text{ mol BaCl}_2} = 0.40 \cdot \frac{\text{mol Cl}^-}{\text{L}}$$

Therefore, the molar concentration of chloride is:

$$\begin{aligned} [\text{Cl}^-] &= [\text{Cl}^-] \text{ from NaCl} + [\text{Cl}^-] \text{ from BaCl}_2 \\ &= 0.10 \text{ M} + 0.40 \text{ M} = 0.50 \text{ M} \end{aligned}$$

22.1.5 Dilution


Dilution refers to the addition of more solvent to a solution. What happens when we do this? Recall that molarity is defined as:

$$M = \frac{n}{V}$$

where *n* is the moles of solute and *V* is the volume of solution. Adding more solvent increases the volume, but the amount of solute remains the same. Therefore, we will now have a larger denominator (*V*), but the same *n*. This means that the molarity decreases. In other words, diluting a solution lowers the concentration.

Dilution is a commonly used procedure in the laboratory to prepare a solution if a solution of higher concentration happens to be in stock. If we use *M*₁ and *V*₁ to represent the molarity and volume of a solution (the “stock solution”), and *M*₂ and *V*₂ as the new molarity and volume after dilution, then:

$$V_1 M_1 = V_2 M_2$$



This is called the dilution formula. This formula simply says that the amount of solute does not change when we do a dilution. Remember that the amount of solute (in moles) is simply the product of V and M . All we are doing when doing a dilution is adding more solvent.

► Example

What is the molarity of the resulting solution if 1.00L of 2.00M NaOH solution is diluted to 4.00L?

Answer: 0.500M

We divide both sides of the dilution formula by the final volume V_2 , in order to solve for the final molarity (M_2):

$$M_2 = \frac{V_1 M_1}{V_2} = \frac{(1.00 \cancel{\text{L}})(2.00 \text{ M})}{4.00 \cancel{\text{L}}} = 0.500 \text{ M}$$

We can see that increasing the total volume 4-fold reduces the molarity to 1/4 of the original concentration; 0.500 is 1/4 of 2.00. The relationship between M and V in the dilution formula is an example of what is called *inverse proportionality*. Two quantities are said to be inversely proportional if their product is a constant. In the case of the dilution formula, the product of V and M is the amount of solute, which does not change when we do dilutions. If two quantities are inversely proportional, then when one increases, the other decreases by the same factor; for example, if one doubles (multiplied by 2), the other is halved (divided by 2).

22.2 Solution Stoichiometry

The amounts of reactants and products involved in a reaction are directly proportional and the mole-to-mole ratio is given by the coefficients in the balanced equation. If we represent *changes* in moles of substances “1” and “2” as n_1 and n_2 , and represent their coefficients as c_1 and c_2 , then:

$$\frac{n_1}{n_2} = \frac{c_1}{c_2}$$

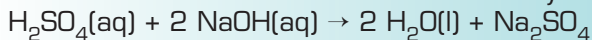
which we can rearrange into a more ready-to-use form:

$$n_2 = n_1 \cdot \frac{c_2}{c_1}$$

If we know how much (in moles) of one substance was consumed or produced in a reaction, we assign it to n_1 , then we multiply it by an appropriate ratio of coefficients to get the amount involved for any of the other substances involved in the ratio. When dealing with reactions in aqueous solution, it is important to remember that the number of moles of solute is just equal to the VM, where V is the volume of solution in liters and M is the molar concentration of the solute.

► Example

Consider the neutralization of sulfuric acid by sodium hydroxide.



How many moles of H_2SO_4 will be neutralized by 25.0 mL of 0.200M NaOH?

Answer: 2.50×10^{-3} mol

We are given molarity and volume of the NaOH solution; therefore, we can use this to calculate moles of NaOH.

$$25.0 \text{ (} 10^{-3} \text{ L)} \times \frac{0.200 \text{ mol NaOH}}{\text{L}} = 5.00 \times 10^{-3} \text{ mol NaOH}$$

Note that we first replaced mL by 10^{-3} L in order to have the answer in moles. From this, we can solve for the moles of H_2SO_4 :

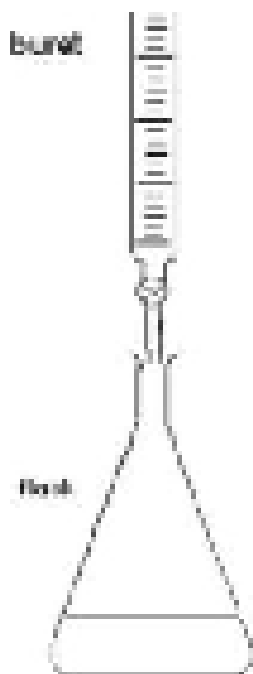
$$(5.00 \times 10^{-3} \text{ mol NaOH}) \times \left(\frac{1 \text{ mol H}_2\text{SO}_4}{2 \text{ mol NaOH}} \right) = 2.50 \times 10^{-3} \text{ mol H}_2\text{SO}_4$$

Titration is a typical laboratory procedure for determining unknown amounts of substances or ions in a sample. The two reactants in a titration are called the *standard* (the “known”) and the *analyte*. (the “unknown”). Titration involves the gradual addition of one reactant (the titrant) to another. The titrant is usually the standard; it is a solution dispensed with a buret as illustrated in Figure 1. The other reactant, usually the analyte, is placed in a flask.

The addition of titrant is stopped when a drastic change is observed in the reaction mixture; the point when this happens is called the *endpoint*. Titrations are designed so that the endpoint very closely approximates the *equivalence point*. At the equivalence point, the mole-to-mole ratio of the standard and analyte is equal to the ratio of their coefficients in the balanced equation.

Traditionally, a small amount of another reagent is added to the flask before the start of a titration in order to be able to determine the endpoint; this reagent is called an *indicator*.

Figure 1. Experimental Setup for Titration



For example, in the titration of an acid by a base, one or two drops of phenolphthalein solution is added to the acid in the flask. The endpoint of the titration occurs when the phenolphthalein changes from being colorless to having a very light pink color. With modern instrumentation, titration endpoints can be determined by monitoring some property of the reaction mixture, such as pH, electrical conductivity and (light) absorbance.

Sometimes, the concentration of a solution meant to be used a standard must first be determined. In this case, we do what is called a *standardization*—a titration is carried out where the solution (titrant) is the unknown and the sample in the flask is the standard. Once this is done, the solution can then be used as a standard for other (unknown) samples in the flask. For example, a solution of NaOH can be used as a standard for determining unknown amounts of acids. But before it can be used, we need to determine its concentration by using it to titrate a precisely known amount of the acid called “KHP” (potassium hydrogen phthalate, or potassium biphthalate, $\text{KHC}_8\text{H}_4\text{O}_4$). In this case, we say that the NaOH solution is being standardized against KHP, KHP is the *primary standard*, and NaOH is a *secondary standard*.




TEST YOURSELF

For answers and other study resources, see:

<http://i-assign.com/ebook/answers/chapter22.htm>.

- How many moles of NaCl are in a 400.0 mL sample of 0.18M NaCl?
A. 0.072 mol B. 72 mol C. 0.45 mol D. 2.2 mol
- How many grams of NaCl are in a 400.0mL sample of 0.18M NaCl?
A. 2.2 g B. 4.2 g C. 7.2 g
- An aqueous solution in the lab is labeled “0.100 M HC₂H₃O₂”. How many moles of acetic acid are in a 25.0 mL sample of this solution?
- An aqueous solution in the lab is labeled “6.00 M HC₂H₃O₂”. How many grams of acetic acid are in a 2.00 L sample of this solution?
- How many moles of sodium ions are in 50.0 mL of 0.400 M Na₂CO₃?
A. 0.0200 mol B. 0.0400 mol C. 0.25 mol D. 6.67×10⁻³ mol
- What is the molarity of a solution if a 2.0 L sample contains 3.0 mol NaOH?
A. 1.5 M B. 0.67 M C. 6.0 M
- What is the molar concentration of NaCl in a solution prepared by dissolving 11.6 g NaCl in enough water to make a 500.0 mL solution?
A. 0.0232 M B. 0.397 M C. 5.80 M
- What is the molar concentration of chloride ions in 0.30M BaCl₂?
A. 0.30M B. 0.15M C. 0.60M D. 0.20M
- What is the molar concentration of sodium ions in a solution that is 0.20M in NaCl and 0.30M in Na₂SO₄?
A. 0.50M B. 0.25M C. 0.70M D. 0.80M
- A solution is prepared by mixing 10.0 mL of 0.100M NaNO₃, 20.0 mL of 0.300M Ca(NO₃)₂, and enough water to bring the total volume up to 50.0 mL. What is the molar concentration of nitrate ions in the resulting solution?
A. 0.200M B. 0.260M C. 0.130 M D. 0.700 M

- 
11. Consider a 0.500 M NaOH(aq). If enough water is added to a 10.0 mL sample of this solution in order to bring up the total volume to 100.0mL, what is the molarity of the resulting solution?
- A. 0.0500M B. 1.00M C. 2.00M D. 5.00M
12. How much water should be added to a 100.0mL sample of 6.000M NaOH in order to dilute the solution to 3.000M?
- A. 100.0 mL B. 200.0 mL
C. enough to bring the total volume to 200.0 mL D. none of the above
13. Consider the neutralization of Mg(OH)₂(s) by HCl(aq).
- $$\text{Mg(OH)}_2(\text{s}) + 2 \text{HCl}(\text{aq}) \rightarrow \text{MgCl}_2(\text{aq}) + 2 \text{H}_2\text{O}(\text{l})$$
- What volume of 0.200M HCl(aq) is required to neutralize 0.200 mol Mg(OH)₂?
- A. 500.0 mL B. 1.00 L C. 2.00 L D. 4.00 L
14. What mass of silver chloride will be formed if 50.0 mL of 0.750 molar silver nitrate is mixed with 70.0 mL of 0.500 molar sodium chloride?
- A. 2.04 g B. 5.02 g C. 5.37 g D. 6.37 g
15. Consider the neutralization of sulfuric acid by sodium hydroxide.
- $$\text{H}_2\text{SO}_4(\text{aq}) + 2 \text{NaOH}(\text{aq}) \rightarrow 2 \text{H}_2\text{O}(\text{l}) + \text{Na}_2\text{SO}_4$$
- What if a 25.00 mL sample of sulfuric acid solution is titrated with 0.500M NaOH. If 25.00 mL of the base was required to reach the endpoint, what is the molarity of the sulfuric acid solution?
- A. 0.125M B. 0.250M C. 0.500M D. 1.00M

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Ideal Gas Behavior

The behavior of gases is best summarized by the equation:

$$PV = nRT$$

This equation is called the ideal gas equation. In this equation P , V , and T are the pressure, volume, and temperature of the gas, n is the amount of gas in moles, and R is a constant. In this chapter, we will examine these quantities in depth.

23.1 Pressure

Pressure is defined as force per unit area. If a force, f , is applied to a surface with an area of A , then the pressure, P , is given by:

$$P = \frac{f}{A}$$

The SI unit for pressure is the Pascal (Pa), or Newton per square meter (N m^{-2}). In terms of the base units,

$$1 \text{ N} = 1 \text{ kg m s}^{-2}$$

$$1 \text{ Pa} = 1 \text{ N m}^{-2} = 1 (\text{kg m s}^{-2})(\text{m}^{-2}) \text{ or } 1 (\text{kg m}^{-1} \text{ s}^{-2})$$

► Example

Calculate the pressure at the bottom of a column of mercury (Hg) liquid that is 76.0 cm high. The density of liquid Hg is 13.6 g/mL or $13.6 \times 10^3 \text{ kg m}^{-3}$.

Answer: $1.01 \times 10^5 \text{ Pa}$

We figure out the pressure that the Hg column exerts on whatever is at the bottom of the column as follows:

- The earth's gravitational pull exerts a downward force on anything; this is called the weight. The weight of the Hg column is equal to its mass (m) times the acceleration due to gravity (g): $f = mg$, where $g = 9.81 \text{ m s}^{-2}$
- According to Newton's second law, if the Hg column is not moving, then the net force on it is zero. This means that

whatever is at the bottom of the column must be exerting an upward force on the column that counteracts the pull of gravity; this is called the “normal force” and is due to net repulsions between the atoms of Hg and those on the surface once the atoms get too close. Thus, the normal force is also equal to mg , but directed upward.

- According to Newton’s third law, the Hg column exerts an equal and opposite force on whatever is at the bottom. Therefore, we conclude that the Hg column exerts a downward force of mg on whatever is at the bottom.
- The pressure on the surface at the bottom of the Hg column is, therefore, mg/A , where A is the cross sectional area of the Hg column. If we assume that the column has a uniform cross sectional area, then the volume (V) of the column is just equal to the cross sectional area times the height (h); $V = Ah$. Therefore, the cross sectional area is equal to V/h . The pressure due to a column of liquid of height h and cross sectional area A is:

$$P = \frac{f}{A} = \frac{mg}{A} = \frac{mg}{\left(\frac{V}{h}\right)} = \frac{mgh}{V}$$

- Density is defined as the ratio of mass (m) to volume (V); $d = m/V$. Substituting d for (m/V) in the preceding equation, we get:

$$P = dgh$$

For a column of Hg that is 76.0 cm (or 0.760 m) high,

$$\begin{aligned} P &= dgh = (13.6 \times 10^3 \text{ kg m}^{-3})(9.81 \text{ ms}^{-2})(0.760 \text{ m}) \\ &= 1.01 \times 10^5 \text{ Pa} \end{aligned}$$

Although we assumed a uniform cross sectional area in the preceding example, it turns out that for any column of liquid, the pressure only depends on the height and density. The formula we derived, $P = dgh$, is valid whether or not the cross sectional area is uniform.

In Chemistry, we typically deal with pressure associated with gases. Pressures of gases are commonly expressed in terms of equivalent heights of Hg column (cm Hg or mm Hg), Torr, atmosphere, bar, mbar (millibar), and psi (pounds per square inch). These units are related as follows:

$$\begin{aligned} 1 \text{ atm} &= 76 \text{ cm Hg} = 760 \text{ mm Hg} = 760 \text{ Torr} \\ &= 1.01325 \times 10^5 \text{ Pa} = 1.01325 \text{ bar} = 1013.25 \text{ mbar} = 14.7 \text{ psi} \end{aligned}$$

It is obvious from the preceding that:

$$1 \text{ mm Hg} = 1 \text{ Torr}$$

$$1 \text{ bar} = 10^5 \text{ Pa} = 1000 \text{ mbar}$$

► Example

Express the pressure due to a 1.00 m column of Hg in cm Hg, mm Hg, Torr, atm, Pa, and bar.

Answer:

We can use heights of Hg in cm or mm as units of pressure. Since 1.00 m is equivalent to 100 cm or 1000 mm,

$$P = 1.00 \text{ m Hg} \cdot \frac{100 \text{ cm Hg}}{1 \text{ m Hg}} = 1.00 \cdot 10^2 \text{ cm Hg}$$

$$P = 1.00 \text{ m Hg} \cdot \frac{1000 \text{ mm Hg}}{1 \text{ m Hg}} = 1.00 \cdot 10^3 \text{ mm Hg}$$

In other units:

$$P = 1.00 \cdot 10^3 \text{ mm Hg} \cdot \frac{1 \text{ Torr}}{1 \text{ mm Hg}} = 1.00 \cdot 10^3 \text{ Torr}$$

$$P = 1.00 \cdot 10^3 \text{ mm Hg} \cdot \frac{1 \text{ atm}}{760 \text{ mm Hg}} = 1.32 \text{ atm}$$

$$P = 1.00 \cdot 10^3 \text{ mm Hg} \cdot \frac{1.01325 \cdot 10^5 \text{ Pa}}{760 \text{ mm Hg}} = 1.33 \cdot 10^5 \text{ Pa} = 1.33 \text{ bar}$$

► Example

What is the pressure underwater at a depth of 50.0 m? Assume the water surface is at sea level; take the density of water as 1.00 g/mL, or $1.00 \times 10^3 \text{ kg m}^{-3}$.

Answer. 5.84 atm

The pressure due to water is:

$$P = dgh = (1.00 \times 10^3 \text{ kg m}^{-3})(9.81 \text{ m s}^{-2})(50.0 \text{ m}) = 4.905 \times 10^5 \text{ Pa}$$

In atmospheres, the pressure due to water is:

$$P = 4.905 \cdot 10^5 \cdot \frac{1 \text{ atm}}{1.01325 \cdot 10^5 \text{ Pa}} = 4.84 \text{ atm}$$

There is an additional pressure of 1.00 atm due to the air above the water surface. So the total pressure is 5.84 atm.

An alternative way of determining the pressure due to water is to use the fact that Hg is 13.6 times denser than water. Therefore, the pressure due to 1 mm Hg is equivalent to the pressure of 13.6 mm H₂O.

$$P = 50.0 \text{ m H}_2\text{O} \cdot \frac{1000 \text{ mm H}_2\text{O}}{1 \text{ m H}_2\text{O}} \cdot \frac{1 \text{ mm Hg}}{13.6 \text{ mm H}_2\text{O}} \cdot \frac{1 \text{ atm}}{760 \text{ mm Hg}}$$
$$= 4.84 \text{ atm}$$

Essentially, we divide the height of water column by 13.6 to get the equivalent height of mercury column.

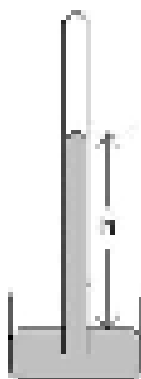
23.2 Gas Pressure Measurement

The pressure of a gas is due to the force exerted by gas particles on a surface (such as the wall of the gas container); the force is the result of collisions of gas particles with the surface.

Nowadays, gas pressure is conveniently measured using electronic sensors. Traditional methods of measuring the pressure of a gas use columns of mercury. Atmospheric pressure is measured using a barometer, which is illustrated in Figure 1.

Imagine a tube with no gas in it (a *vacuum*), sealed at the top, is inverted and opened into a pool of liquid mercury. The atmospheric pressure pushing down on the pool will cause the liquid to rise up the tube. This is similar to what happens if you suck the air out of a straw that is dipped in a glass of water. The atmospheric pressure on the water causes it to rise up the straw. At sea level, the typical atmospheric pressure will cause the Hg to rise to a height (h) of about 76 cm above the surface of the pool, provided the space above the Hg column is a vacuum. It is for this reason that a pressure of 1 atmosphere (abbreviated

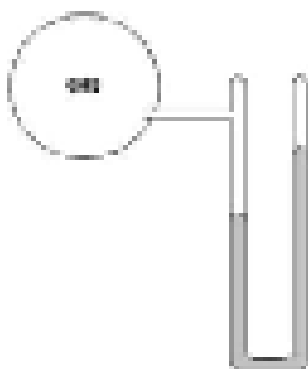
Figure 1. Barometer



as 1 atm) is defined to be equivalent to the pressure due to a mercury column that is *exactly* 76 cm high. The actual atmospheric pressure varies depending on where you are and the prevailing weather conditions. In other words, atmospheric pressure is hardly ever exactly 1 atm; to avoid confusion, it is preferable to refer to atmospheric pressure as *barometric pressure*.

For samples of gases, the pressure is measured using a manometer, a U-shaped tube filled with mercury. In a close-end manometer, Figure 2, the gas is connected to one arm and the space above the Hg in the other arm is a vacuum. The pressure of the gas is manifested as a difference in the height of the Hg in the arms. The mercury level in the arm connected to the gas would be lower. If it is lower by h cm, then the pressure of the gas is h cm Hg.

Figure 2. Close-end Manometer



► Example

A gas is connected to a close-end manometer. If the difference in mercury levels is 20.0 cm, what is the pressure of the gas in Torr?

Answer: 2.00×10^2 Torr

The pressure of the gas is 20.0 cm Hg, which is equivalent to 200 mm Hg, or 2.00×10^2 mm Hg. But 1 mm Hg is equivalent to 1 Torr. So, the pressure of the gas is 2.00×10^2 Torr.

Another common setup for measuring gas pressure involves an open-end manometer, as illustrated in Figures 3 and 4. One arm of the manometer is connected to the gas and the other arm is open to the atmosphere. If the pressure of the gas is equal to the prevailing barometric pressure, then the mercury levels will be the same in both arms. If the pressure of the gas is higher than the prevailing barometric pressure, the Hg level will be

lower in the arm connected to the gas as illustrated in Figure 3. If the difference in height is h , then the pressure of the gas is: $P_{\text{gas}} = P_{\text{barometric}} + h$

Figure 3. Open-end Manometer; $P_{\text{gas}} > P_{\text{barometric}}$

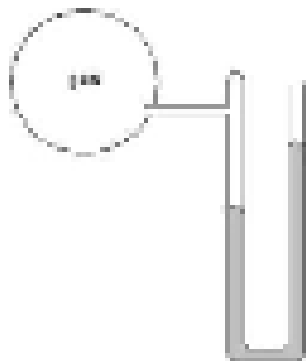
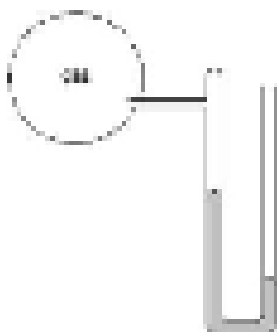


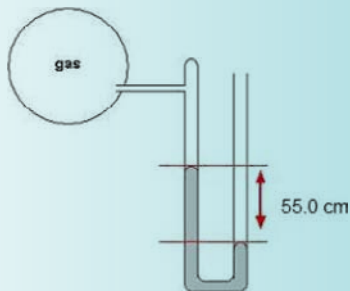
Figure 4. Open-end Manometer; $P_{\text{gas}} < P_{\text{barometric}}$



If the pressure is lower than the prevailing barometric pressure, the Hg level will be higher in the arm connected to the gas as illustrated in Figure 4. If the difference in height is h , then the pressure of the gas is: $P_{\text{gas}} = P_{\text{barometric}} - h$

► **Example**

What is the pressure of the gas in the figure illustrated below if the right arm of the manometer is open to the atmosphere and the prevailing barometric pressure is 1.00 atm.



Answer: 21.0 cm Hg

The pressure of the gas is lower than the barometric pressure:

$$P = P_{\text{barometric}} - h.$$

The barometric pressure is given as 1.00 atm, which is equivalent to 76.0 cm Hg. Therefore:

$$P = 76.0 \text{ cm Hg} - 55.0 \text{ cm Hg} = 21.0 \text{ cm Hg}$$

Blood pressure measurements are, in fact, measurements of air pressure in the cuff that is wrapped around a person's arm. Air is pumped into the cuff and the air pressure in the cuff is monitored as the air is released. The device used to monitor the pressure is called a sphygmomanometer.

23.3 Gas Laws Relating P, V, and T

The ideal gas equation, $PV = nRT$, summarizes several laws that describe the behavior of gases at low pressures. In this section, we discuss laws based on studies of how the pressure (P), volume (V), and temperature (T) are related for a fixed amount of gas (i.e. constant n).

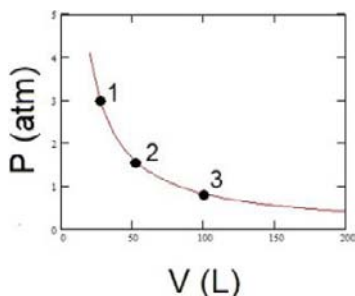
23.3.1 Boyle's Law

Robert Boyle discovered the relationship between P and V for a fixed amount of gas at constant T . He found that P and V are inversely proportional. When two quantities are inversely proportional, it means that if one increases, the other decreases by the same factor. Mathematically, we say that two quantities are inversely proportional if their product is a constant:

$$PV = \text{constant}$$

We can see that this is consistent with the ideal gas equation; for a fixed amount of gas (constant n) at constant T , the right-hand side of the ideal gas equation is constant since R is also a constant. If we were to plot P vs. V at constant T , we would get a curve similar to that shown in Figure 5. Any plot at constant T is called an *isotherm*. The isotherm shown in Figure 5 is for one mole of an ideal gas at 1000K. At any point on the isotherm, the

Figure 5. PV Isotherm



product PV has the same value; that value is nRT . For the points labeled “1”, “2”, and “3” we can say that:

$$P_1 V_1 = P_2 V_2 = P_3 V_3$$

It is easy to see from the graph that the volume doubles from point 1 to point 2 while the pressure is halved. Similarly, from point 2 to point 3, volume is doubled while pressure is halved.

► Example

A 25.0 L sample of gas, initially at 1.00 atm expands to 50.0 L at constant temperature. Calculate the final pressure.

Answer. 0.500 atm

The problem explicitly states that T is constant. There is nothing in the problem that indicates a possible change in amount of gas; so, n is also constant. Therefore, Boyle's Law is applicable for this problem; if we refer to the initial pressure and volume as P_1 and V_1 , and to the final pressure and volume as P_2 and V_2 , then:

$$P_1 V_1 = P_2 V_2$$

Solving for the final pressure, P_2 , we get:

$$P_2 = \frac{P_1 V_1}{V_2} = \frac{(1.00 \text{ atm})(25.0 \cancel{\text{ L}})}{50.0 \cancel{\text{ L}}} = 0.500 \text{ atm}$$

We can see that doubling the volume causes the pressure to be cut in half.

If we rearrange the ideal gas equation so that only P is on the left-hand-side, we get:

$$P = nRT \left(\frac{1}{V} \right)$$

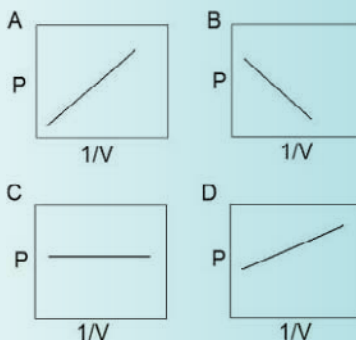
If nRT is constant, then a plot of P vs. $1/V$ is a straight line. The standard form for the equation of a straight line is:

$$y = mx + b$$

where m is the slope and b is the y -intercept. If we let $y = P$ and $x = (1/V)$, we can see that the slope, m , is equal to nRT , and the y -intercept, b , is equal to zero.

► Example

Which of the four graphs below illustrates Boyle's Law? Assume the bottom left corners of the graphs shown below correspond to $(0,0)$.



Answer. A

If we plot P vs. $1/V$, we are letting $y = P$ and $x = 1/V$ and we get a straight line with a slope of nRT , and a y -intercept of zero.

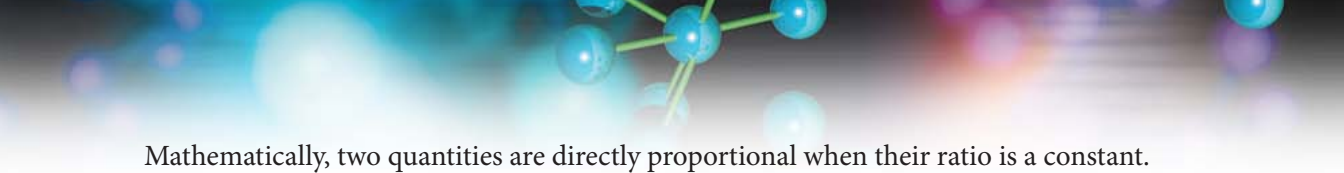
$$P = nRT \left(\frac{1}{V} \right)$$

$$y = mx + b$$

Since n , R , and T are positive numbers, the slope is positive. The graph that fits this description is A. Graph B has a negative slope. Graph C has a zero slope. Graph D has a positive slope, but its y -intercept is not zero. Graphs B and C also have nonzero y -intercepts.

23.3.2 Charles' Law

Jacques Charles discovered the relationship between V and T for a fixed amount of gas at constant P . Joseph Gay-Lussac first published the discovery; thus, the law is sometimes known as Charles' and Gay-Lussac's law. The modern statement of Charles' law states that V and T are directly proportional at constant n and P . When two quantities are directly proportional, it means that when one changes, the other also changes by the same factor.



Mathematically, two quantities are directly proportional when their ratio is a constant. Therefore:

$$\frac{V}{T} = \text{constant}$$

We can see that this is consistent with the ideal gas equation. If we rearrange the ideal gas equation to solve for V/T :

$$\frac{V}{T} = \frac{nR}{P}$$

we can see that the right-hand-side is constant if n and P are constants. If we were to plot V vs. T , we expect to get a straight line.

It is very important to note that T in the equations above refer to the absolute temperature in Kelvin. The temperature in Kelvin is obtained by adding 273.15 to the Celsius temperature,

► Example

A 10.0 L sample of gas initially at 300.0K is heated to 600.0K at constant pressure. What is the final volume of the gas?

Answer. 20.0 L

The problem explicitly states that P is constant. There is nothing in the problem that indicates a possible change in amount of gas; so, n is also constant. Therefore, Charles' Law is applicable for this problem; if we refer to the initial volume and temperature as V_1 and T_1 , and refer to the final volume and temperature as V_2 and T_2 , then:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Solving for V_2 , we get:

$$V_2 = \frac{V_1}{T_1} T_2 = \left(\frac{10.0 \text{ L}}{300.0 \text{ K}} \right) (600.0 \text{ K}) = 20.0 \text{ L}$$

We can see that doubling of the temperature leads to a doubling of the volume.

23.3.3 Amontons' Law

Guillaume Amontons discovered the relationship between P and T at constant n and V . He found that P and T are directly proportional at constant n and V . Amontons' Law is erroneously called Gay-Lussac's law in some textbooks. Mathematically, this means that:

$$\frac{P}{T} = \text{constant}$$

We can see that this is consistent with the ideal gas equation if we rearrange the ideal gas equation to solve for P/T . We get:

$$\frac{P}{T} = \frac{nR}{V}$$

and see that the right-hand-side is, indeed, constant when n and V are constant.

► Example

A fixed-volume container contains a gas at 300.0K, 1.00 atm. If the temperature is increased to 600.0K, calculate the final pressure.

Answer. 2.00 L

The problem says that V is constant (“fixed volume”) and there is nothing to indicate that there is a change in the amount of gas (so n is also constant). If we refer to the initial pressure and temperature as P_1 and T_1 , and to the final temperature as P_2 and T_2 , Amontons’ law says that:

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

Solving for P_2 , we get:

$$P_2 = \frac{P_1}{T_1} T_2 = \left(\frac{1.00 \text{ atm}}{300.0 \text{ K}} \right) (600.0 \text{ K}) = 2.00 \text{ L}$$

23.3.4 Combined Gas Law

The relationship between P , V , and T for a fixed amount of gas can be combined into just one equation.

$$\frac{PV}{T} = \text{constant}$$

Once again, we can see that this is consistent with the ideal gas equation, which we can rearrange to:

$$\frac{PV}{T} = nR$$

to show that PV/T is indeed equal to a constant for a fixed amount of gas (constant n). The combined gas law is useful for determining how one of the three quantities change if changes in the other two are known; we simply use the equation:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$



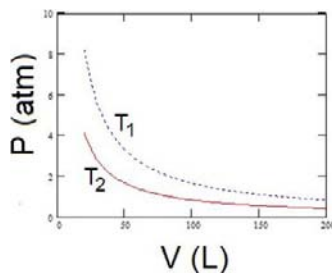
TEST YOURSELF

For answers and other study resources, see:

<http://i-assign.com/ebook/answers/chapter23.htm>.

1. What is the pressure due to a vertical column of mercury that is 760.0 mm long?
A. 760.0 Torr B. 760.0 Pa C. 760.0 atm D. 760.0 bar
2. What is the pressure due to a vertical column of water that is 760 mm long? (use the following densities: water 1.00 g/mL, Hg is 13.6 g/mL)
A. 7.6×10^2 Torr B. 1.0×10^5 Torr C. 7.4×10^{-2} atm
3. A gas bulb is connected to an open-end mercury manometer and the liquid level in the arm connected to the gas bulb is found to be 15.0 cm lower than in the arm that is open to the atmosphere. The prevailing barometric pressure is 755 mm Hg. What is the pressure of the gas in the bulb?
A. 905 Torr B. 770 Torr C. 740 Torr D. 605 Torr
4. A gas bulb is connected to an open-end mercury manometer and the liquid level in the arm connected to the gas bulb is found to be 20.0 mm higher than in the arm that is open to the atmosphere. The prevailing barometric pressure is 758 mm Hg. What is the pressure of the gas in the bulb?
A. 778 Torr B. 760 Torr C. 756 Torr D. 738 Torr
5. What is the final pressure of a gas, originally at (30.0 L, 250.0 Torr) if it is compressed to 15.0 L at constant temperature?
A. 125 Torr B. 235 Torr C. 280 Torr D. 500 Torr
6. If the pressure of a gas is tripled at constant temperature, the volume...
A. is tripled
B. is reduced to 1/3 of the original volume
C. increases 9-fold
D. decreases by 3 L
7. If the volume of a gas increases from 8.0L to 2.0L at constant temperature, the pressure...
A. is quadrupled
B. is reduced to (1/4) of the original pressure
C. increases by 6.0 atm

8. Which of the two PV isotherms shown below represents data at a higher temperature (for the same sample of gas)?



9. What is the final volume of a gas, originally at (25.0 L, 25.00°C) if it is heated to 50.00°C at constant pressure?
- A. 12.5 L B. 27.1 L C. 50.0 L
10. What is the final volume of a gas, originally at (30.0 L, 250.0 Torr, 25°C) if its pressure and temperature are changed to (500.0 Torr, 115°C)?
- A. 19.5 L B. 46.0 L C. 69.0 L D. 78.1 L

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Counting Gas Particles

When dealing with any pure substance, in any physical state (solid, liquid, or gas), we can count the particles that make up a sample by simply dividing the mass of the sample by the molar mass. Unfortunately, weighing gases is a cumbersome process.

It is easier to count particles in a gas sample by measuring three properties of the sample: pressure (P), volume (V), and temperature (T). If we know these three, we can calculate the number of moles of particles in the sample.

24.1 Gas Particles

A gas sample is a collection of particles, which can either be molecules or free atoms. Strictly speaking, the term molecule refers to a group of two or more atoms that are sharing electrons (or covalently bonded). By free atom, we mean a single neutral atom that is not bonded to any other atom. When discussing gases, people tend to use molecule as a generic term for both molecule and free atom; the more precise term to use is particle.

► Example

Which gas sample has more gas particles: 1 mol CH_4 or 1 mol He?

Answer: Same. Each CH_4 molecule counts as one particle; each He atom counts as one particle.

► Example

Which gas sample has more atoms: 1 mol CH_4 or 1 mol He?

Answer: CH_4

One mole of CH_4 has 5 moles of atoms, **one mole of C** and **4 moles of H**. One mole of He atom has one mole of atoms.

24.2 The Ideal Gas Equation

If we know the pressure (P), volume (V), and temperature (T) of a gas sample, we can calculate the number of moles of gas particles in the sample by rearranging the ideal gas equation:

$$PV = nRT$$

to solve for n:

$$n = \frac{PV}{RT}$$

The value and unit for R depends on the units used for P and V. The most commonly used units for P and V in Chemistry are atmosphere and liter. Therefore, it is convenient to memorize the value of R as:

$$R = 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

If we have P and V values expressed in other units, we just convert those to atmosphere and liter.

▶ Example

How many moles of particles are in a 22.4 L sample of air at STP. STP stands for standard temperature and pressure, which corresponds to the 1 atm and 273.15K (which is the freezing point of water at 1 atm).

Answer: 1.00 mol

To solve for n, we divide both sides of the ideal gas equation by (RT), and we get:

$$n = \frac{PV}{RT} = \frac{(1 \text{ atm})(22.4 \text{ L})}{(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(273.15 \text{ K})} = 1.00 \text{ mol}$$

For determining significant figures in the final answer, treat the STP values (1 atm and 273.15K) as exact.

The ideal gas equation is, strictly speaking, valid only at very low pressures. At typical conditions, room temperature and a pressure close to 1 atmosphere, calculations based on the ideal gas equation could be in error by up to about 1%. Thus, calculations of n at ordinary conditions are probably reliable to only about 3–4 significant figures.

24.3 Avogadro's Law

The *molar volume* (V_m) of a gas is defined as the volume that one mole would occupy; mathematically, it is just the ratio of V to n :

$$V_m = \frac{V}{n}$$

If the ideal gas equation is applicable, then the molar volume is given by:

$$V_m = \frac{V}{n} = \frac{RT}{P}$$

We can see that at a given temperature and pressure, the molar volume is constant; all the terms on the right-hand side of the preceding equation (R , T , and P) are constants.

► Example

What is the molar volume of any gas at STP?

Answer: 22.4 L mol^{-1}

$$\begin{aligned} V_m &= \frac{V}{n} = \frac{RT}{P} \\ &= \frac{(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(273.15 \text{ K})}{1 \text{ atm}} = 22.4 \text{ L mol}^{-1} \end{aligned}$$

Whenever the ratio of two things is constant, we say that they are directly proportional. Therefore, we can say that at a given T and P , *the volume of a gas sample is directly proportional to the number of moles of gas particles in the gas sample*. This is known as *Avogadro's Law*. When we say that V and n are directly proportional, it means that:

- if $n = 0$, then $V = 0$, and
- if n changes, so does V (by the same factor).

If we have twice as many gas particles, the gas would occupy twice as much volume (at the same T , P). If we have 3 times as many gas particles, the gas would occupy 3 times as much volume (at the same T , P). Another way of stating Avogadro's law is to say that: *at the same T and P , equal volumes of gas contain equal number of particles*.

► Example

Which of the following gas samples contains the most number of molecules at the same temperature and pressure?

Sample A. 2.00 L CH₄

Sample B. 1.00 L H₂

Sample C. 2.00 L He

Sample D. 4.00 L He

Answer: Sample D

Since volume is directly proportional to n (at the same T,P), equal volumes mean equal number of gas particles. Samples A and C have the same number of particles. Sample D has twice as many; its volume is twice that of sample A or C. Sample B has half as many gas particles; its volume is only half that of sample A or C.

► Example

Which of the following gas samples contains the most number of atoms at the same temperature and pressure?

Sample A. 2.00 L CH₄

Sample B. 1.00 L H₂

Sample C. 2.00 L He

Sample D. 4.00 L He

Answer: Sample A

Since we do not have enough information to calculate number of particles, let "x" be the number of particles in sample B (which has the fewest).

- For sample A, there are 2x particles since its volume is twice that of sample B. Since each particle is a CH₄ molecule, each particle is made up of 5 atoms (one C and four H). Therefore, sample A has:

$$2x \text{ particles} \frac{5 \text{ atoms}}{1 \text{ particle}} = 10x \text{ atoms}$$

- For sample B, the number of particles is x; this times 2 atoms per particle gives us 2x atoms.
- For sample C, there are 2x particles since its volume is twice that of sample B. Since each particle is a free He atom, we also have 2x atoms.
- For sample D, there are 4x particles since its volume is 4 times that of sample B. Each particle is a free He atom; therefore, we also have 4x atoms.

24.4 Gas Mixtures

The ideal gas equation is a very powerful equation in that if it is applicable, it does not depend on the nature of the gas particles. We can use it for pure gaseous substances as well as gaseous mixtures.

24.4.1 Partial Pressure

Partial pressure is defined as the pressure that a component of a gas mixture would exert if it were alone in the container. Therefore, if “A” is a component of a gas mixture, its partial pressure, P_A , is simply:

$$P_A = \frac{n_A RT}{V}$$

assuming the ideal gas equation is applicable. In a fixed volume container at constant temperature, we can see that the partial pressure and number of moles of any component are directly proportional. The more moles present, the higher the partial pressure.

► Example

What are the partial pressures of O_2 and N_2 in a 25.0 L sample containing 1.00 mol O_2 and 4.00 mol N_2 at 300.0 K? What is the total pressure?

Answer: 0.985 atm, 3.94 atm, and 4.92 atm

The partial pressure of O_2 is:

$$\begin{aligned} P_{O_2} &= n_{O_2} \left(\frac{RT}{V} \right) \\ &= (1.00 \text{ mol}) \frac{(0.08206 \cancel{\text{ L}} \text{ atm mol}^{-1} \text{ K}^{-1})(300.0 \text{ K})}{25.0 \cancel{\text{ L}}} = 0.985 \text{ atm} \end{aligned}$$

Similarly, we can calculate the partial pressure of N_2 and find it to be 3.94 atm.

$$\begin{aligned} P_{N_2} &= n_{N_2} \left(\frac{RT}{V} \right) \\ &= (4.00 \text{ mol}) \frac{(0.08206 \cancel{\text{ L}} \text{ atm mol}^{-1} \text{ K}^{-1})(300.0 \text{ K})}{25.0 \cancel{\text{ L}}} = 3.94 \text{ atm} \end{aligned}$$

and the total pressure is:

$$\begin{aligned} P_{\text{total}} &= n_{\text{total}} \left(\frac{RT}{V} \right) \\ &= (5.00 \text{ mol}) \frac{(0.08206 \cancel{\text{ L}} \text{ atm mol}^{-1} \text{ K}^{-1})(300.0 \text{ K})}{25.0 \cancel{\text{ L}}} = 4.92 \text{ atm} \end{aligned}$$

24.4.2 Dalton's Law of Partial Pressures

Dalton's Law of Partial Pressures states that the pressure of a gas mixture is equal to the sum of the partial pressures of its components. We can see that this is consistent with the ideal gas equation. In general, for a mixture of A, B, C, etc..., the total pressure is:

$$P = n_{\text{total}} \left(\frac{RT}{V} \right) = (n_A + n_B + n_C + \dots) \left(\frac{RT}{V} \right)$$

or:

$$P = n_A \left(\frac{RT}{V} \right) + n_B \left(\frac{RT}{V} \right) + n_C \left(\frac{RT}{V} \right) + \dots = P_A + P_B + P_C + \dots$$

► Example

In any enclosed vessel containing liquid water, the partial pressure of water vapor is called the vapor pressure of water; it is a constant value (at a given temperature) that we can look up. At 298K, it is 23.8 Torr. A sample of H_2 is collected over water at 298K. If the pressure of the sample is 750.0 Torr, what is the partial pressure of H_2 ?

Answer: 726.2 Torr

Dalton's law says that the total pressure is equal to the sum of the partial pressures of the components. The components in this case are hydrogen and water vapor. Therefore:

$$P_{\text{total}} = P_{\text{hydrogen}} + P_{\text{water_vapor}}$$

which we can rearrange to solve for the partial pressure of hydrogen:

$$\begin{aligned} P_{\text{hydrogen}} &= P_{\text{total}} - P_{\text{water_vapor}} \\ &= 750.0 \text{ Torr} - 23.8 \text{ Torr} = 726.2 \text{ Torr} \end{aligned}$$

24.4.3 Partial Pressure and Mole Fraction

Mole fraction is defined as the ratio of the number of moles of a component to the total number of moles in a mixture. If a mixture contains n_1 moles of component “1” and total moles of n_{total} , then the mole fraction of component “1” is:

$$x_1 = \frac{n_1}{n_{\text{total}}}$$

Using the ideal gas equation, we can show that the mole fraction of a component of any gas mixture is equal to the ratio of its partial pressure to the total pressure. For component “1”:

$$x_1 = \frac{n_1}{n_{\text{total}}} = \frac{P_1 \left(\frac{V}{RT} \right)}{P_{\text{total}} \left(\frac{V}{RT} \right)} = \frac{P_1}{P_{\text{total}}}$$

► Example

About 21% of molecules in a typical air sample are O_2 molecules. We say that the mole percent of O_2 is 21%, or that the mole fraction of O_2 is 0.21. What is the partial pressure of O_2 in an air sample if the total pressure of the sample is 1.20 atm?

Answer. 0.25 atm

We are not given the volume and temperature of this mixture, so we cannot calculate the partial pressure of O_2 using the defining formula for partial pressure. However, we can determine the partial pressure from the mole fraction and total pressure. If x_1 is the mole fraction of O_2 and P_1 is its partial pressure, then:

$$x_1 = \frac{P_1}{P_{\text{total}}}$$

which we can rearrange to solve for P_1 :

$$P_1 = x_1 P_{\text{total}} = (0.21)(1.20 \text{ atm}) = 0.25 \text{ atm}$$

24.5 Stoichiometry Involving Gases

The amounts of reactants and products involved in a reaction are directly proportional and the mole-to-mole ratio is given by the coefficients in the balanced equation. If we represent *changes* in moles of substances “1” and “2” as n_1 and n_2 , and represent their coefficients as c_1 and c_2 , then:

$$\frac{n_1}{n_2} = \frac{c_1}{c_2}$$

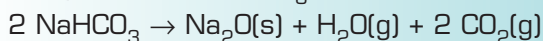
which we can rearrange into a more ready-to-use form:

$$n_2 = n_1 \cdot \frac{c_2}{c_1}$$

If we know how much (in moles) of one substance was consumed or produced in a reaction, we assign it to n_1 , then we multiply it by an appropriate ratio of coefficients to get the amount involved for any of the other substances involved in the ratio. When dealing with reactions involving gases, it is important to remember that the number of moles of gas particles can be calculated from the ideal gas equation.

▶ Example

Suppose 22.4 L of CO_2 were collected at STP from the decomposition of NaHCO_3 :



How much $\text{Na}_2\text{O}(\text{s})$ was also produced?

Answer: First, calculate moles of CO_2 produced. STP means $T = 273.15\text{K}$, $P = 1.00\text{ atm}$

$$n = \frac{PV}{RT} = \frac{(1 \text{ atm})(22.4 \text{ L})}{(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(273.15 \text{ K})} = 1.00 \text{ mol}$$

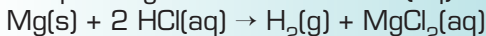
Therefore, we can calculate moles of Na_2O , by multiplying moles of CO_2 with the ratio of the coefficients of Na_2O and CO_2 :

$$1.00 \text{ mol CO}_2 \cdot \frac{1 \text{ mol Na}_2\text{O}}{2 \text{ mol CO}_2} = 0.500 \text{ mol Na}_2\text{O}$$

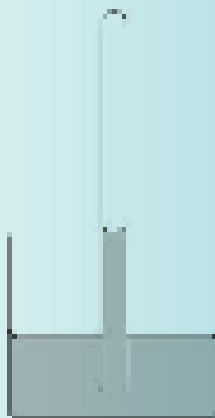
It is often convenient to use pressure measurements to monitor the progress of a reaction that involves gases. When the reaction mixture contains more than one gaseous substance, it is useful to know partial pressures.

▶ Example

A strip of Mg is reacted with HCl(aq):



and the H_2 gas was collected over water as illustrated below. As such, the gas is a mixture of H_2 and water vapor, $\text{H}_2\text{O}(\text{g})$. Suppose the volume of gas collected at 298K is 2.50 L, the water level inside the tube is 10.0 cm above the water level outside, and the prevailing barometric pressure is 755 Torr, how much HCl was consumed in the reaction? The vapor pressure of water at 298K is 23.8 Torr.



Answer: 0.195 mol HCl

The pressure of the gas is less than the barometric pressure; the difference is equal to the pressure due the water column (which is given as 10.0 cm high).

$$\begin{aligned} P &= 755 \text{ Torr} - \left(10.0 \text{ cm H}_2\text{O} \times \frac{1 \text{ cm Hg}}{13.6 \text{ cm H}_2\text{O}} \times \frac{10 \text{ mm Hg}}{1 \text{ cm Hg}} \times \frac{1 \text{ Torr}}{1 \text{ mm Hg}} \right) \\ &= 747.6 \text{ Torr} \end{aligned}$$

This should only have 3 significant digits, but we keep an extra digit to minimize round-off error in subsequent calculations. This is equal to the sum of the partial pressures of $\text{H}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$. We can therefore solve for the partial pressure of H_2 .

$$P_{\text{hydrogen}} = P - P_{\text{water_vapor}} = 747.6 \text{ Torr} - 23.8 \text{ Torr} = 723.8 \text{ Torr}$$

In atmospheres, the partial pressure of H_2 is:

$$P_{\text{hydrogen}} = 723.8 \text{ Torr} \cdot \frac{1 \text{ atm}}{760 \text{ Torr}} = 0.9524 \text{ atm}$$

Finally, we can calculate moles of H_2 , using $PV = nRT$:

$$\begin{aligned} n_{\text{hydrogen}} &= \frac{P_{\text{hydrogen}} V}{RT} \\ &= \frac{(0.9524 \text{ atm})(2.50 \text{ L})}{(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(298 \text{ K})} = 0.09737 \text{ mol} \end{aligned}$$

To calculate moles of HCl consumed, we use the coefficients of H_2 and HCl in the balanced equation.

$$0.0974 \text{ mol } H_2 \cdot \frac{2 \text{ mol HCl}}{1 \text{ mol } H_2} = 0.195 \text{ mol HCl}$$




TEST YOURSELF

For answers and other study resources, see:

<http://i-assign.com/ebook/answers/chapter24.htm>.

- Which gas sample has more gas particles?
A. 1.0 mol CH_4 B. 2.5 mol O_2 C. same
- What is the mass of a 248.0 mL sample of oxygen gas at 100.00°C and 0.500 atm?
A. 0.130 g B. 0.484 g C. 2.03 g
- A mixture of 1.00 g H_2 and an unknown amount of He occupies 22.4 L at STP. What is the mass of helium in the sample?
A. 0.496 g B. 0.503 g C. 2.02 g D. 4.00 g
Hint: calculate total moles (n), subtract moles of H_2 from n to get moles of He; convert moles of He to grams.
- A flask is open to the atmosphere and contains 300.0 mL of air at room temperature (298K); the prevailing barometric pressure is 755 Torr. The flask is heated to 596K . How many moles of air molecules are in the flask initially? How many moles of air molecules remain after the flask is heated? Hint: P and V are constant.
- Suppose a fixed-volume container initially contains 2.00 moles of gas at 0.500 atm. The gas decomposes and, hours later, the pressure (at the same temperature) is found to be 0.800 atm. How many moles of gas are present in the final mixture?
- Which of the following gas samples has the smallest volume at 300K and 125 Torr?
A. 1.00 mol H_2 B. 2.00 mol He C. 2.00 mol CH_4
- Which of the following gas samples has the smallest volume at 300K and 125 Torr?
A. 1.00 g H_2 B. 2.00 g He C. 2.00 mol CH_4
- Hydrogen gas is collected over water at 25°C . The vapor pressure of water at this temperature is 23.8 Torr. If the total pressure of the gas is 755.0 Torr, what is the partial pressure of hydrogen?
A. 731.2 Torr B. 778.8 Torr C. 23.8 Torr D. None of the above

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9. A 5.0 mg sample of gas “X” is found to have a pressure of 0.100 atm at 298K in a given container. A 10.0 mg sample of gas “Y” placed in the same container is found to have a pressure of 0.150 atm at 298K. What would be the total pressure of a mixture of 5.0 mg “X” and 10.0 mg “Y” in the same container at 298K? (assume no reaction)
- A. 0.050 atm B. 0.105 atm C. 0.250 atm D. 2.0 atm
10. A mixture containing 0.200 mol H₂ and 0.300 mol N₂ has a total pressure of 720.0 Torr. What is the partial pressure of H₂ in the mixture?
- A. 144 Torr B. 216 Torr C. 288 Torr D. 360 Torr
11. What is the partial pressure of O₂ in a mixture consisting of 16.0 g O₂ and 4.0 g He if the total pressure is 850.0 Torr?
12. A piece of Mg ribbon is reacted with hydrochloric acid. If 224 mL of hydrogen gas is produced at 25.00°C, 1.00 atm, how much HCl was consumed? The reaction is:
- $$\text{Mg(s)} + 2 \text{HCl(aq)} \rightarrow \text{MgCl}_2\text{(aq)} + \text{H}_2\text{(g)}$$
13. Consider the combustion of urea:
- $$2 \text{CO(NH}_2)_2\text{(s)} + 3 \text{O}_2\text{(g)} \rightarrow 2 \text{CO}_2\text{(g)} + 2 \text{N}_2\text{(g)} + 4 \text{H}_2\text{O(l)}$$
- Suppose 3.00 g of urea were burned in excess oxygen in a fixed-volume 1.00-L sealed container that initially contained 2.00 atm of O₂ at 298K. Estimate the final pressure in the container at 298K.
14. Consider the hypothetical reaction: 2 A(g) → B(g) + 3 C(g)
- Suppose a fixed-volume container initially contains 2.00 mol of pure A(g) at a pressure of 0.500 atm. Hours later, the pressure, at the same temperature, is found to be 0.800 atm. How many moles of B(g) are present in the final mixture?

Chemistry

The Core Concepts

About the Authors

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Dr. Glenn V. Lo is a Professor of Chemistry and Assistant Dean of the College of Arts and Sciences at Nicholls State University in Thibodaux, Louisiana. He has a B.S. in Chemistry (cum laude) from the University of the Philippines (1982), and a Ph.D. (Physical Chemistry) from Kansas State University (1989). He did postdoctoral work at the Université Joseph Fourier in France. His graduate work involved laser-induced fluorescence studies and spectral simulations. More recent research projects involved semiclassical dynamics simulations.

Dr. Lo's main interest is in improving science education. He has published in the Journal of Chemical Education and the Chemical Educator. In 1999, he co-developed an online homework system used by thousands of high school and college chemistry students worldwide. An improved version of the system is currently accessible at <http://i-assign.com>. Dr. Lo's recent projects include a professional development program for high school physical science teachers (sponsored by the Louisiana Systemic Initiatives Program) and the development of video assessment library for Chemistry (<http://chemqa.blogspot.com>). He is the director for the Region I tournament of the Louisiana science olympiad (<http://www.nicholls.edu/scienceolympiad>), which serves New Orleans and surrounding parishes (counties).

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Michael A. Janusa received his B.S. from Louisiana Tech University in 1985 and a Ph.D. from Louisiana State University in 1993. He taught chemistry at Nicholls State University for ten years before accepting the position of Professor and Chair of the Chemistry Department at Stephen F. Austin State University in 2003. Dr. Janusa teaches General Chemistry, Inorganic, Analytical, and Environmental Chemistry. Known for his clear, well organized lectures, Dr. Janusa has received several awards for excellence in teaching. His research interest focuses on the environmental science area. He holds a U.S. patent in complexing heavy metals with bagasse (sugar cane by-product).