CHEM 0106: CHEMISTRY OF THE ENVIRONMENT



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CHEM 0106 - Chemistry of the Environment (b)

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Glossary

Glossary

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Licensing

*A detailed breakdown of this resource's licensing can be found in **Back Matter/Detailed Licensing**.*

CHAPTER OVERVIEW

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1.1: Expressing Numbers

Learning Objective

- Learn to express numbers properly

Quantities have two parts: the number and the unit. The number tells "how many." It is important to be able to express numbers properly so that the quantities can be communicated properly.

Standard Notation

Standard notation is the straightforward expression of a number. Numbers such as 17, 101.5, and 0.00446 are expressed in standard notation. For relatively small numbers, standard notation is fine. However, for very large numbers, such as 306,000,000, or for very small numbers, such as 0.000000419, standard notation can be cumbersome because of the number of zeros needed to place nonzero numbers in the proper position.

Scientific Notation

Scientific notation is an expression of a number using powers of 10. Powers of 10 are used to express numbers that have many zeros:

Table shows the powers of 10. Left side has 10 to a specific power and right side has the equation for the specified power.

10^0	= 1
10^1	= 10
10^2	= 100 = 10 × 10
10^3	= 1,000 = 10 × 10 × 10
10^4	= 10,000 = 10 × 10 × 10 × 10

and so forth.

The raised number to the right of the 10 indicates the number of factors of 10 in the original number. (Scientific notation is sometimes called *exponential notation*.) The exponent's value is equal to the number of zeros in the number expressed in standard notation.

Small numbers can also be expressed in scientific notation but with negative exponents:

Table shows the powers of 10 with negative exponents. Left side has 10 to a specific power and right side has the equation for the specified power.

10^{-1}	= 0.1 = 1/10
10^{-2}	= 0.01 = 1/100
10^{-3}	= 0.001 = 1/1,000
10^{-4}	= 0.0001 = 1/10,000

and so forth. Again, the value of the exponent is equal to the number of zeros in the denominator of the associated fraction. A negative exponent implies a decimal number less than one.

A number is expressed in scientific notation by writing the first nonzero digit, then a decimal point, and then the rest of the digits. The part of a number in scientific notation that is multiplied by a power of 10 is called the *coefficient*. We determine the power of 10 needed to make that number into the original number and multiply the written number by the proper power of 10. For example, to write 79,345 in scientific notation,

$$79,345 = 7.9345 \times 10,000 = 7.9345 \times 10^4$$

Thus, the number in scientific notation is 7.9345×10^4. For small numbers, the same process is used, but the exponent for the power of 10 is negative:

$$0.000411 = 4.11 \times \frac{1}{10,000} = 4.11 \times 10^{-4}$$

Typically, the extra zero digits at the end or the beginning of a number are not included (Figure 1.1.1).



Figure 1.1.1: "The Blue Marble" is a famous photograph of the Earth taken on December 7, 1972, by the crew of the Apollo 17 spacecraft en route to the Moon at a distance of about 29,000 kilometers. This is $2.9 \times 10^4\ km$. It shows Africa, Antarctica, and the Arabian Peninsula.The earth is about 93,000,000 miles from the sun. In scientific notation, this is $9.3 \times 10^7\ miles$. (Public Domain; NASA/Apollo 17 crew; taken by either Harrison Schmitt or Ron Evans.)

✔ Example 1.1.1: Expressing Numbers in Scientific Notation

Express these numbers in scientific notation.

a. 306,000
b. 0.00884
c. 2,760,000
d. 0.000000559

Solution

a. The number 306,000 is 3.06 times 100,000, or 3.06 times 10^5. In scientific notation, the number is 3.06×10^5.
b. The number 0.00884 is 8.84 times 1/1,000, which is 8.84 times 10^{-3}. In scientific notation, the number is 8.84×10^{-3}.
c. The number 2,760,000 is 2.76 times 1,000,000, which is the same as 2.76 times 10^6. In scientific notation, the number is written as 2.76×10^6. Note that we omit the zeros at the end of the original number.
d. The number 0.000000559 is 5.59 times 1/10,000,000, which is 5.59 times 10^{-7}. In scientific notation, the number is written as 5.59×10^{-7}.

? Exercise 1.1.1

Express these numbers in scientific notation.

a. 23,070
b. 0.0009706

Answer a

2.307×10^4

Answer b

9.706×10^{-4}

Another way to determine the power of 10 in scientific notation is to count the number of places you need to move the decimal point to get a numerical value between 1 and 10. The number of places equals the power of 10. This number is positive if you move the decimal point to the right and negative if you move the decimal point to the left:

$$\underset{\substack{\nwarrow \nwarrow \nwarrow \nwarrow \\ 4\ 3\ 2\ 1}}{56,900} = 5.69 \times 10^4 \qquad \underset{\substack{\nearrow \nearrow \nearrow \nearrow \nearrow \\ 1\ 2\ 3\ 4\ 5}}{0.000028} = 2.8 \times 10^{-5}$$

56900 can be written as 5.69 times 10 to the fourth power. 0.000028 can be written as 2.8 times 10 to the negative fifth power.

Many quantities in chemistry are expressed in scientific notation. When performing calculations, you may have to enter a number in scientific notation into a calculator. Be sure you know how to correctly enter a number in scientific notation into your calculator. Different models of calculators require different actions for properly entering scientific notation. If in doubt, consult your instructor immediately (Figure 1.1.2).

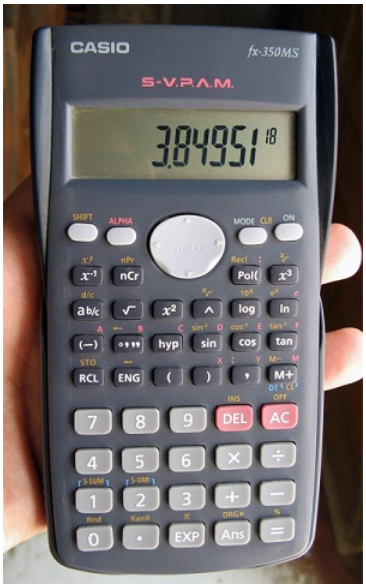


Figure 1.1.2: This calculator shows only the coefficient and the power of 10 to represent the number in scientific notation. Thus, the number being displayed is 3.84951×10^{18}, or $3,849,510,000,000,000,000$. Source: "Casio" Asim Bijarani is licensed under Creative Commons Attribution 2.0 Generic.

Key Takeaways

- Standard notation expresses a number normally.
- Scientific notation expresses a number as a coefficient times a power of 10.
- The power of 10 is positive for numbers greater than 1 and negative for numbers between 0 and 1.

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1.2: Accuracy and Precision



Figure 1.2.1 (Public Domain; Daniel Arizpe via Commons Wikimedia, High School Basketball Game [commons.wikimedia.org])

How do professional basketball players improve their shooting accuracy?

Basketball is one of those sports where you need to hit the target. A football field goal kicker might have room for some deviation from a straight line – for college and pro football there is an 18 foot 6 inch space for the ball to go through. In basketball, the basket is only 18 inches across and the ball is a little less than 10 inches across – not much room for error. The ball has to be on target in order to go into the basket and score.

Accuracy and Precision

In everyday speech, the terms **accuracy** and **precision** are frequently used interchangeably. However, their scientific meanings are quite different. Accuracy is a measure of how close a measurement is to the correct or accepted value of the quantity being measured. Precision is a measure of how close a series of measurements are to one another. Precise measurements are highly reproducible, even if the measurements are not near the correct value. Darts thrown at a dartboard are helpful in illustrating accuracy and precision.

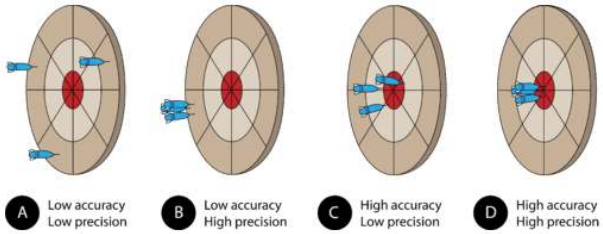


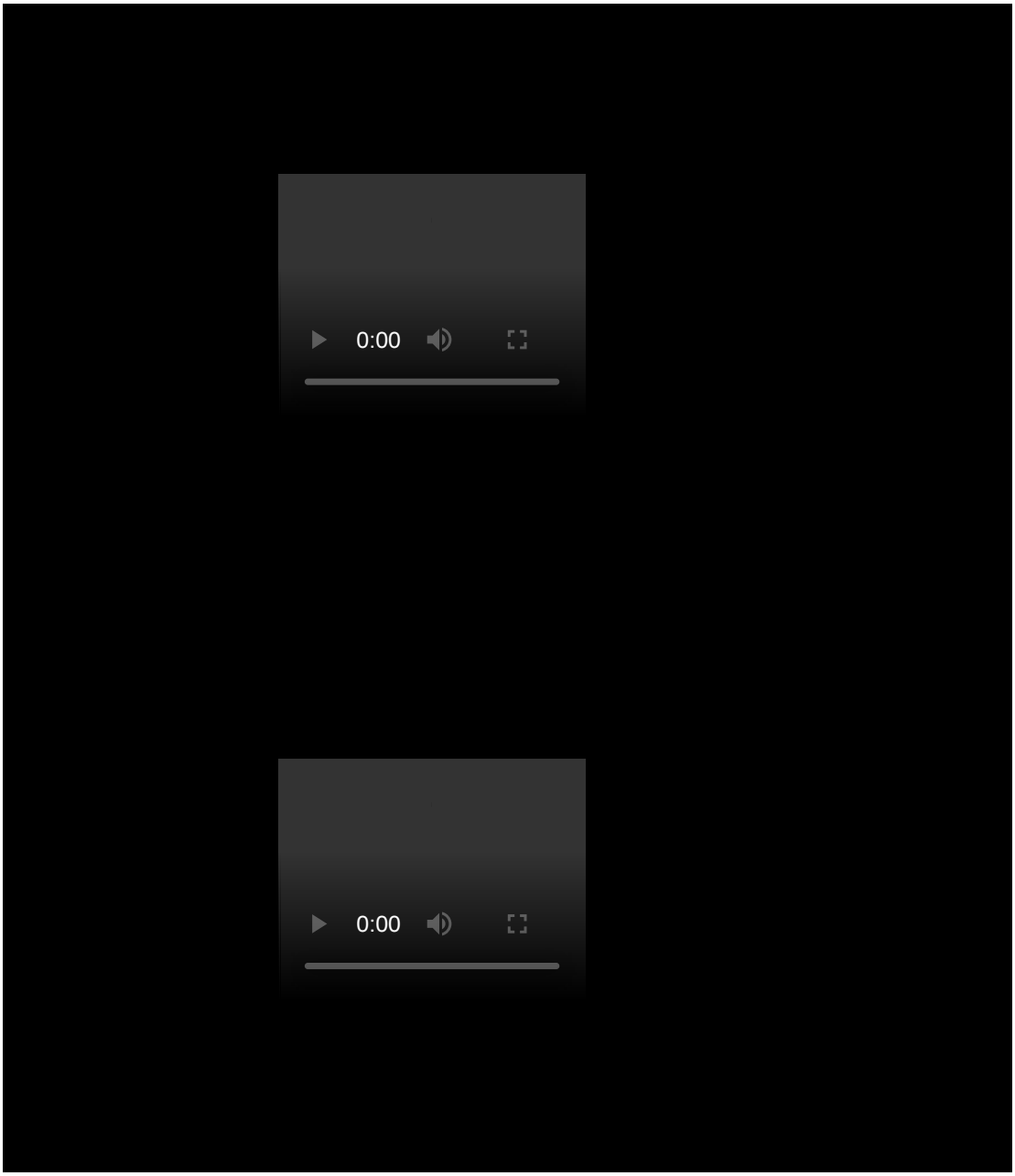
Figure 1.2.2: The distribution of darts on a dartboard shows the difference between accuracy and precision. (CC BY-NC 3.0; Christopher Auyeung via CK-12 Foundation)

Assume that three darts are thrown at the dartboard, with the bulls-eye representing the true, or accepted, value of what is being measured. A dart that hits the bulls-eye is highly accurate, whereas a dart that lands far away from the bulls-eye displays poor accuracy. The figure above demonstrates four possible outcomes:

a. The darts have landed far from each other and far from the bulls-eye. This grouping demonstrates measurements that are neither accurate nor precise.
b. The darts are close to one another, but far from the bulls-eye. This grouping demonstrates measurements that are precise, but not accurate. In a laboratory situation, high precision with low accuracy often results from a systematic error. Either the measurer makes the same mistake repeatedly, or the measuring tool is somehow flawed. A poorly calibrated balance may give the same mass reading every time, but it will be far from the true mass of the object.
c. The darts are not grouped very near to each other, but are generally centered around the bulls-eye. This demonstrates poor precision, but fairly high accuracy. This situation is not desirable in a lab situation because the "high" accuracy may simply be random chance and not a true indicator of good measuring skill.
d. The darts are grouped together and have hit the bulls-eye. This demonstrates high precision and high accuracy. Scientists always strive to maximize both in their measurements.



Figure 1.2.3: Students in a chemistry lab are making careful measurements with a series of volumetric flasks. Accuracy and precision are critical in every experiment. (CK-12 Curriculum Materials license; CK-12 Foundation via CK-12 Foundation)



Summary

- Accuracy is a measure of how close a measurement is to the correct or accepted value of the quantity being measured.
- Precision is a measure of how close a series of measurements are to one another.

Review

1. Define accuracy.
2. Define precision.
3. What can be said about the reproducibility of precise values?

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1.3: Percent Error

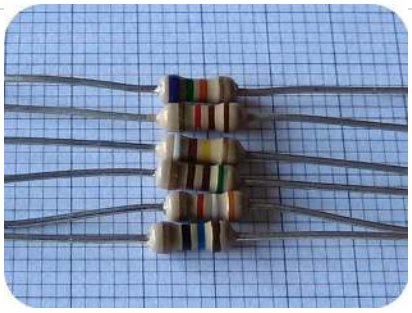


Figure 1.3.1 (Public Domain; Vald Kliper via Wikipedia)

How does an electrical circuit work?

A complicated piece of electronic equipment may contain several resistors that have the role of controlling the voltage and current in the electrical circuit. If there is too much current, the apparatus malfunctions. Conversely, too little current means the system simply will not perform. The resistor values are always given with an error range. A resistor may have a stated value of 200 ohms, but a 10% error range, meaning the resistance could be anywhere between 195 and 205 ohms. By knowing these values, an electronics person can design and service the equipment to make sure that it functions properly.

Percent Error

An individual measurement may be accurate or inaccurate, depending on how close it is to the true value. Suppose that you are doing an experiment to determine the density of a sample of aluminum metal. The **accepted value** of a measurement is the true or correct value based on general agreement with a reliable reference. For aluminum, the accepted density is $2.70\ \text{g/cm}^3$. The **experimental value** of a measurement is the value that is measured during the experiment. Suppose that in your experiment, you determine an experimental value for the aluminum density to be $2.42\ \text{g/cm}^3$. The **error** of an experiment is the difference between the experimental and accepted values.

$$\text{Error} = \text{experimental value} - \text{accepted value}$$

If the experimental value is less than the accepted value, the error is negative. If the experimental value is larger than the accepted value, the error is positive. Often, error is reported as the absolute value of the difference in order to avoid the confusion of a negative error. The **percent error** is the absolute value of the error, divided by the accepted value, and multiplied by 100%.

$$\%\ \text{Error} = \frac{|\text{experimental value} - \text{accepted value}|}{\text{accepted value}} \times 100\%$$

To calculate the percent error for the aluminum density measurement, we can substitute the given values of $2.45\ \text{g/cm}^3$ for the experimental value and $2.70\ \text{g/cm}^3$ for the accepted value.

$$\%\ \text{Error} = \frac{\left|2.45\ \text{g/cm}^3 - 2.70\ \text{g/cm}^3\right|}{2.70\ \text{g/cm}^3} \times 100\% = 9.26\%$$

If the experimental value is equal to the accepted value, the percent error is equal to 0. As the accuracy of a measurement decreases, the percent error of that measurement rises.



Summary

- Definitions of accepted value and experimental values are given.
- Calculations of error and percent error are demonstrated.

Review

1. Define accepted value.
2. Define experimental value
3. What happens as the accuracy of the measurement decreases?

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1.4: Measurement Uncertainty



Figure 1.4.1 (CC BY-SA 4.0; Tony Webster via Commons Wikimedia, Police Line Crime Scene [commons.wikimedia.org])

How do police officers identify criminals?

After a bank robbery has been committed, police will ask witnesses to describe the thieves. They will usually get an answer such as "medium height". Others may say something along the lines of "between 5 foot 8 inches and 5 foot 10 inches". In both cases, there is a significant amount of uncertainty about the height of the criminals.

Measurement Uncertainty

Some error or **uncertainty** always exists in any measurement. The amount of uncertainty depends both upon the skill of the measurer and upon the quality of the measuring tool. While some balances are capable of measuring masses only to the nearest 0.1 g, other highly sensitive balances are capable of measuring to the nearest 0.001 g or even better. Many measuring tools, such as rulers and graduated cylinders, have small lines which need to be carefully read in order to make a measurement. The figure below shows two rulers making the same measurement of an object (indicated by the blue arrow).

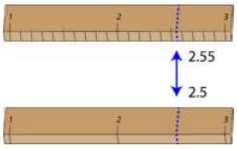


Figure 1.4.2: Uncertainty in measurement. (CC BY-NC-SA 3.0; Christopher Auyeung via CK-12 Foundation)

With either ruler, it is clear that the length of the object is between 2 and 3 cm. The bottom ruler contains no millimeter markings. With that ruler, the tenths digit can be estimated and the length may be reported as 2.5 cm. However, another person may judge that the measurement is 2.4 cm or perhaps 2.6 cm. While the 2 is known for certain, the value of the tenths digit is uncertain.

The top ruler contains marks for tenths of a centimeter (millimeters). With this ruler, the same object may be measured as 2.55 cm. The measurer is capable of estimating the hundredths digit because he can be certain that the tenths digit is a 5. Again, another measurer may report the length to be 2.54 cm or 2.56 cm. In this case, there are two certain digits (the 2 and the 5), with the hundredths digit being uncertain. Clearly, the top ruler is a superior ruler for measuring lengths as precisely as possible.



Summary

- Uncertainty exists in all measurements.
- The degree of uncertainty is affected in part by the quality of the measuring tool.

Review

1. What is uncertainty in measurements?
2. Why is the top ruler more reliable in measuring length than the bottom ruler?
3. How could the top ruler be made more accurate?

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1.5: Significant Figures



Figure 1.5.1 (Public Domain; User:WhisperToMe/Wikimedia Commons via Wikipedia)

How fast do you drive?

As you enter the town of Jacinto City, Texas, a sign tells you that the speed limit is 30 miles per hour. But what if you happen to be driving 31 miles an hour? Are you in trouble? Probably not, because there is a certain amount of leeway built into enforcing the regulation. Most speedometers do not measure the vehicle speed very accurately and could easily be off by a mile or so (on the other hand, radar measurements are much more accurate). So, a couple of miles per hour difference won't matter that much. However, if you stretch the limits any further, you may end up receiving a traffic ticket.

Significant Figures

The **significant figures** in a measurement consist of all the certain digits in that measurement, plus one uncertain or estimated digit. In the ruler illustration below, the bottom ruler gave a length with 2 significant figures, while the top ruler gave a length with 3 significant figures. In a correctly reported measurement, the final digit is significant but not certain. Insignificant digits are not reported. With either ruler, it would not be possible to report the length at $2.553\ \text{cm}$, as there is no possible way that the thousandths digit could be estimated. The 3 is not significant and would not be reported.

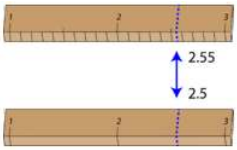


Figure 1.5.2: Measurement with two different rulers. (CC BY-NC-SA 3.0; Christopher Auyeung via CK-12 Foundation)

When you look at a reported measurement, it is necessary to be able to count the number of significant figures. The table below details the rules for determining the number of significant figures in a reported measurement. For the examples in the table, assume that the quantities are correctly reported values of a measured quantity.

Figure 1.5.1: Significant Figure Rules

Rule	Examples
1. All nonzero digits in a measurement are significant.	• 237 has three significant figures. • 1.897 has four significant figures.
2. Zeros that appear between other nonzero digits are always significant.	• 39,004 has five significant figures. • 5.02 has three significant figures.
3. Zeros that appear in front of all of the nonzero digits are called left-end zeros. Left-end zeros are never significant.	• 0.008 has one significant figure. • 0.000416 has three significant figures.
4. Zeros that appear after all nonzero digits are called right-end zeros. Right-end zeros in a number that lacks a decimal point are not significant.	• 140 has two significant figures. • 75,210 has four significant figures.
5. Right-end zeros in a number with a decimal point are significant. This is true whether the zeros occur before or after the decimal point.	• 620.0 has four significant figures. • 19.000 has five significant figures.

It needs to be emphasized that to say a certain digit is not significant, does not mean that it is not important or can be left out. Though the zero in a measurement of 140 may not be significant, the value cannot simply be reported as 14. An insignificant zero functions as a placeholder for the decimal point. When numbers are written in scientific notation, this becomes more apparent. The measurement 140 can be written as 1.4×10^2 with two significant figures in the coefficient. For a number with left-end zeros, such as 0.000416, it can be written as 4.16×10^{-4} with 3 significant figures. In some cases, scientific notation is the only way to correctly indicate the correct number of significant figures. In order to report a value of 15,000,000 with four significant figures, it would need to be written as 1.500×10^7. The right-end zeros after the 5 are significant. The original number of 15,000,000 only has two significant figures.



Summary

- Significant figures give an indication of the certainty of a measurement.
- Rules allow decisions to be made about how many digits to use in any given situation.

Review

1. What does a significant figure tell us?
2. What is a left-end zero?
3. What is a right-end zero?
4. What does an insignificant zero do?

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1.6: Uncertainty in Multiplication and Division



Figure 1.6.1 (Public Domain; Adrian Pingstone (User:Arpingstone/Wikimedia Commons) via Wikipedia)

Who should report the numbers - you or your calculator?

Calculators do just what is asked of them—no more and no less. However, they sometimes can get a little out of hand. If you multiply 2.48 times 6.3, you get an answer of 15.687, a value that ignores the number of significant figures in either number. Division with a calculator is even worse. When you divide 12.2 by 1.7, the answer you obtain is 7.176470588. Neither piece of data is accurate to nine decimal places, but the calculator does not know that. The human being operating the instrument has to make the decision about how many places to report.

Uncertainty in Multiplication and Division

The density of a certain object is calculated by dividing the mass by the volume. Suppose that a mass of $37.46\ \text{g}$ is divided by a volume of $12.7\ \text{cm}^3$. The result on a calculator would be:

$$D = \frac{m}{V} = \frac{37.46\ \text{g}}{12.7\ \text{cm}^3} = 2.949606299\ \text{g/cm}^3$$

The value of the mass measurement has four significant figures, while the value of the volume measurement has only three significant figures. For multiplication and division problems, the answer should be rounded to the same number of significant figures as the measurement with the least number of significant figures. Applying this rule results in a density of $2.95\ \text{g/cm}^3$, with three significant figures—the same as the volume measurement.



1.6.1 Example

Perform the following calculations, rounding the answers to the appropriate number of significant figures.

A. $0.048\ \text{m} \times 32.97\ \text{m}$

B. $14,570\ \text{kg} \div 5.81\ \text{L}$

Solution

Step 1: Plan the problem.

Analyze each of the measured values to determine how many significant figures should be in the result. Perform the calculation and round appropriately. Apply the correct units to the answer. When multiplying or dividing, the units are also multiplied or divided.

Step 2: Calculate.

A. $0.048\ \text{m} \times 32.97\ \text{m} = 1.6\ \text{m}^2$ Round to two significant figures because 0.048 has two.

B. $14,570\ \text{kg} \div 5.81\ \text{L} = 2510\ \text{kg/L}$ Round to three significant figures because 5.81 has three.

? Exercise 1.6.1

How many significant figures should the answer contain?

$10.61 \times 12.133 \times 3.25$

Answer

=418; 3 significant figures

Summary

- For multiplication and division problems, the answer should be rounded to the same number of significant figures as the measurement with the least number of significant figures.

Review

1. Perform the calculation and round your answer with the correct number of significant figures.
   a. $78.2 \div 32\ \text{cm}^3$
   b. $3.0\ \text{m/s} \times 9.21\ \text{s}$
2. What happens to units in multiplication and division problems?

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1.7: Uncertainty in Addition and Subtraction



Figure 1.7.1 (Public Domain; User:Septagram/Wikipedia via Wikipedia)

How old do you think this calculator is?

Calculators are great devices. Their invention has allowed for quick computation at work, school, and other places where manipulation of numbers needs to be done rapidly and accurately. But they are only as good as the numbers put into them. The calculator cannot determine how accurate each set of numbers is, and the answer given on the screen must be assessed by the user for reliability.

Uncertainty in Addition and Subtraction

Consider two separate mass measurements: $16.7\ \text{g}$ and $5.24\ \text{g}$. The first mass measurement, $(16.7\ \text{g})$, is known only to the tenths place, or to one digit after the decimal point. There is no information about its hundredth place and so that digit cannot be assumed to be zero. The second measurement, $(5.24\ \text{g})$, is known to the hundredths place, or to two digits after the decimal point.

When these masses are added together, the result on a calculator is $16.7 + 5.24 = 21.94\ \text{g}$. Reporting the answer as $21.94\ \text{g}$ suggests that the sum is known all the way to the hundredths place. However, that cannot be true because the hundredths place of the first mass was completely unknown. The calculated answer needs to be rounded in such a way as to reflect the certainty of each of the measured values that contribute to it. For addition and subtraction problems, the answer should be rounded to the same number of decimal places as the measurement with the least number of decimal places. The sum of the above masses would be properly rounded to a result of $21.9\ \text{g}$.

Example 1.7.1

Determine the combined molecular mass of a glucose molecule and a maltose molecule.

Glucose molecule = $180.156\ \frac{g}{mol}$

Maltose molecule = $342.3\ \frac{g}{mol}$

Solution

$180.156 + 342.4 = 522.456$

When adding and subtracting we know to look at the least number of decimals in our starting values; in this case 342.3 has only 1 digit after the decimal, so we need to round our answer to the same place.

\(522.456\to 522.5\frag{g}{mol}

When working with whole numbers, pay attention to the last significant digit that is to the left of the decimal point, and round your answer to that same point. For example, consider the subtraction: $78,500\ \text{m} - 362\ \text{m}$. The calculated result is $78,138\ \text{m}$. However, the first measurement is known only to the hundreds place, as the 5 is the last significant digit. Rounding the result to that same point means that the correct result is $78,100\ \text{m}$.

Example 1.7.2

What is $4200 + 540 = ?$

Solution

$4200 + 540 = 4740$

To determine where to round our answer, we look at our starting numbers to see which has the fewest number of decimal places. They both have 0 so we round to the nearest whole number, 4740.



Summary

- For addition and subtraction problems, the answer should be rounded to the same number of decimal places as the measurement with the least number of decimal places.

Review

1. What is the basic principle to use in working with addition and subtraction?
2. What do you pay attention to when working with whole numbers?

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1.8: Scientific Dimensional Analysis

Conversion Factors

Many quantities can be expressed in several different ways. The English system measurement of 4 cups is also equal to 2 pints, 1 quart, and $\frac{1}{4}$ of a gallon.

$$4 \text{ cups} = 2 \text{ pints} = 1 \text{ quart} = 0.25 \text{ gallon}$$

Notice that the numerical component of each quantity is different, while the actual amount of material that it represents is the same. This is because the units are different. We can establish the same set of equalities for the metric system:

$$1 \text{ meter} = 10 \text{ decimeters} = 100 \text{ centimeters} = 1000 \text{ millimeters}$$

The metric system's use of powers of 10 for all conversions makes this quite simple.

Whenever two quantities are equal, a ratio can be written that is numerically equal to 1. Using the metric examples above:

$$\frac{1 \text{ m}}{100 \text{ cm}} = \frac{100 \text{ cm}}{100 \text{ cm}} = \frac{1 \text{ m}}{1 \text{ m}} = 1$$

The $\frac{1 \text{ m}}{100 \text{ cm}}$ is called a **conversion factor**. A conversion factor is a ratio of equivalent measurements. Because both 1 m and 100 cm represent the exact same length, the value of the conversion factor is 1. The conversion factor is read as "1 meter per 100 centimeters". Other conversion factors from the cup measurement example can be:

$$\frac{4 \text{ cups}}{2 \text{ pints}} = \frac{2 \text{ pints}}{1 \text{ quart}} = \frac{1 \text{ quart}}{0.25 \text{ gallon}} = 1$$

Since the numerator and denominator represent equal quantities in each case, all are valid conversion factors.

Scientific Dimensional Analysis

Conversion factors are used in solving problems in which a certain measurement must be expressed with different units. When a given measurement is multiplied by an appropriate conversion factor, the numerical value changes, but the actual size of the quantity measured remains the same. **Dimensional analysis** is a technique that uses the units (dimensions) of the measurement in order to correctly solve problems. Dimensional analysis is best illustrated with an example.

1.8.1 Example

How many seconds are in a day?

Solution

Step 1: List the known quantities and plan the problem.

Known

- 1 day = 24 hours
- 1 hour = 60 minutes
- 1 minute = 60 seconds

Unknown

The known quantities above represent the conversion factors that we will use. The first conversion factor will have day in the denominator so that the "day" unit will cancel. The second conversion factor will then have hours in the denominator, while the third conversion factor will have minutes in the denominator. As a result, the unit of the last numerator will be seconds and that will be the units for the answer.

Step 2: Calculate.

$$1 \text{ d} \times \frac{24 \text{ hr}}{1 \text{ d}} \times \frac{60 \text{ min}}{1 \text{ hr}} \times \frac{60 \text{ s}}{1 \text{ min}} = 86,400 \text{ s}$$

Applying the first conversion factor, the "d" unit cancels and $1 \times 24 = 24$. Applying the second conversion factor, the "hr" unit cancels and $24 \times 60 = 1440$. Applying the third conversion factor, the "min" unit cancels and $1440 \times 60 = 86,400$. The

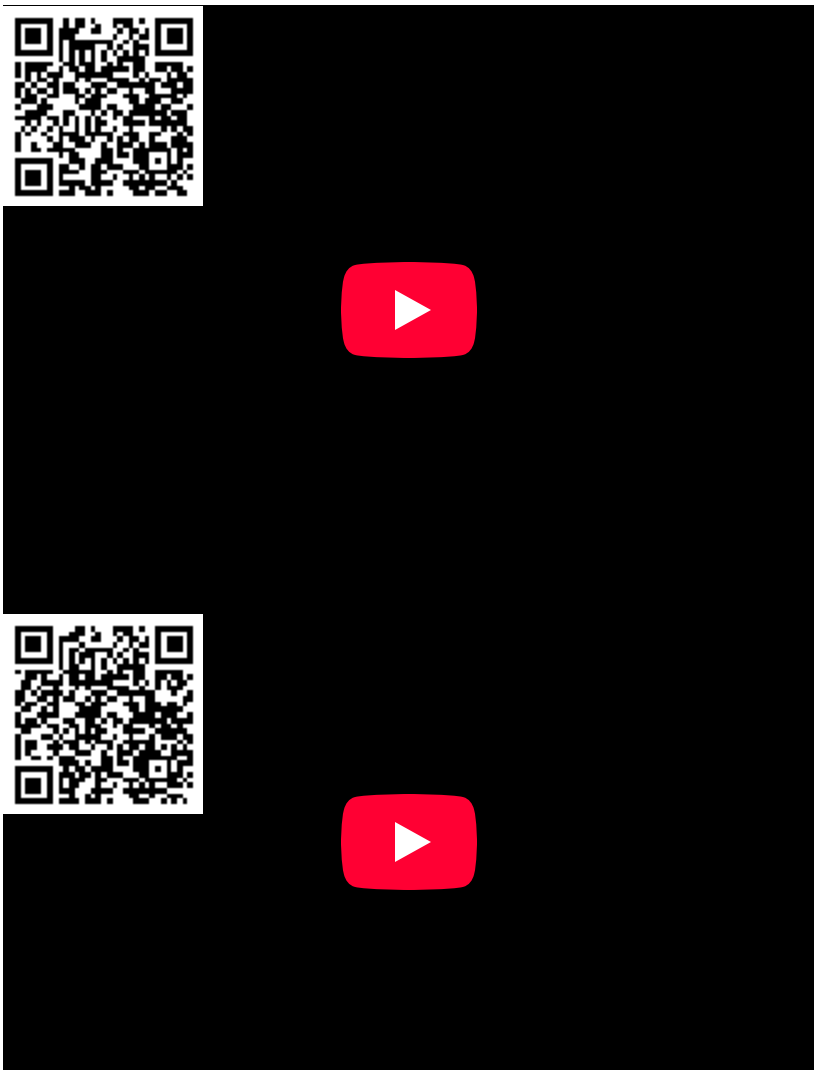
unit that remains is "s" for seconds.

Step 3: Think about your result.

Seconds is a much smaller unit of time than days, so it makes sense that there are a very large number of seconds in one day.

Summary

- A conversion factor is a ratio of equivalent measurements.
- Dimensional analysis is a technique that uses the units (dimensions) of the measurement to solve problems.



Review

1. What is a conversion factor?
2. What is dimensional analysis?
3. How many meters are in 3.7 km?
4. How many kg in 12980 g?

Explore More

Use the link below to answer the following questions**:** http://www.felderbooks.com/papers/units.html

1. What do we always need to express measurements correctly?
2. What does dimensional analysis tell you?
3. How do you know that you have set the problem up incorrectly?

4. How do you know that you have set the problem up correctly?

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1.9: Metric Unit Conversions



Figure 1.9.1 (Public Domain; the US Army via Wikipedia)

How can a number of track laps be converted to a distance in meters?

You are training for a 10-kilometer run by doing laps on a 400-meter track. You ask yourself how many times you need to run around the track in order to cover ten kilometers (...more than you realize). By using dimensional analysis, you can easily determine the number of laps needed to cover the $10\ \text{km}$ distance.

Metric Unit Conversions

The metric system's many prefixes allow quantities to be expressed in many different units. Dimensional analysis is useful to convert from one metric system unit to another.

1.9.1 Example

A particular experiment for science class requires $120\ \text{mL}$ of a solution. The science teacher knows that he will need to make enough solution for 40 experiments to be performed throughout the day. How many liters of solution should he prepare?

Solution

Step 1: List the known quantities and plan the problem.

Known

- 1 experiment requires $120\ \text{mL}$
- $1\ \text{L} = 1000\ \text{mL}$

Unknown

Since each experiment requires $120\ \text{mL}$ of solution and the teacher needs to prepare enough for 40 experiments, multiply 120 by 40 to get $4800\ \text{mL}$ of solution needed. Now you must convert mL to L by using a conversion factor.

Step 2: Calculate.

$$4800\ \text{mL} \times \frac{1\ \text{L}}{1000\ \text{mL}} = 4.8\ \text{L}$$

Note that the conversion factor is arranged so that the mL unit is in the denominator and thus cancels out, leaving L as the remaining unit in the answer.

Step 3:Think about your result.

A liter is much larger than a milliliter, so it makes sense that the number of liters required is less than the number of milliliters.

Two-Step Metric Unit Conversions

Some metric conversion problems are most easily solved by breaking them down into more than one step. When both the given unit and the desired unit have prefixes, one can first convert to the simple (un-prefixed) unit, followed by a conversion to the desired unit. The following example will illustrate this method.

1.9.2 Example

Convert 4.3 cm to μm.

Solution

Step 1: List the known quantities and plan the problem.

Known

- $1\text{ m} = 100\text{ cm}$
- $1\text{ m} = 10^6\ \mu\text{m}$

Unknown

You may need to consult a table for the multiplication factor represented by each metric prefix. First convert cm to m, then convert m to μm.

Step 2: Calculate.

$$4.3\text{ cm} \times \frac{1\text{ m}}{100\text{ cm}} \times \frac{10^6\ \mu\text{m}}{1\text{ m}} = 43,000\ \mu\text{m}$$

Each conversion factor is written so that the unit of the denominator cancels with the unit of the numerator of the previous factor.

Step 3: Think about your result.

A micrometer is a smaller unit of length than a centimeter, so the answer in micrometers is larger than the number of centimeters given.



Summary

- Dimensional analysis can be used to carry out metric unit conversions.

Review

1. Perform the following conversions.
   a. 0.074 km to m
   b. 24,600 µg to g
   c. 4.9 × 107 µg to kg
   d. 84 dm to mm

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1.10: Derived Units



Figure 1.10.1 (Public Domain; User:Joegrimes/Wikipedia via Commons Wikimedia, Farm landly sander [commons.wikimedia.org])

How has farming evolved?

As farming becomes more expensive and less profitable (at least for small farms), farmers might decide to sell their land to builders who want to erect commercial or residential properties. In order to sell, an accurate property title is needed. The dimensions of the farm must be determined, and the acreage calculated from those dimensions.

Dimensional Analysis and Derived Units

Some units are combinations of SI base units. A **derived unit** is a unit that results from a mathematical combination of SI base units. We have already discussed volume and energy as two examples of derived units. Some others are listed in the table below:

Derived SI Units

Quantity	Symbol	Unit	Unit Abbreviation	Derivation
Area	A	square meter	m^2	$\text{length} \times \text{width}$
Volume	V	cubic meter	m^3	$\text{length} \times \text{width} \times \text{height}$
Density	D	kilograms/cubic meter	$\mathrm{kg/m}^3$	\(\frac{\text{mass}}{\text{volume}}\0
Concentration	c	moles/liter	$\mathrm{mol/L}$	$\frac{\text{amount}}{\text{volume}}$
Speed (velocity)	v	meters/second	$\mathrm{m/s}$	$\frac{\text{length}}{\text{time}}$
Acceleration	a	meters/second/second	$\mathrm{m/s}^2$	$\frac{\text{speed}}{\text{time}}$
Force	F	newton	N	$\text{mass} \times \text{acceleration}$
Energy	E	joule	J	$\text{force} \times \text{length}$

Using dimensional analysis with derived units requires special care. When units are squared or cubed as with area or volume, the conversion factors themselves must also be squared. Shown below is the conversion factor for cubic centimeters and cubic meters.

$$\left(\frac{1\ \mathrm{m}}{100\ \mathrm{cm}}\right)^3 = \frac{1\ \mathrm{m}^3}{10^6\ \mathrm{cm}^3} = 1$$

Because a cube has 3 sides, each side is subject to the conversion of 1 m to 100 cm. Since 100 cubed is equal to 1 million $\left(10^6\right)$, there are $10^6\ \mathrm{cm}^3$ in $1\ \mathrm{m}^3$. Two convenient volume units are the liter (which is equal to a cubic decimeter) and the milliliter, which is equal to a cubic centimeter. The conversion factor would be:

$$\left(\frac{1\ \mathrm{dm}}{10\ \mathrm{cm}}\right)^3 = \frac{1\ \mathrm{dm}^3}{1000\ \mathrm{cm}^3} = 1$$

There are thus $1000\ \mathrm{cm}^3$ in $1\ \mathrm{dm}^3$, which is the same thing as saying there are $1000\ \mathrm{mL}$ in $1\ \mathrm{L}$.

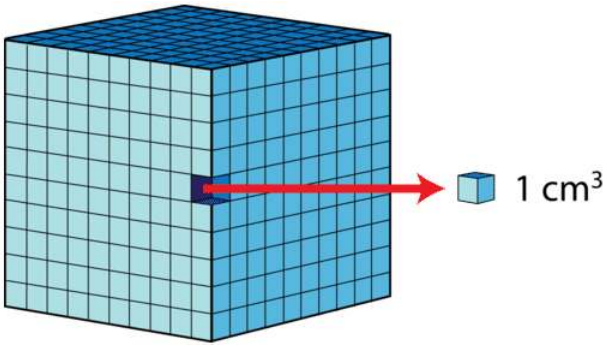


Figure 1.10.2: There are 1000 cm^3 in 1 dm^3. Since a cm^3 is equal to a mL and a dm^3 is equal to a L, we can say that there are 1000 mL in 1 L. (CC BY-NC 3.0; Christopher Auyeung via CK-12 Foundation)

1.10.1 Example

Convert 3.6×10^8 mm^3 to mL.

Solution

Step 1: List the known quantities and plan the problem.

Known

- $1\ m = 1000\ mm$
- $1\ mL = 1\ cm^3$
- $1\ m = 100\ cm$

Unknown

This problem requires multiple steps and the technique for converting with derived units. Simply proceed one step at a time: mm^3 to m^3 to $cm^3 = mL$.

Step 2: Calculate.

$$3.6\ mm^3 \times \left(\frac{1\ m}{1000\ mm}\right)^3 \times \left(\frac{100\ cm}{1\ m}\right)^3 \times \frac{1\ mL}{1\ cm^3} = 0.0036\ mL$$

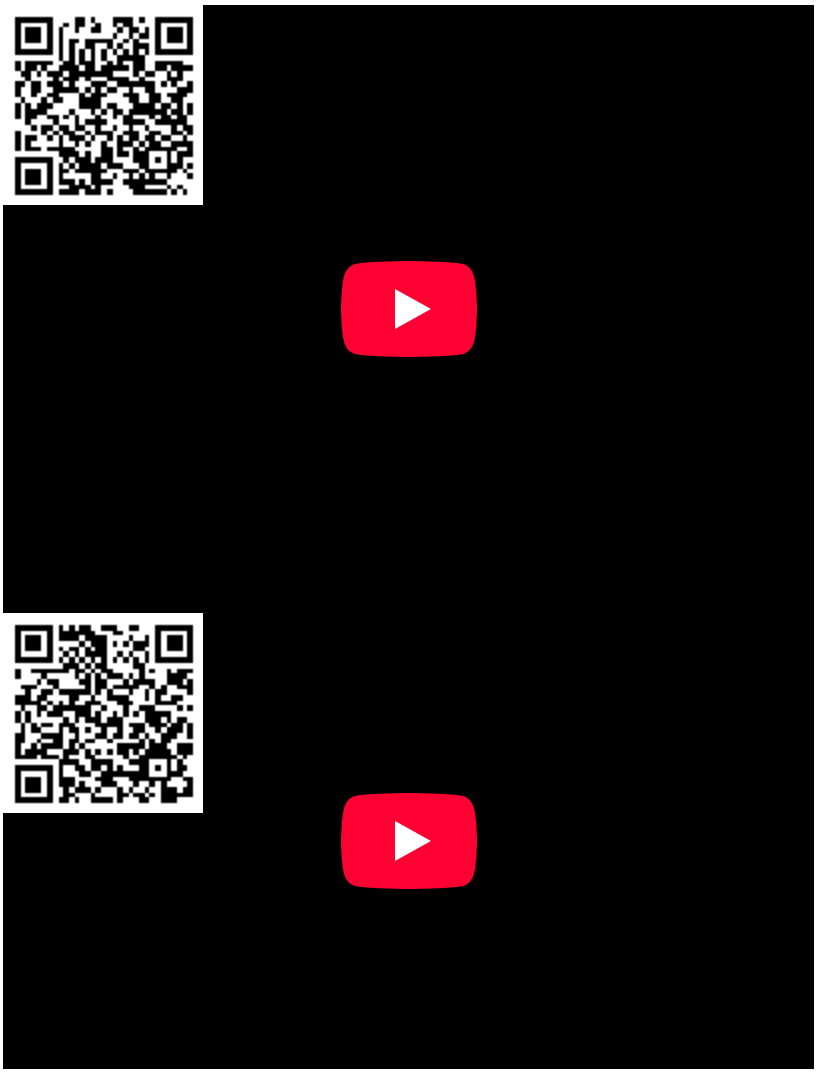
Numerically, the steps are to divide 3.6 by 10^9, followed by multiplying by 10^6. You may find that you can shorten the problem by a step by first determining the conversion factor from mm to cm, and using that instead of first converting to m. There are 10 mm in 1 cm.

$$3.6\ mm^3 \times \left(\frac{1\ cm}{10\ mm}\right)^3 \times \frac{1\ mL}{1\ cm^3} = 0.0036\ mL$$

In this case, 3.6/1000 gives the same result of 0.0036.

Step 3: Think about your result.

Cubic millimeters are much smaller than cubic centimeters, so the final answer is much less than the original number of mm^3.



Summary

- A derived unit is a unit that results from a mathematical combination of SI base units.
- Calculations involving derived units follow the same principles as other unit conversion calculations.

Review

1. What is a derived unit?
2. Convert 0.00722 km^3 to m^3
3. Convert 129 cm^3 to L
4. Convert 4.9 × 105 μm^3 to mm^3

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1.11: Density



Figure 1.11.1 (CC BY 2.0; Tony Hisgett (Flickr:ahisgett) via Flickr)

How do logs stay afloat in water?

After trees are cut, logging companies often move the raw material down a river to a sawmill where it can be shaped into building materials or other products. The logs float on the water because they are less dense than the water they are in. Knowledge of density is important in the characterization and separation of materials. Information about density allows us to make predictions about the behavior of matter.

Density

A golf ball and a table tennis ball are about the same size. However, the golf ball is much heavier than the table tennis ball. Now imagine a similar size ball made out of lead. That would be very heavy indeed! What are we comparing? By comparing the mass of an object relative to its size, we are studying a property called **density**. Density is the ratio of the mass of an object to its volume.

$$\text{Density} = \frac{\text{mass}}{\text{volume}}$$

Density is an intensive property, meaning that it does not depend on the amount of material present in the sample. Water has a density of $1.0\ \text{g/mL}$ That density is the same whether you have a small glass of water or a swimming pool full of water. Density is a property that is constant for the particular identity of the matter being studied.

The SI unit of density is kilograms per cubic meter $\left(\text{kg/m}^3\right)$, since the kg and the m are the SI units for mass and length respectively. In everyday usage in a laboratory, this unit is awkwardly large. Most solids and liquids have densities that are conveniently expressed in grams per cubic centimeter $\left(\text{g/cm}^3\right)$. Since a cubic centimeter is equal to a milliliter, density units can also be expressed as g/mL. Gases are much less dense than solids and liquids, so their densities are often reported in g/L. Densities of some common substances at 20^oC are listed in the table below.

Table 1.11.1: Densities of Some Common Substances

Liquids and Solids	**Density at 20^oC (g/mL)**	**Gases**	**Density at 20^oC (g/L)**
Ethanol	0.79	Hydrogen	0.084
Ice (0^oC)	0.917	Helium	0.166
Corn oil	0.922	Air	1.20
Water	0.998	Oxygen	1.33
Water (4^oC)	1.000	Carbon dioxide	1.83
Corn syrup	1.36	Radon	9.23
Aluminum	2.70		
Copper	8.92		
Lead	11.35		
Mercury	13.6		
Gold	19.3		

Since most materials expand as temperature increases, the density of a substance is temperature dependent, and usually decreases as temperature increases.

Ice floats in water, and it can be seen from the table that ice is less dense. Corn syrup, being more dense, would sink if placed in water.

1.11.1 Example

An $18.2\ \text{g}$ sample of zinc metal has a volume of $2.55\ \text{cm}^3$. Calculate the density of zinc.

Solution

Step 1: List the known quantities and plan the problem.

Known

- Mass $= 18.2\ \text{g}$
- Volume $= 2.55\ \text{cm}^3$

Unknown

Use the equation for density, $D = \frac{m}{V}$, to solve the problem.

Step 2: Calculate.

$$D = \frac{m}{V} = \frac{18.2\ \text{g}}{2.55\ \text{cm}^3} = 7.14\ \text{g/cm}^3$$

Step 3: Think about your result.

If $1\ \text{cm}^3$ of zinc has a mass of about 7 grams, then 2 and a half cm^3 will have a mass about 2 and a half times as great. Metals are expected to have a density greater than that of water, and zinc's density falls within the range of the other metals listed above.

Since density values are known for many substances, density can be used to determine an unknown mass or an unknown volume. Dimensional analysis will be used to ensure that units cancel appropriately.

1.11.2 Example

1. What is the mass of $2.49\ \text{cm}^3$ of aluminum?
2. What is the volume of $50.0\ \text{g}$ of aluminum?

Solution

Step 1: List the known quantities and plan the problem.

Known

- Density $= 2.70\ \text{g/cm}^3$
- 1. Volume $= 2.49\ \text{cm}^3$
- 2. Mass $= 50.0\ \text{g}$

Unknown

- 1. Mass $=?\ \text{g}$
- 2. Volume $=?\ \text{cm}^3$

Use the equation for density, $D = \frac{m}{V}$, and dimensional analysis to solve each problem.

Step 2: Calculate.

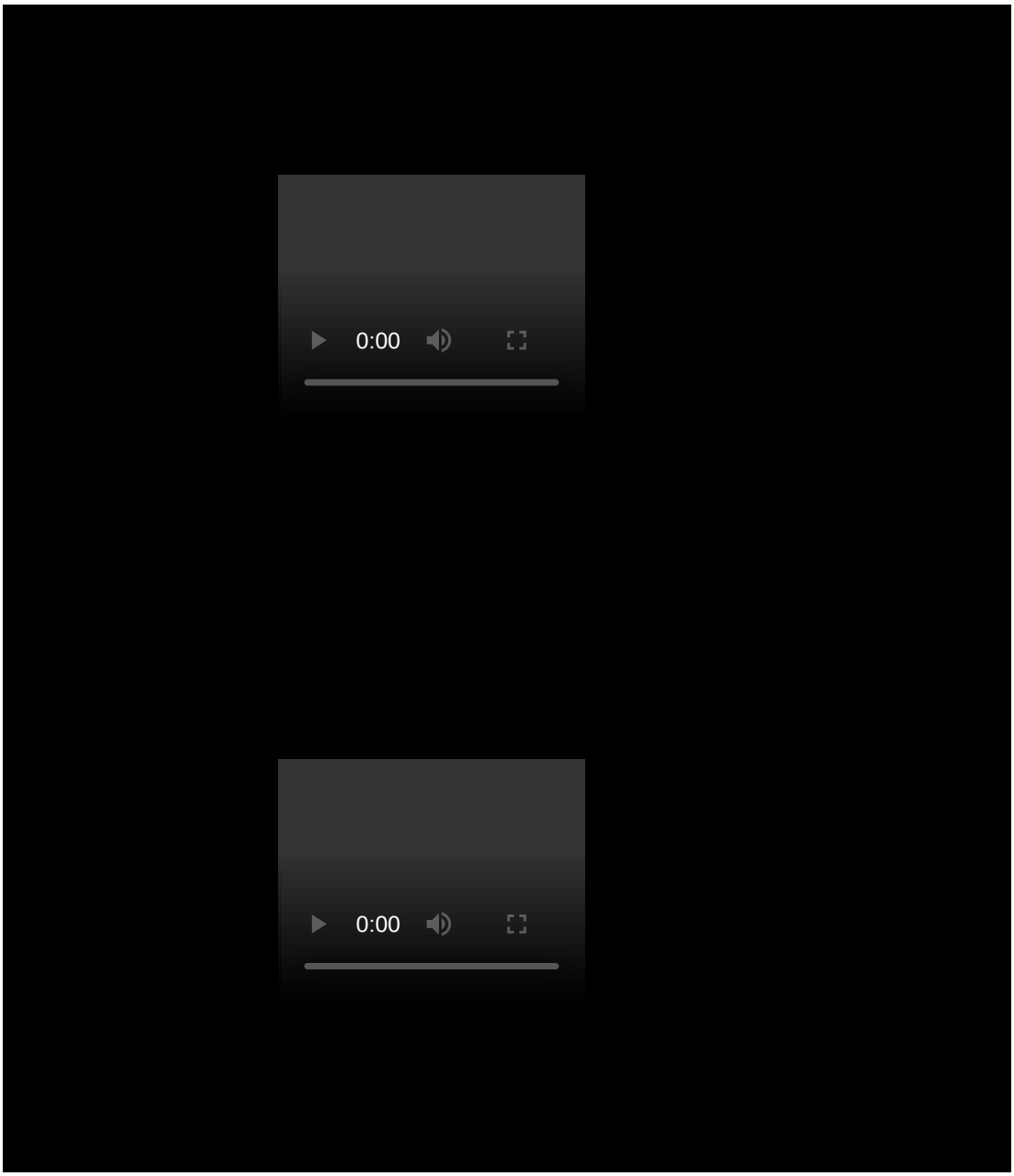
$$1.\ \ 2.49\ \text{cm}^3 \times \frac{2.70\ \text{g}}{1\ \text{cm}^3} = 6.72\ \text{g}$$

$$2.\ \ 50.0\ \text{g} \times \frac{1\ \text{cm}^3}{2.70\ \text{g}} = 18.5\ \text{cm}^3$$

In problem 1, the mass is equal to the density multiplied by the volume. In problem 2, the volume is equal to the mass divided by the density.

Step 3: Think about your results.

Because a mass of $1\ \text{cm}^3$ of aluminum is $2.70\ \text{g}$ the mass of about $2.5\ \text{cm}^3$ should be about 2.5 times larger. The $50\ \text{g}$ of aluminum is substantially more than its density, so that amount should occupy a relatively large volume.



Summary

- Density is the ratio of the mass of an object to its volume.
- Gases are less dense than either solids or liquids.
- Both liquid and solid materials can have a variety of densities.
- For liquids and gases, the temperature will affect the density to some extent.

Review

1. Define “density.”
2. Are gases more or less dense that liquids or solids at room temperature?
3. How does temperature affect the density of a material?
4. A certain liquid sample has a volume of 14.7 mL and a mass of 22.8 grams. Calculate the density.
5. A material with a density of 2.7 grams/mL occupies 35.6 mL. How many grams of the material are there?
6. A certain material has a density of 19.3 g/mL. What is the material?

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CHAPTER OVERVIEW

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2.1: Democritus' Idea of the Atom



Figure 2.1.1 (CC by 2.0; Justin Norris (Flickr:JustinMN) via Flickr)

What would the philosophers do?

People enjoy getting together to discuss things, whether it is how your favorite sports team is doing, what the best new movie is, the current politics, or any number of other topics. Often the question is raised about who is right and who is wrong. If the football game is to be played this coming weekend, all we can do is offer opinions as to its outcome. The game has not been played yet, so we don't know who will actually win.

The ancient Greek philosophers did a lot of discussing, with part of their conversations concerning the physical world and its composition. There were different opinions about what made up matter. Some felt one thing was true while others believed another set of ideas. Since these scholars did not have laboratories and had not developed the idea of the experiment, they were left to debate. Whoever could offer the best argument was considered right. However, often the best argument had little to do with reality.

One of the on-going debates had to do with sand. The question posed was: into how small of pieces can you divide a grain of sand? The prevailing thought at the time, pushed by Aristotle, was that the grain of sand could be divided indefinitely, that you could always get a smaller particle by dividing a larger one and there was no limit to how small the resulting particle could be.



Figure 2.1.2: Into how small of pieces can you divide a grain of sand? (Public Domain; User:(WT-shared) Shoestring/WTS.Wikivoyage via Wikipedia)

Since Aristotle was such an influential philosopher, very few people disagreed with him. However, there were some philosophers who believed that there was a limit to how small a grain of sand could be divided. One of these philosophers was Democritus (~460-370 B.C.E.), often referred to as the "laughing philosopher" because of his emphasis on cheerfulness. He taught that there were substances called **atoms** and that these atoms made up all material things. The atoms were unchangeable, indestructible, and always existed.



Figure 2.1.3: Democritus. (Public Domain; Antoine Coypel via Wikipedia)

The word "**atom**" comes from the Greek $\alpha\tau o\mu o\sigma$ and means "indivisible". The atomists of the time (Democritus being one of the leading atomists) believed there were two realities that made up the physical world: atoms and void. There were an infinite number of atoms, but different types of atoms had different sizes and shapes. The void was the empty space in which the atoms moved and collided with one another. When these atoms collided with one another, they might repel each other or they might connect in clusters, held together by tiny hooks and barbs on the surfaces of the atoms.



Aristotle disagreed with Democritus and offered his own idea of the composition of matter. According to Aristotle, everything was composed of four elements: earth, air, fire, and water. Deomcritus' theory better explained things, but Aristotle was more influential, so his ideas prevailed. It took almost two thousand years before scientists came around to seeing the atom as Democritus did.



How right was Democritus?

It is very interesting that Democritus had the basic idea of atoms, even though he had no experimental evidence to support his thinking. We now know more about how atoms hold together in "clusters" (compounds), but the basic concept existed over two thousand years ago. We also know that atoms can be further subdivided, but there is still a lower limit to how small we can break up that grain of sand.

Summary

- Greek philosophers debated many ideas.
- Aristotle and others believed that a grain of sand could be divided indefinitely.
- Democritus believed there was a lower limit to the division of a grain of sand.

Review

1. How did the ancient Greek philosophers spend their time?
2. What approach did they not have for studying nature?
3. Who was the most influential philosopher of that time?
4. What was the major contribution Democritus made to the thinking of his day?
5. List characteristics of atoms according to Democritus.

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2.2: Conservation of Mass



Figure 2.2.1 (CC BY 2.0; Douglas Heriot via Flickr)

Have you ever lost a screw?

The following situation happens all too often. You have taken apart a piece of equipment to clean it up. When you put the equipment back together, somehow you have an extra screw or two. Or you find out that a screw is missing that was a part of the original equipment. In either case, you know something is wrong. You expect to end up with the same amount of material that you started with, not with more or less than what you had originally.

Law of Conservation of Mass

By the late 1700s, chemists accepted the definition of an element as a substance that cannot be broken down into a simpler substance by ordinary chemical means. It was also clear that elements combine with one another to form more complex substances called compounds. The chemical and physical properties of these compounds are different than the properties of the elements from which they were formed. There were questions about the details of these processes.

In the 1790s, a greater emphasis began to be placed on the quantitative analysis of chemical reactions. Accurate and reproducible measurements of the masses of reacting elements and the compounds they form led to the formulation of several basic **laws**. One of these is called the law of **conservation of mass**, which states that during a chemical reaction, the total mass of the **products** must be equal to the total mass of the **reactants**. In other words, mass cannot be created or destroyed during a chemical reaction, but is always conserved.

As an example, consider the reaction between silver nitrate and sodium chloride. These two compounds will dissolve in water to form silver chloride and sodium nitrate. The silver chloride does not dissolve in water, so it forms a solid that we can filter off. When we evaporate the water, we can recover the sodium nitrate formed. If we react 58.5 grams of sodium chloride with 169.9 grams of silver nitrate, we start with 228.4 grams of materials. After the reaction is complete and the materials separated, we find that we have formed 143.4 grams of silver chloride and 85.0 grams of sodium nitrate, giving us a total mass of 228.4 grams for the products. So, the total mass of reactants equals the total mass of products, a proof of the law of conservation of mass.



Summary

- The law of conservation of mass states that, during a chemical reaction, the total mass of the products must be equal to the total mass of the reactants.

Review

1. The law of conservation of mass states that, during a chemical reaction, the total _____ of the products must be equal to the total _____ of the reactants.
2. Describe an example of the law of conservation of mass.

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2.3: Dalton's Atomic Theory



Figure 2.3.1 (Public Domain; Luca della Robbia, photographed by Jastrow via Wikipedia)

"Pick a little, talk a little, pick a little, talk a little,

Cheep cheep cheep, talk a lot, pick a little more"

These lyrics from the musical "Music Man" sum up the way science was done for centuries. The lyrics refer to a group of gossiping ladies, but the outcome was the same. The Greek and Roman philosophers debated, discussed, and sometimes even attacked one another. But the mode of discovery was talk. There was no experimentation—the idea had not yet been thought of. So science did not develop very far, and there was no reliable way to establish what was true and what was false.

John Dalton

While it must be assumed that many more scientists, philosophers, and others studied the composition of matter after Democritus, a major leap forward in our understanding of the composition of matter took place in the 1800s with the work of the British scientist John Dalton. He started teaching school at age twelve, and was primarily known as a teacher. In his twenties, he moved to the growing city of Manchester, where he was able to pursue some scientific studies. His work in several areas of science brought him a number of honors. When he died, over 40,000 people in Manchester marched at his funeral.

Dalton studied the weights of various elements and compounds. He noticed that matter always combined in fixed ratios based on weight, or volume in the case of gases. Chemical compounds always contain the same proportion of elements by mass, regardless of amount, which provided further support for Proust's law of definite proportions. Dalton also observed that there could be more than one combination of two elements.



Figure 2.3.2: John Dalton. (Public Domain; Henry Roscoe (author), William Henry Worthington (engraver), and Joseph Allen (painter) via Wikipedia)

Dalton's Atomic Theory (1804)

From his own experiments and observations, as well as the work of his peers, Dalton proposed a new theory of the **atom**. This later became known as Dalton's **atomic theory**. The general tenets of this theory are as follows:

- All matter is composed of extremely small particles called atoms.
- Atoms of a given element are identical in size, mass, and other properties. Atoms of different elements differ in size, mass, and other properties.
- Atoms cannot be subdivided, created, or destroyed.
- Atoms of different elements can combine in simple whole number ratios to form chemical compounds.
- In chemical reactions, atoms are combined, separated, or rearranged.

Dalton's atomic theory has been largely accepted by the scientific community, with the exception of three changes. We now know that (1) an atom can be further subdivided, (2) all atoms of an element are not identical in mass, and (3) using nuclear fission and fusion techniques, we can create or destroy atoms by changing them into other atoms.

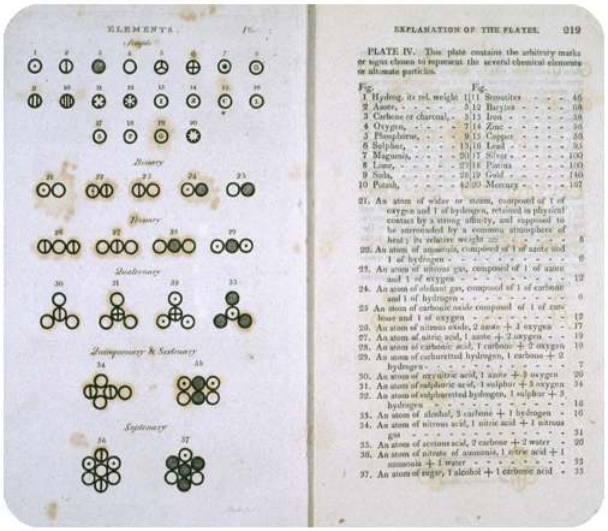


Figure 2.3.3: Dalton's symbols. (Public Domain; John Dalton via Wikipedia)



Summary

- Dalton proposed his atomic theory in 1804.
- The general tenets of this theory are:
  - All matter is composed of extremely small particles called atoms
  - Atoms cannot be subdivided, created, or destroyed.
  - Atoms of a given element are identical in size, mass, and other properties. Atoms of different elements differ in size, mass, and other properties.
  - Atoms of different elements can combine in whole number ratios to form chemical compounds;
  - In chemical reaction, atoms are rearranged, combined, or separated.

Review

1. Did Dalton believe that atoms could be created or destroyed?
2. According to Dalton's theory, all atoms of the same _____ are identical in size, mass, and other properties.
3. What parts of the theory are not considered valid any more?

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2.4: Electrons

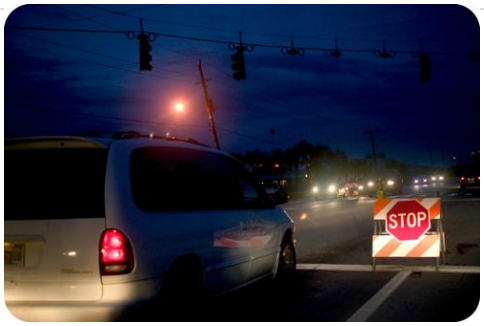


Figure 2.4.1 (Public Domain; Andrea Booher, FEMA via Wikipedia)

What causes a power outage?

In a power outage, all your electrical equipment suddenly stops working. The radio was on just a minute ago and now it is silent. What happened? Somewhere between a power generator and your electrical device was an interruption. Power stopped flowing through the wires and into your radio. That “power” turns out to be electrons that move through the wires and cause an electrical current to flow.

Is There Anything Inside an Atom?

As the nineteenth century began to draw to a close, the concept of atoms was well-established. We could determine the mass of different atoms and had some good ideas about the atomic composition of many compounds. Dalton’s atomic theory held that atoms were indivisible, so scientists did not ask questions about what was inside the atom – it was solid and could not be broken down further. But then things began to change.

The Electron

In 1897, English physicist J.J. Thomson (1856-1940) experimented with a device called a cathode ray tube, in which an electric current was passed through gases at low pressure. A cathode ray tube consists of a sealed glass tube fitted at both ends with metal disks called electrodes. The electrodes are then connected to a source of electricity. One electrode, called the anode, becomes positively charged while the other electrode, called the cathode, becomes negatively charged. A glowing beam (the cathode ray) travels from the cathode to the anode.

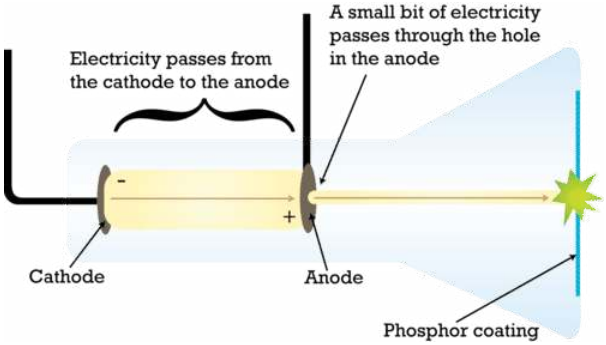


Figure 2.4.2 (CC BY-NC 3.0; Christopher Auyeung via CK-12 Foundation)

Earlier investigations by Sir William Crookes and others had been carried out to determine the nature of the cathode ray. Thomson modified and extended these experiments in an effort to learn about these mysterious rays. He discovered two things, which supported the hypothesis that the cathode ray consisted of a stream of particles.

- When an object was placed between the cathode and the opposite end of the tube, it cast a shadow on the glass.
- A cathode ray tube was constructed with a small metal rail between the two electrodes. Attached to the rail was a paddle wheel capable of rotating along the rail. Upon starting up the cathode ray tube, the wheel rotated from the cathode towards the anode. This proved that the cathode ray was made of particles which must have mass. Crooke had first observed this phenomenon and attributed it to pressure by these particles on the wheel. Thomson correctly surmised that these particles were producing heat, which caused the wheel to turn.

In order to determine if the cathode ray consisted of charged particles, Thomson used magnets and charged plates to deflect the cathode ray. He observed that cathode rays were deflected by a **magnetic field** in the same manner as a wire carrying an electric current, which was known to be negatively charged. In addition, the cathode ray was deflected away from a negatively charged metal plate and towards a positively charged plate.

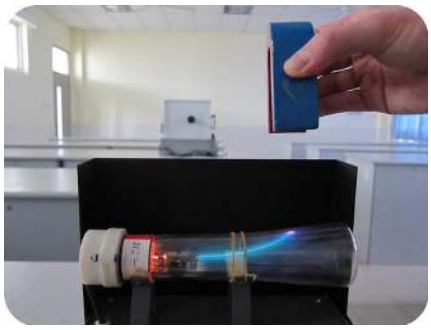


Figure 2.4.3 (CC BY 2.0; Micah Sittig via Flickr)

Thomson knew that opposite charges attract one another, while like charges repel one another. Together, the results of the cathode ray tube experiments showed that cathode rays are actually streams of tiny negatively charged particles moving at very high speeds. While Thomson originally called these particles corpuscles, they were later named electrons.

Thomson conducted further experiments, which allowed him to calculate the charge-to-mass ratio $\frac{e}{m_e}$ of the electron. In units of coulombs to grams, this value is 1.8×10^8 Coulombs/gram. He found that this value was a constant and did not depend on the gas used in the cathode ray tube or on the metal used as the electrodes. He concluded that electrons were negatively charged subatomic particles present in atoms of all elements.



Summary

- Cathode rays are deflected by a magnetic field.
- The rays are deflected away from a negatively charged electrical field and toward a positively charge field.
- The charge/mass ratio for the electron is 1.8×10^8 Coulombs/gram.

Review

1. What subatomic particle creates electric power, and how does it do it?
2. Whose work did Thomson repeat and revise?
3. What experiment did Thomson perform that showed cathode rays to be particles?
4. How did he show that these particles had a charge on them?
5. Did the cathode ray have positive or negative charge?

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2.5: Protons



Figure 2.5.1 (Public Domain; Adrian Pingstone (User:Arpingstone/Wikimedia Commons) via Wikipedia)

Can you name this car?

Describing what we can see is a fairly easy matter. If we are asked to describe the sports car illustrated below, we could all quickly come up with a fairly accurate description. A person knowledgeable about cars would include more details, but everyone would have the basic information in their description.

What makes the description easy to come up with? We can see it, we have a common language to describe it (size, color, construction), and we have a basic idea of what it is (a car, not a house or a tree). Scientists have far more difficulty in describing things they cannot see. There is no way to look directly at an atom and see its detailed structure. When a discovery is first made, there is often no language to use to tell others exactly what it is. This was the problem in talking about the atom and its structure.

Putting the Puzzle Pieces Together

Research builds upon itself – one piece connects to another. Sometimes the puzzle doesn't seem to make sense because some of the pieces are missing at the moment. Each finding gives a clearer picture of the whole and also raises new questions. The detective work that led to the discovery of the proton was built upon finding pieces to the puzzle and putting them together in the right way.

The electron was discovered using a cathode ray tube. An electric current was passed from the cathode (the negative pole) to the anode (positive pole). Several experiments showed that particles were emitted at the cathode and that these particles had a negative charge. These experiments demonstrated the presence of electrons.

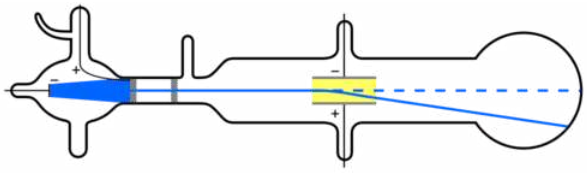


Figure 2.5.2: JJ Thomson's experiment with cathode rays. (Public Domain; User:Kurzon/Wikimedia Commons via Wikipedia)

If cathode rays are electrons that are given off by the metal atoms of the cathode, then what remains of the atoms that have lost those electrons? We know several basic things about electrical charges. They are carried by particles of matter. Millikan's experiment showed that they exist as whole-number multiples of a single basic unit. Atoms have no overall electrical charge, meaning that each and every atom contains an exactly equal number of positively and negatively charged particles. A hydrogen atom is the simplest kind of atom with only one electron. When that electron is removed, a positively charged particle should remain.

Discovery of the Proton

In 1886, Eugene Goldstein (1850-1930) discovered evidence for the existence of this positively charged particle. Using a cathode ray tube with holes in the cathode, he noticed that there were rays traveling in the opposite direction from the cathode rays. He called these **canal rays** and showed that they were composed of positively charged particles. The **proton** is the positively charged subatomic particle present in all atoms. The mass of the proton is about 1840 times the mass of the electron.



Summary

- When an electron is removed from a hydrogen atom, a proton remains.
- Goldstein observed rays traveling in the opposite direction of the cathode rays in a cathode ray tube.
- He demonstrated that these rays were positive particles and called the canal rays.

Review

1. Why is it easy to describe things we can see?
2. Why did researchers believe that the particle left after electrons were emitted as cathode rays had to be positive?
3. Atoms, which are always neutral in electric charge, contain electrons as well as protons and neutrons. An electron has an electrical charge of -1. If an atom has three electrons, infer how many protons it has.
4. How many electrons does it take to weight the same as one proton?

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2.6: Neutrons



Figure 2.6.1 (Public Domain; Sidney Paget via Wikipedia)

Was Sherlock Holmes real or the product of someone's imagination?

The most famous detective in history and literature never existed. Sherlock Holmes was the creation of the British author Sir Arthur Conan Doyle. This mythical person had capabilities far beyond those of mere mortals. Holmes was capable of spotting the tiniest clue, the smallest piece of evidence to solve the crime. He could link all sorts of seemingly irrelevant data into a coherent whole to clear up whatever mystery he was dealing with.

The Quest for the Neutron

Clues are generally considered to involve the presence of something – a footprint, a piece of fabric, a bloodstain, something tangible that we can measure directly. The discoveries of the electron and the proton were accomplished with the help of those kinds of clues. Cathode ray tube experiments showed both the negatively charged electrons emitted by the cathode and the positively charged proton (also emitted by the cathode). The **neutron** was initially found not by a direct observation, but by noting what was not found.

Research had shown the properties of the electron and the proton. Scientists learned that approximately 1,837 electrons weighed the same as one proton. There was evidence to suggest that electrons went around the heavy nucleus composed of protons. Charge was balanced with equal numbers of electrons and protons which made up an electrically neutral atom. But there was a problem with this model – the atomic number (number of protons) did not match the atomic weight. In fact, the atomic number was usually about half the atomic weight. This indicated that something else must be present. That something must weigh about the same as a proton, but could not have a charge – this new particle had to be electrically neutral.

In 1920, Ernest Rutherford tried to explain this phenomenon through the presence of another particle in the nucleus. He proposed that the "extra" particles were protons and electrons that had combined into a new particle in the nucleus (this did not turn out to be the case). These new particles would have a mass very similar to a proton, but would be electrically neutral since the positive charge of the proton and the negative charge of the electron would cancel each other out.

In 1930, German researchers bombarded the element beryllium with alpha particles (helium nuclei containing two protons and two neutrons with a charge of +2). The particles produced in this process had strong penetrating power, which suggested they were fairly large. In addition, they were not affected by a magnetic field, so they were electrically neutral. The French husband-wife research team of Frederic and Irene Joliot-Curie used these new "rays" to bombard paraffin, which was rich in protons. The unknown particles produced a large emission of protons from the paraffin.

The English physicist James Chadwick (1891-1974) repeated these experiments and studied the energy of these particles. By measuring velocities, he was able to show that the new particle has essentially the same mass as a proton. So we now have a third subatomic particle with a mass equal to that of a proton, but with no charge. This particle is called the neutron. Chadwick won the Nobel Prize in Physics in 1935 for his research.



Neutron Applications

Neutrons can be used in a variety of ways. One important use is in nuclear **fission** to produce new isotopes. A neutron will collide with a large atom (such as uranium) and cause it to split into smaller atoms, such as in figure below.

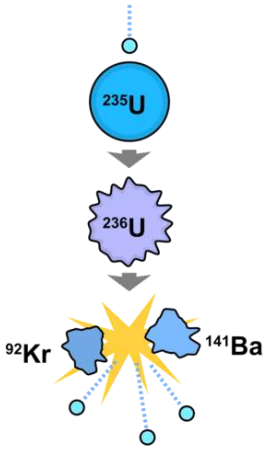


Figure 2.6.2: A neutron collides with a large atom, splitting it into smaller atoms. (Public Domain; User:Fastfission/Wikimedia Commons via Wikipedia)

Nuclear reactors utilize **chain reactions** involving neutrons to heat water which drive turbines for the generation of electricity. When a neutron collides with a large atom, the atom splits with the release of more neutrons and also a large amount of energy. The energy converts water to steam for the turbine, while the neutrons serve to continue the chain reaction (see figure below).

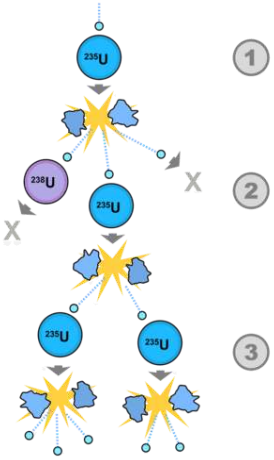


Figure 2.6.3: How nuclear fission produces new isotopes. (Public Domain; User: Fastfission/Wikimedia Commons via Wikipedia)

Summary

- Rutherford proposed that "extra" particles in nucleus were combinations of protons and electrons.
- Bombardment of beryllium with alpha particles produced large, neutral particles.
- Chadwick determined the mass of the neutron.
- Nuclear fission produces new elements.
- Nuclear reactors use chain reactions to produce heat.

Review

1. How did Rutherford try to explain the differences between the number of protons in the nucleus and the atomic weight?
2. What did German researchers find when they bombarded beryllium with alpha particles?
3. What did Chadwick determine about these new particle (observed by the German scientist and the Curies)?

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2.7: Atomic Nucleus



Figure 2.7.1 (Credit: Charles Hamm; Source: http://commons.wikimedia.org/wiki/File:Close_up_of_Hand_Cut_Jigsaw_Puzzle.JPG(opens in new window); License: CC by 3.0(opens in new window))

How is science like a jigsaw puzzle?

Many people enjoy putting jigsaw puzzles together. As the different pieces go together, the picture begins to become clearer. When the puzzle is completed, you see that what had been a confused collection of individual components that made little or no sense by themselves fit together to give a clear picture.

Science works the same way as a jigsaw puzzle. Different researchers make individual discoveries that answer a specific question or questions. When enough data are gathered, we get a better understanding of a process or a structure. The experiments of Crooke, Millikan, Rutherford, and many others gave us pieces of the puzzle that is the atomic nucleus.

Different Models of the Nucleus

After the electron and proton were discovered, people began to try to build a picture of the atom. The Thomson model had electrons mixed in with a positive core of some sort that provided electrical neutrality. Rutherford showed that this model was incomplete. His picture of the atom involved a small solid core that alpha particles could zoom past with very few collisions. So the picture of the atom became a little clearer – electrons surrounded a very small core nucleus. The discovery of the neutron helped fill out the picture even more. We now have protons and neutrons in a concentrated center of the atom with electrons surrounding the nucleus.

One problem still existed. We have a number of positively charged protons in the nucleus. Why don't they push each other apart? Physicists postulate a strong nuclear force that acts at very short distances. At these distances the attraction between protons is greater than the force causing the positive charges to push each other away. Neutrons are also involved in this process somehow. So the strong force holds protons together, it holds neutrons together, and it causes protons and neutrons to be attracted to one another.



Summary

- Rutherford proposed a model of the atomic nucleus which had a solid core.
- Physicists postulate a strong nuclear force holds the protons and neutrons together in the nucleus of the atom.

Review

1. How did Rutherford change our thinking about atomic structure?
2. What is our current picture of the atom?
3. Why is the presence of positively charged protons a problem with current models of the atom?
4. How do we explain why the nucleus does not fall apart?

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2.8: Atomic Number



Figure 2.8.1 (CK-12 Curriculum Materials license; CK-12 Foundation via CK-12 Foundation)

What is unique about each one of us?

For the vast majority of people, it is not their name, because it is quite possible for others in the world to have the same name (check it out by doing an internet search for your name and see how many other of "you" there are). It is not your physical description. Eye-witnesses to crime scenes often pick the wrong person when trying to identify the criminal.

There may be some unique identifiers for us. If you have a cell phone in your name, nobody else in the world has that number. Email addresses are different for each of us, which is a good thing since we can email almost anywhere in the world. Our DNA is unique, but getting a DNA analysis is expensive and time-consuming, so we really don't want to have to explore that.

Organizing the Elements

One of the goals of science is to discover the order in the universe and to organize information that reflects that order. As information about the different elements was made known, efforts were made to see if there were patterns in all of the data. An early attempt to organize data was made by Mendeleev, who developed the first periodic table. His data set was based on **atomic weights** and was instrumental in providing clues as to the possible identity of new elements. Once we learned the details of the atomic nucleus, the table was based on the number of protons in the nucleus, called the **atomic number** of the element.

Atomic Number

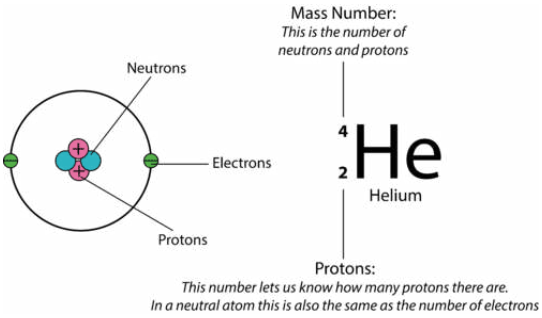


Figure 2.8.2: How can you determine the atomic number of an element. (Public Domain; User:Materialscientist/Wikimedia Commons via Wikipedia)

The atomic number (Z) of an element is the number of protons in the nucleus of each atom of that element. This means that the number of protons is the characteristic which makes each element unique compared to all other elements. Elements are different because of their atomic number. The **periodic table** displays all of the known elements and is arranged in order of increasing atomic number. In this table, an element's atomic number is indicated above the elemental symbol. Hydrogen, at the upper left of the table, has an atomic number of 1. Every hydrogen atom has one proton in its nucleus. Following on the table is helium, whose atoms have two protons in the nucleus. Lithium atoms have three protons, and so forth.

Since atoms are neutral, the number of electrons is equal to the number of protons. Hydrogen atoms all have one electron occupying the space outside of the nucleus. Manganese (atomic number 25) would have twenty-five protons and twenty-five electrons.

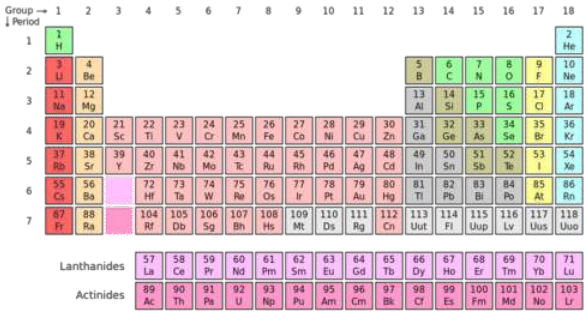


Figure 2.8.3: The periodic table classifies elements by atomic number. (Public Domain; User:Cepheus/Wikimedia Commons via Wikipedia)

The classification of elements by atomic number allows us to understand many properties of the atom and makes it possible to predict behaviors instead of just having to memorize everything.



Summary

- The atomic number (Z) of an element is the number of protons in the nucleus of each atom of that element
- The number of electrons is equal to the number of protons in an atom of an element.

Review

1. What is the atomic number of an atom? Why is this number important?
2. Using a periodic table, what is the atomic number of helium have
3. How many protons are in the following elements:?
    a. Ne
    b. Ca
    c. Pt
4. Write the symbol for the element with the following atomic number:
    a. 18
    b. 41
    c. 82
    d. 12

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2.9: Isotopes



Figure 2.9.1 (Public Domain; Chief Photographer's Mate Johnny Bivera, U.S. Navy via Wikipedia)

Are all the members of the football team shown above identical?

They are on the same team and are all known by the same team name, but there are individual differences among the players. We do not expect the kicker to be as big as the quarterback. The tight end is very likely to weigh less than the defensive tackle on the other side of the ball. They play as a unit, but they have different weights and heights.

What are Isotopes?

The history of the atom is full of some of these differences. Although John Dalton stated in his atomic theory of 1804 that all atoms of an element are identical, the discovery of the neutron began to show that this assumption was not correct. The study of radioactive materials (elements that spontaneously give off particles to form new elements) by Frederick Soddy (1877-1956) gave important clues about the internal structure of atoms. His work showed that some substances with different radioactive properties and different atomic masses were in fact the same element. He coined the term **isotope** from the Greek roots isos (ίσος "equal") and topos (τόπος "place"). He described isotopes as, "Put colloquially, their atoms have identical outsides but different insides." Soddy won the Nobel Prize in Chemistry in 1921 for his work.

As stated earlier, not all atoms of a given element are identical. Specifically, the number of neutrons can be variable for many elements. As an example, naturally occurring carbon exists in three forms. Each carbon atom has the same number of protons (6), which is its atomic number. Each carbon atom also contains six electrons in order to maintain electrical neutrality. However the number of neutrons varies as six, seven, or eight. Isotopes are atoms that have the same number atomic number, but different mass numbers due to a change in the number of neutrons.

The three isotopes of carbon can be referred to as carbon-12 ($^{12}_{6}C$), carbon-13 ($^{13}_{6}C$), and carbon-14 ($^{14}_{6}C$) refers to the nucleus of a given isotope of an element. A carbon atom is one of three different nuclides. Most elements naturally consist of mixtures of isotopes. Carbon has three natural isotopes, while some heavier elements can have many more. Tin has ten stable isotopes, the most of any element.

While the presence of isotopes affects the mass of an atom, it does not affect its chemical reactivity. Chemical behavior is governed by the number of electrons and the number of protons. Carbon-13 behaves chemically in exactly the same way as the more plentiful carbon-12.



Summary

- Isotopes are atoms that have the same atomic number, but different mass numbers due to a change in the number of neutrons.
- The term nuclide refers to the nucleus of a given isotope of an element.
- The atomic mass of an atom equals the sum of the protons and the neutrons.

Review

1. What are isotopes?
2. Why do different isotopes of an element generally have the same physical and chemical properties?
3. How would the nucleus of the hydrogen-1 and hydrogen-2 differ?
4. Relate the concepts of isotope and mass number.
5. All oxygen atoms have eight protons, and most have eight neutrons as well. What is the mass number of an oxygen isotope that has nine neutrons? What is the name of this isotope?
6. An isotope of yttrium has 39 protons and 59 neutrons. What is the mass number of that isotope?
7. An isotope with a mass number of 193 has 116 neutrons. What is the atomic number of this isotope?
8. An isotope of barium (atomic number 56) has an mass of 138. How many neutrons are in the nucleus of this isotope?
9. Relate the concepts of isotope and mass number.

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2.10: Atomic Mass Unit



Figure 2.10.1 (Public Domain; Derek Jensen (User:Tysto/Wikimedia Commons) via Wikipedia)

The current system of measurement in the United States is a hodge-podge of different units, many of which are hard to interconvert. We at least have standardized units these days, unlike centuries past. At one time, measurements of length were defined as the distance from the end of one appendage to another. For example, the yard was defined as the distance from the king's nose to the tip of his thumb, when his arm was stretched out.

Standardized measurements make it possible for people everywhere to get the same amount of something. Note the red and white labels on the gas pump pictured below. These labels certify that the gas pump has been checked, and is pumping an accurate gallon of gas. Standard measurements in science are very important so that we can compare experimental data from one lab to another, and make sure that we are all talking about the same thing.

Atomic Mass

Masses of individual atoms are very, very small. Using a modern device called a mass spectrometer, it is possible to measure such miniscule masses. An atom of oxygen-16, for example, has a mass of 2.66×10^{-23} g. While comparisons of masses measured in grams would have some usefulness, it is far more practical to have a system that will allow us to more easily compare relative atomic masses. Scientists decided on using the carbon-12 nuclide as the reference standard by which all other masses would be compared. By definition, one atom of carbon-12 is assigned a mass of 12 **atomic mass units** (amu). An atomic mass unit is defined as a mass equal to one twelfth the mass of an atom of carbon-12. The mass of any isotope of any element is expressed in relation to the carbon-12 standard. For example, one atom of helium-4 has a mass of 4.0026 amu An atom of sulfur-32 has a mass of 31.972 amu

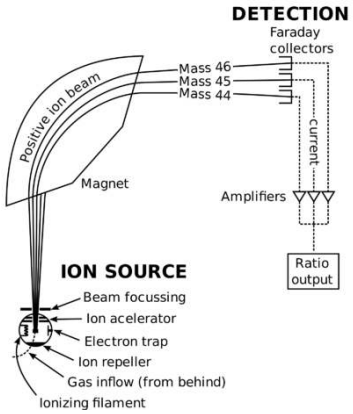


Figure 2.10.2: Mass spectrometer schematic. (Public Domain; Devon Fyson, based on image created by the U.S. Geological Survey via Wikipedia)

The carbon-12 atom has six protons and six neutrons in its nucleus for a mass number of 12. Since the nucleus accounts for nearly all of the mass of the atom, a single proton or single neutron has a mass of approximately 1 amu. However, as seen by the helium and sulfur examples, the masses of individual atoms are not whole numbers. This is because an atom's mass is affected very slightly by the interactions of the various particles within the nucleus, and the small mass of the electron is taken into account.



Summary

- Carbon-12 is the reference for all atomic mass calculations.
- An atomic mass unit is defined as a mass equal to one twelfth the mass of an atom of carbon-12.
- The mass of an atom is affected by the interactions of particles within the nucleus.

Review

1. What instrument is used to measure the mass of atoms?
2. How much does a single oxygen-16 atom weigh in grams?
3. What is the reference standard for atomic mass units?
4. How is an atomic mass unit defined?
5. Why are the numbers for atomic mass of individual atoms not whole numbers?

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2.11: Early History of the Periodic Table



Figure 2.11.1 (Public Domain; User:Raysonho/Wikimedia Commons via Commons Wikimedia, File:SteacieLibrary.jpg [commons.wikimedia.org])

When you go to the library to find a book, how do you locate it?

If it is a fiction book, you look by author since the fiction materials are filed by the author's last name. If you are looking for a non-fiction publication, you look in a catalog (most likely on a computer these days). The book you are looking for will have a number by the title. This number refers to the Dewey Decimal system, developed by Melvil Dewey in 1876 and used in over 200,000 libraries throughout the world. Another system in wide use is the Library of Congress approach, developed in the late 1800s-early 1900s to organize the materials in the federal Library of Congress. This method is one of the most widely used ways to organize libraries in the world. Both approaches organize information so that people can easily find what they are looking for. Chemistry information also needs to be organized so we can see patterns of properties in elements.

Early Attempts to Organize Elements

By the year 1700, only a handful of elements had been identified and isolated. Several of these, such as copper and lead, had been known since ancient times. As scientific methods improved, the rate of discovery dramatically increased. With the ever-increasing number of elements, chemists recognized that there may be some kind of systematic way to organize the elements. The question was: how?

A logical way to begin grouping elements together was by their chemical properties. (In other words, putting elements in separate groups based on how they reacted with other elements.) In 1829, a German chemist, Johann Dobereiner (1780-1849), placed various groups of three elements into groups called **triads**. One such triad was lithium, sodium, and potassium. Triads were based on both physical, as well as chemical, properties. Dobereiner found that the atomic masses of these three elements, as well as other triads, formed a pattern. When the atomic masses of lithium and potassium were averaged together $\left(\frac{(6.94+39.10)}{2} = 23.02\right)$, it was approximately equal to the atomic mass of sodium (22.99). These three elements also displayed similar chemical reactions, such as vigorously reacting with the members of another triad: chlorine, bromine, and iodine. While Dobereiner's system would pave the way for future ideas, a limitation of the triad system was that not all of the known elements could be classified in this way.

English chemist John Newlands (1838-1898) ordered the elements in increasing order of atomic mass and noticed that every eighth element exhibited similar properties. He called this relationship the "Law of **Octaves**". Unfortunately, there were some elements that were missing and the law did not seem to hold for elements that were heavier than calcium. Newlands' work was largely ignored and even ridiculed by the scientific community in his day. It was not until years later that another more extensive periodic table effort would gain much greater acceptance, and that the pioneering work of John Newlands would be appreciated.

No.		No.		No.		No.		No.		No.		No.	
H	1	F	8	Cl	15	Co & Ni	22	Br	29	Pd	36	I	42	Pt & Ir	50
Li	2	Na	9	K	16	Cu	23	Rb	30	Ag	37	Cs	44	Os	51
G	3	Mg	10	Ca	17	Zn	24	Sr	31	Cd	38	Ba & V	45	Hg	52
Bo	4	Al	11	Cr	19	Y	25	Ce & La	33	U	40	Ta	46	Tl	53
C	5	Si	12	Ti	18	In	26	Zr	32	Sn	39	W	47	Pb	54
N	6	P	13	Mn	20	As	27	Di & Mo	34	Sb	41	Nb	48	Bi	55
O	7	S	14	Fe	21	Se	28	Ro & Ru	35	Te	43	Au	49	Th	56

Figure 2.11.2 (Public Domain; John Alexander Reina Newlands via Commons Wikimedia, Newlands Periodiska System 1866 [commons.wikimedia.org])



Summary

- Johann Dobereiner organized elements into groups called triads.
- John Newlands proposed the "Law of Octaves" for organizing the elements.

Review

1. List some elements known since ancient times?
2. What properties were the basis of the triad system?
3. Why did Dobereiner believe that lithium, sodium, and potassium belonged in a triad?
4. What was a shortcoming of the triad system?
5. How did Newlands arrange the element?
6. What was a problem with the “Law of Octaves"?

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2.12: Mendeleev's Periodic Table



Figure 2.12.1 (CC BY-NC 3.0; Laura Guerin via CK-12 Foundation)

When you study for a test, how do you approach the task?

One useful way to study for a test is to use flashcards. To make them, write down vocabulary words, foreign language terms, math formulas, chemistry reactions—anything you want to learn. Then sort these cards into categories and topics that go together. This organization of information helps you see patterns in the material so that you can tie different ideas together and make better sense of them.

The periodic table was first built using a set of cards. With this strategy, Dmitri Mendeleev, the creator of the periodic table, could organize and rearrange material until patterns emerged.

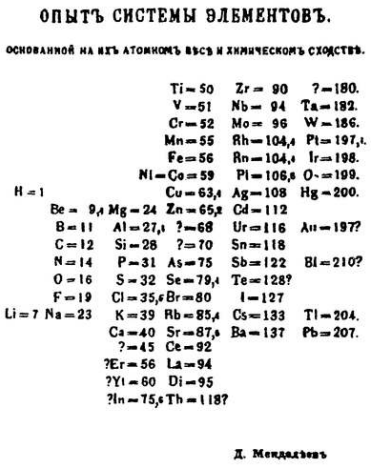
Mendeleev's Periodic Table

In 1869, Russian chemist and teacher Dmitri Mendeleev (1836-1907) published a periodic table of the elements. The following year, German chemist Lothar Meyer independently published a very similar table. Mendeleev is generally given more credit than Meyer because his table was published first, and because of several key insights that he made regarding the table.



Figure 2.12.2: Dmitri Mendeleev. (Public Domain; Unknown via Wikipedia)

Mendeleev was writing a chemistry textbook for his students and wanted to organize all of the known elements at that time according to their chemical properties. He famously organized the information for each element onto separate note cards that were then easy to rearrange as needed. He discovered that when he placed them in order of increasing atomic mass, certain similarities in chemical behavior repeated at regular intervals. This type of a repeating pattern is called "periodic". A pendulum that swings back and forth in a given time interval is periodic, as is the movement of the moon around the Earth.



ОПЫТЪ СИСТЕМЫ ЭЛЕМЕНТОВЪ.

основанной на ихъ атомномъ вѣсѣ и химическомъ сходствѣ.

			Ti = 50	Zr = 90	? = 180.
			V = 51	Nb = 94	Ta = 182.
			Cr = 52	Mo = 96	W = 186.
			Mn = 55	Rh = 104,4	Pt = 197,1.
			Fe = 56	Ru = 104,4	Ir = 198.
			Ni = Co = 59	Pl = 106,6	O = 199.
H = 1			Cu = 63,4	Ag = 108	Hg = 200.
	Be = 9,4	Mg = 24	Zn = 65,2	Cd = 112	
	B = 11	Al = 27,4	? = 68	Ur = 116	Au = 197?
	C = 12	Si = 28	? = 70	Sn = 118	
	N = 14	P = 31	As = 75	Sb = 122	Bi = 210?
	O = 16	S = 32	Se = 79,4	Te = 128?	
	F = 19	Cl = 35,5	Br = 80	I = 127	
Li = 7	Na = 23	K = 39	Rb = 85,4	Cs = 133	Tl = 204.
		Ca = 40	Sr = 87,6	Ba = 137	Pb = 207.
		? = 45	Ce = 92		
		?Er = 56	La = 94		
		?Yt = 60	Di = 95		
		?In = 75,6	Th = 118?		

Д. Менделѣевъ

Figure 2.12.3: Mendeleev's 1869 periodic table. (Public Domain; Dmitri Mendeleev via Wikipedia)

In the figure above, atomic mass increases from top to bottom of vertical columns, with successive columns going left to right. As a result, elements that are in the same horizontal row are groups of elements that were known to exhibit similar chemical properties. One of Mendeleev's insights is illustrated by the elements tellurium (Te) and iodine (I). Notice that tellurium is listed before iodine even though its atomic mass is higher. Mendeleev reversed the order because he knew that the properties of iodine were much more similar to those of fluorine (F), chlorine (Cl), and bromine (Br) than they were to oxygen (O), sulfur (S), and selenium (Se). He simply assumed that there was an error in the determination of one or both of the atomic masses. This turned out not to be the case, but Mendeleev was indeed correct to group these two elements as he did.

Notice that there are several places in the table that have no chemical symbol, but are instead labeled with a question mark. Between zinc (Zn) and arsenic (As) are two such missing elements. Mendeleev believed that elements with atomic masses of 68 and 70 would eventually be discovered and that they would fit chemically into each of those spaces. Listed in the table below are other properties that Mendeleev predicted for the first of these two missing elements, which he called "eka-aluminum", compared with the element gallium.

Mendeleev's predicted properties for Eka-aluminum and gallium.

	Eka-Aluminum (Ea)	**Gallium** (Ga)
Atomic Mass	$68\ \mathrm{amu}$	$69.9\ \mathrm{amu}$
Melting Point	Low	$30.15^{\circ}\mathrm{C}$
Density	$5.9\ \mathrm{g/cm^3}$	$5.94\ \mathrm{g/cm^3}$
Formula of Oxide	$\mathrm{Ea_2O_3}$	$\mathrm{Ga_2O_3}$

The element gallium was discovered four years after the publication of Mendeleev's table, and its properties matched up remarkably well with eka-aluminum, fitting into the table exactly where he had predicted. This was also the case with the element that followed gallium, which was eventually named germanium.

Mendeleev's periodic table gained wide acceptance with the scientific community and earned him credit as the discoverer of the periodic law. Element number 101, synthesized in 1955, is named **mendelevium** after the founder of the periodic table. It was, however, several years after Mendeleev died before the several discrepancies with the atomic masses could be explained, and before the reasons behind the repetition of chemical properties could be fully explained.



Summary

- Mendeleev published his periodic table in 1869.
- His organization of elements was based on atomic mass.
- Mendeleev's periodic table made it possible to predict properties of elements that had not yet been discovered.

Review

1. When did Mendeleev publish his periodic table?
2. Who else came out with a periodic table at about the same time?
3. Why was Mendeleev’s table considered to be superior?
4. What element did Mendeleev predict to exist?
5. What element was named after Mendeleev?

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2.13: Periodic Law



Figure 2.13.1: Copy and Paste Caption here. (CC-BY 2.0; Christopher Fynn via Flickr, Mysore - Fruit vendor [www.flickr.com])

How are these items related to one another?

We have all enjoyed looking around a market for delicious foods to eat later at home. When you get to the market you know you need to get fruits, vegetables and grains to ensure you eat a balanced diet. In the market, these items are all grouped together to make it easier to find the type of fruit, vegetable or grain you are looking for; it would be inconvenient if the different fruits were all scattered in different places. The periodic table is organized in a similar way, ensuring similar elements are found in the same group or period.

The Periodic Law

When Mendeleev put his periodic table together, nobody knew about the existence of the nucleus. It was not until 1911 that Rutherford conducted his gold foil experiment that demonstrated the presence of the nucleus in the atom. Just two years later, in 1913, English physicist Henry Moseley (1887-1915) examined x-ray spectra of a number of chemical elements. He would shoot x-rays through crystals of the element and study the wavelengths of the radiation that he detected. Moseley found that there was a relationship between wavelength and atomic number. His results led to the definition of atomic number as the number of protons contained in the nucleus of each atom. He then realized that the elements of the periodic table should be arranged in order of increasing atomic number, rather than increasing atomic mass.

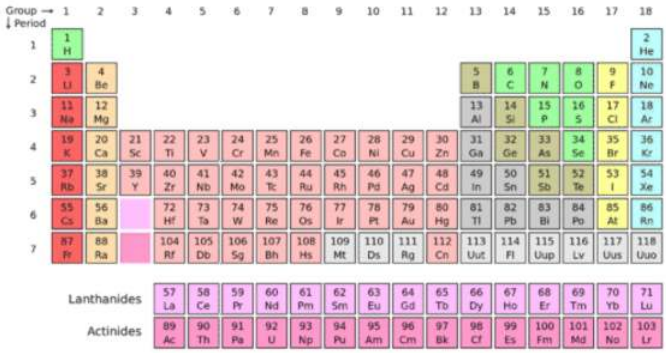


Figure 2.13.2 (Public Domain; User:Cepheus/Wikimedia Commons via Commons Wikimedia, Periodic Table [commons.wikimedia.org])

When ordered by atomic number, the discrepancies within Mendeleev's table disappeared. Tellurium has an atomic number of 52, while iodine has an atomic number of 53. So even though tellurium does indeed have a greater atomic mass than iodine, it is properly placed before iodine in the periodic table. Mendeleev and Moseley are credited with being most responsible for the modern **periodic law**: When elements are arranged in order of increasing atomic number, there is a periodic repetition of their chemical and physical properties. The result is the periodic table as we know it today. Each new horizontal row of the periodic table corresponds to the beginning of a new **period** because a new principal energy level is being filled with electrons. Elements with similar chemical properties appear at regular intervals, within the vertical columns called **groups**.



Summary

- Elements of the periodic table are arranged in order of increasing atomic number.
- The periodic law states: "When elements are arranged in order of increasing atomic number, there is a periodic repetition of their chemical and physical properties."

Review

1. Did Mendeleev know about the nucleus of an atom?
2. Who discovered the relationship between wavelength of X-rays and atomic number?
3. What did Moseley conclude from his research?
4. What is the “periodic law”?
5. What do the vertical columns (groups) in the periodic table represent?

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2.14: Modern Periodic Table- Periods and Groups

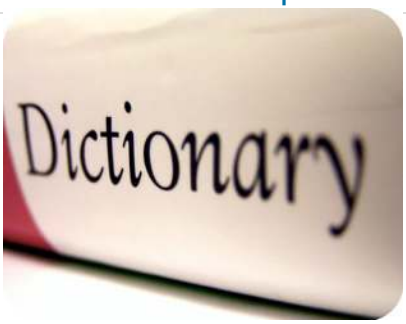


Figure 2.14.1 (Copyright; author via source)

How has the English dictionary evolved over time?

Language changes with time. New words enter the language and old words often disappear from lack of use. Dictionaries are published so that people can keep up with changes in language and know how to use words properly. These publications may be in print, as is the law dictionary below, or they may be electronic. Dictionaries can be found on the internet and apps are available for smartphones. Dictionaries are invaluable for good, reliable communication.

The Modern Periodic Table

The periodic table has undergone extensive changes in the time since it was originally developed by Mendeleev and Moseley. Many new elements have been discovered, while others have been artificially synthesized. Each fits properly into a **group** of elements with similar properties. The periodic table is an arrangement of the elements in order of their atomic numbers, so that elements with similar properties appear in the same vertical column or group.

The figure below shows the most commonly used form of the periodic table. Each square shows the chemical symbol of the element along with its name. Notice that several of the symbols seem to be unrelated to the name of the element: Fe for iron, Pb for lead, etc. Most of these are the elements that have been known since ancient times and have symbols based on their Latin names. The atomic number of each element is written above the symbol.

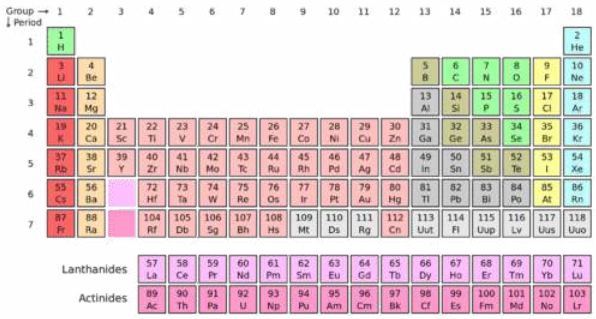


Figure 2.14.2 (Public Domain; User:Cepheus/Wikimedia Commons via Wikipedia)

A **period** is a horizontal row of the periodic table. There are seven periods in the periodic table, with each one beginning at the far left. A new period begins when a new principal energy level begins filling with electrons. Period 1 has only two elements (hydrogen and helium), while periods 2 and 3 have 8 elements. Periods 4 and 5 have 18 elements. Periods 6 and 7 have 32 elements, because the two bottom rows that are separate from the rest of the table belong to those periods. These two rows are pulled out in order to make the table itself fit more easily onto a single page.

A group is a vertical column of the periodic table, based on the organization of the outer shell electrons. There are a total of 18 groups. There are two different numbering systems that are commonly used to designate groups, and you should be familiar with both. The traditional system used in the United States involves the use of the letters A and B. The first two groups are 1A and 2A, while the last six groups are 3A through 8A. The middle groups use B in their titles. Unfortunately, there was a slightly different system in place in Europe. To eliminate confusion, the International Union of Pure and Applied Chemistry (IUPAC) decided that the official system for numbering groups would be a simple 1 through 18 from left to right. Many periodic tables show both systems simultaneously.

Most recent depictions of the periodic table show an incomplete seventh period. In fact, many of those seventh period elements were not known before the early twentieth century. Many elements have been synthesized by bombarding known elements with sub-atomic particles such as neutrons or alpha particles. Uranium has been used in this manner to produce elements 93-100. Larger elements (atomic numbers 101 and above) are formed by fusing nuclei of smaller elements together.

These synthetic elements tend to be very unstable, often existing for less than a second, so little is known about them. Elements up to atomic number 112 are known (not in any detail, however), and some evidence for elements 113 and above had been put forth, with elements 114 and 116 being added to the table in 2011. In December 2015, the IUPAC verified the existence of four new elements 113, 115, 117, and 118 and approved their addition to the periodic table.

The following are the new element names and their origins:

- Element 113 was named Nihonium, symbol Nh, proposed by Japanese researchers after the Japanese word Nihon, which means Japan.
- A team of scientists from Russia and the United States named element 115, Moscovium, symbol Mc, after Moscow and element 117, Tennessine, symbol Ts, after Tennessee.
- The Russian team that discovered element 118 named it Oganesson, symbol Og, after Yuri Oganessian, a prolific element hunter.

These elements complete the seventh period or row of the periodic table.

The video below reviews groups and trends in the periodic table:



Watch the additional videos below to learn more about the newly identified and named chemical elements:

Element Name and Symbol: Nihonium (Nh)

Atomic Number: 113



Element Name and Symbol: Moscovium (Mc)

Atomic Number: 115



Element Name and Symbol: Tennessine (Ts)

Atomic Number: 117



Element Name and Symbol: Oganesson (Og)

Atomic Number: 118



Summary

- The periodic table is arranged in order of atomic number.
- A period is a horizontal row of the periodic table.
- A group is a vertical row of the periodic table.

Review

1. How is today’s periodic table different from the one that Mendeleev published?
2. Are all the elements in today’s periodic table naturally occurring? Explain your answer.
3. What is a “period"? What does it represent?
4. What is a “group"? What does it represent?
5. Why are there two different numbering systems for groups?

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2.15: Metals



Figure 2.15.1 (Public Domain; User:Brianiac/Wikipedia via Wikipedia)

Can you guess what types of metals these screws are made of?

Screws come in all sizes and shapes. They are all (well, almost all) made of some kind of metal. But they have differences in size, shape, and type of metal. Physical characteristics also differ. Some screws are long, and others are short. One screw may have a flat-head slot while another screw may have a Phillips-head. Some of the screws in the picture below are used to fasten things together, and others are used to hang heavy objects on a wall.

Chemists classify materials in many ways. We can sort elements on the basis of their electron arrangements. The way the electrons are distributed determines the chemical properties of the element. Another way is to classify elements based on physical properties. Some common physical properties are color, volume, and density. Other properties that allow us to sort on the basis of behavior are conduction of heat and electricity, malleability (the ability to be hammered into very thin sheets), ductility (the ability to be pulled into thin wires), melting point, and boiling point. Three broad classes of elements based on physical properties are metals, nonmetals, and metalloids.

Metals

A metal is an element that is a good conductor of heat and electricity. Metals are also malleable, which means that they can be hammered into very thin sheets without breaking. They are ductile, which means that they can be drawn into wires. When a fresh surface of any metal is exposed, it will be very shiny because it reflects light well. This is called luster. All metals are solid at room temperature with the exception of mercury (Hg), which is a liquid. Melting points of metals display a very wide variance. The melting point of mercury is -39°C, while the highest melting metal is tungsten (W), with a melting point of 3422°C. The elements in blue in the periodic table below are metals. About 80 percent of the elements are metals.

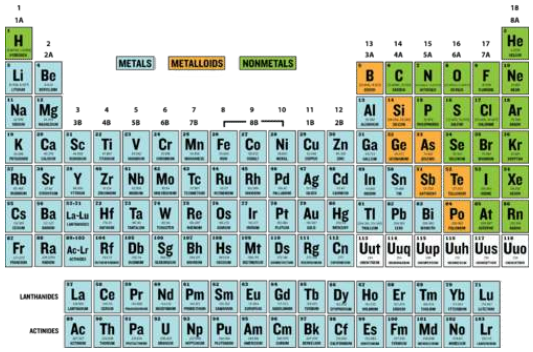


Figure 2.15.2 (CC BY-NC-SA 3.0; Christopher Auyeung via CK-12 Foundation)

Gold has been used by many civilizations for making jewelry (see figure below). This metal is soft and easily shaped into a variety of items. Since gold is very valuable and often used as currency, gold jewelry has also often represented wealth.



Figure 2.15.3: Gold jewelry. (Public Domain; User:Dorieo21/Wikimedia Commons via Wikipedia)

Copper is a good conductor of electricity and is very flexible and ductile. This metal is widely used to conduct electric current in a variety of appliances, from lamps to stereo systems to complex electronic devices (see figure below).



Figure 2.15.4: Copper wire exposed. (Public Domain; Scott Ehardt via Wikipedia)

Mercury is the only metal to exist as a liquid at room temperature (see figure below). This metal was extensively used in thermometers for decades until information about its toxicity became known. Mercury switches were once common, but are no longer used. However, new federally-mandated energy-efficient light bulbs that are now used contain trace amounts of mercury and represent a hazardous waste.



Figure 2.15.5: Pouring Mercury. (CC BY 3.0; User:Bionerd/Wikimedia Commons and User:Materialscientist/Wikimedia Commons via Wikipedia)

Summary

- Metals are good conductors of heat and electricity.
- Metals are malleable and ductile
- All metals are solids at room temperature with the exception of mercury
- Gold, silver, iron, and mercury are typical metals.

Review

1. What properties of an element are affected by electron distribution?
2. Define malleability.
3. Define ductility.
4. State one reason gold is used in jewelry.
5. Why is mercury no longer used in many devices?

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2.16: Nonmetals



Figure 2.16.1 (Public Domain; Neville Street via Wikipedia)

When we sort parts in our shop or garage, we often classify them in terms of common properties. One container might hold all the screws (possibly sub-divided by size and type). Another container would be for nails. Maybe there is a set of drawers for plumbing parts.

When you get finished, you could also have a collection of things that don't nicely fit a category. You define them in terms of what they are not. They are not electrical components, or sprinkler heads for the yard, or parts for the car. These parts may have some common properties, but are a variety of items.

Nonmetals

In the chemical world, these "spare parts" would be considered nonmetals, loosely defined as not having the properties of metals. A **nonmetal** is an element that is generally a poor conductor of heat and electricity. Most properties of nonmetals are the opposite of metals. There is a wider variation in properties among the nonmetals than among the metals. Nonmetals exist in all three states of matter. The majority are gases, such as nitrogen and oxygen. Bromine is a liquid. A few are solids, such as carbon and sulfur. In the solid state, nonmetals are **brittle**, meaning that they will shatter if struck with a hammer. The solids are not lustrous. Melting points are generally much lower than those of metals. The green elements in the table below are nonmetals.

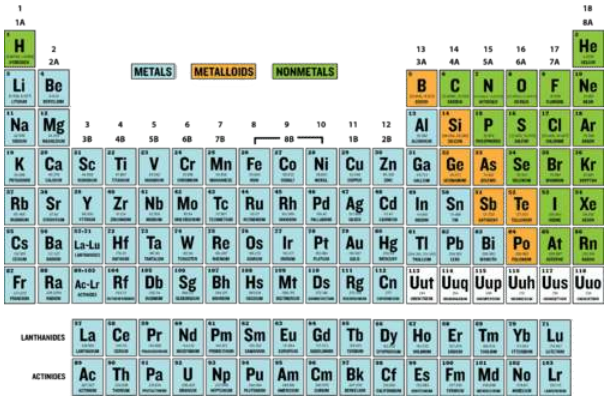


Figure 2.16.2: Copy and Paste Caption here. (CC BY-NC-SA 3.0; Christopher Auyeung via CK-12 Foundation)

Nonmetals have a wide variety of uses. Sulfur can be employed in gunpowder, fireworks, and matches to facilitate ignition (see Figure below). This element is also widely used as an insecticide, a fumigant, or a means of eliminating certain types of fungus. An important role for sulfur is the manufacture of rubber for tires and other materials. First discovered in 1839 by Charles Goodyear, the process of vulcanization makes the rubber more flexible and elastic as well as being more resistant to changes in temperature. A major use of sulfur is for the preparation of sulfur-containing compounds such as sulfuric acid.



Figure 2.16.3: Sulfur. (Public Domain; Ben Mills (Wikimedia: Benjah-bmm27) via Wikipedia)

Bromine is a versatile compound, used mainly in manufacture of flame-retardant materials, especially important for children's clothing (see Figure below). For treatment of water in swimming pools and hot tubs, bromine is beginning to replace chlorine as a disinfectant because of its higher effectiveness. When incorporated into compounds, bromine atoms play important roles in pharmaceuticals for treatment of pain, cancer, and Alzheimer's disease.

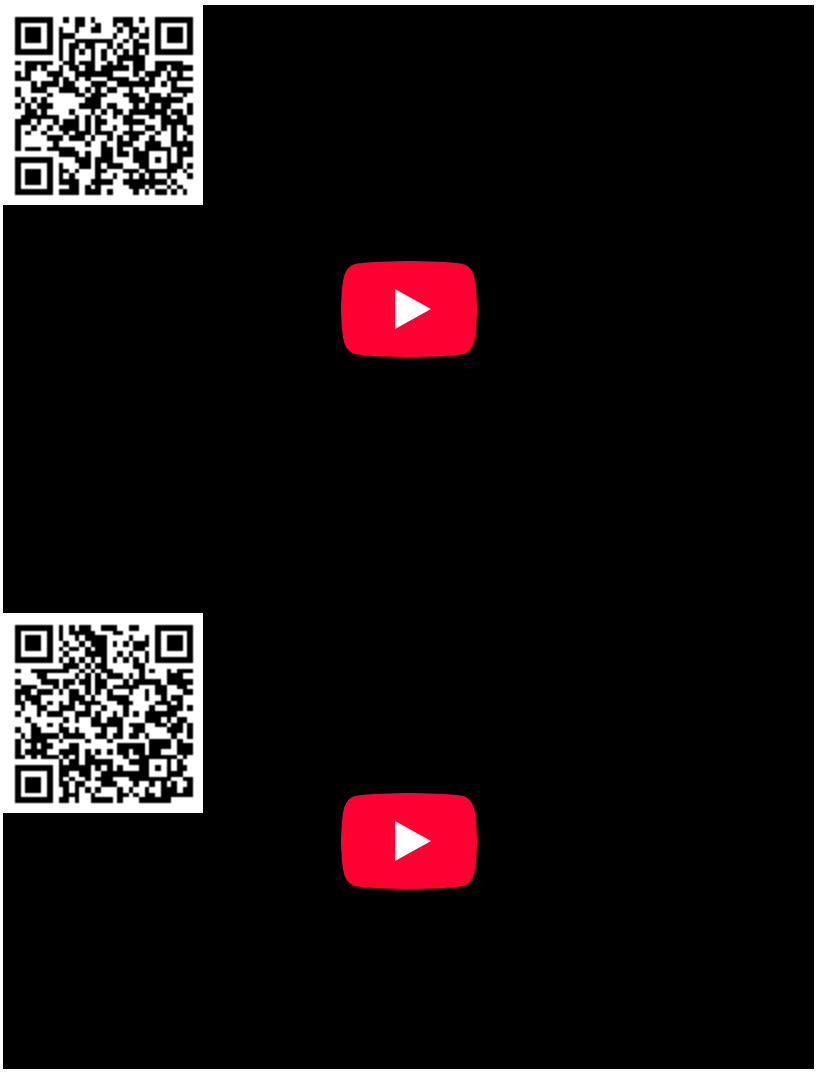


Figure 2.16.4: Bromine. (CC BY 3.0; User:Jurii/Wikimedia Commons via Wikipedia)

Helium is one of the many nonmetals that is a gas. Other nonmetal gases include hydrogen, fluorine, chlorine, and all the group eighteen noble (or inert) gases. Helium is chemically non-reactive, so it is useful for applications such as balloons (see figure below) and lasers, where non-flammability is extremely important. Liquid helium exists at an extremely low temperature and can be used to cool superconducting magnets for imaging studies (MRI, magnetic resonance imaging). Leaks in vessels and many types of high-vacuum apparatus can be detected using helium. Inhaling helium changes the speed of sound, producing a higher pitch in your voice. This is definitely an unsafe practice and can lead to physical harm and death.



Figure 2.16.5: Blimp. (Public Domain; Derek Jensen (Wikimedia: Tysto) via Wikipedia)



Summary

- Nonmetals are generally poor conductors of heat and electricity.
- Properties of nonmetals are usually the opposite of properties of metals
- Nonmetals can be solid, liquid, or gas at room temperature depending upon the element.
- Sulfur, bromine, and helium are typical nonmetals.

Review

1. What are the properties of nonmetals?
2. List the states of matter in which nonmetals can exist and give one example of each state.
3. What are the physical properties and uses of sulfur?
4. What are the physical properties and uses of bromine?
5. What are the physical properties and uses of helium?

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2.17: Metalloids

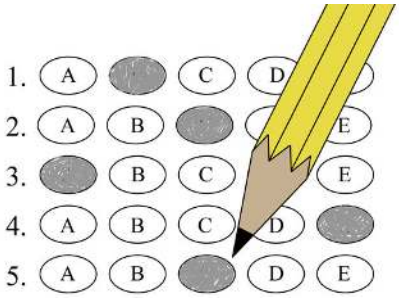


Figure 2.17.1 (CC BY-NC 3.0; Laura Guerin via CK-12 Foundation)

Have you ever taken a multiple-choice test?

Most of the time the answers are specific choices – is the answer possibility a or possibility b? Quite often you can "think through" the choices to come up with the correct answer. More frustrating is the choice "none of the above." You feel very uncertain checking that possibility.

Metalloids

Some elements are "none of the above." They don't fit neatly into the categories of metal or non-metal because of their characteristics. A **metalloid** is an element that has properties that are intermediate between those of metals and nonmetals. Metalloids can also be called semimetals. On the periodic table, the elements colored yellow, which generally border the stair-step line, are considered to be metalloids. Notice that aluminum borders the line, but it is considered to be a metal since all of its properties are like those of metals.

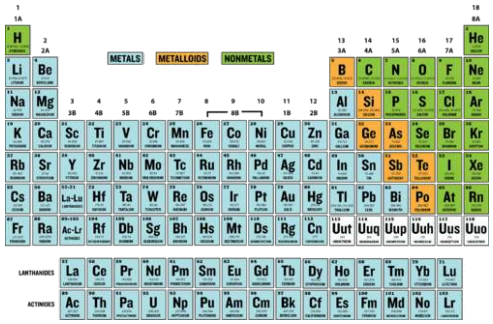


Figure 2.17.2 (CC BY-NC-SA 3.0; Christopher Auyeung via CK-12 Foundation)



Examples of Metalloids

Silicon is a typical metalloid (see figure below). It has luster like a metal, but is brittle like a nonmetal. Silicon is used extensively in computer chips and other electronics because its electrical conductivity is in between that of a metal and a nonmetal.



Figure 2.17.3: Silicon. (Public Domain; User:Enricoros/Wikipedia via Wikipedia)

Boron is a versatile element that can be incorporated into a number of compounds (see figure below). Borosilicate glass is extremely resistance to thermal shock. Extreme changes in the temperature of objects containing borosilicates will not create any damage to the material, unlike other glass compositions, which would crack or shatter. Because of their strength, boron filaments are used as light, high-strength materials for airplanes, golf clubs, and fishing rods. Sodium tetraborate is widely used in fiberglass as insulation and also is employed in many detergents and cleaners.

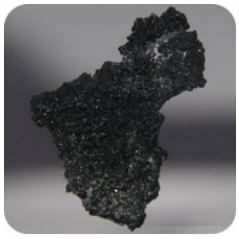


Figure 2.17.4: Boron. (CCSA;CC-BY 3.0; User:Jurii/Wikimedia Commons via Wikipedia)

Arsenic has long played a role in murder mysteries, being used to commit the foul deed (see figure below). This use of the material is not very smart since arsenic can be easily detected on autopsy. We find arsenic in pesticides, herbicides, and insecticides, but the use of arsenic for these applications is decreasing due to the toxicity of the metal. Its effectiveness as an insecticide has led arsenic to be used as a wood preservative.

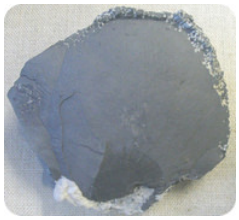


Figure 2.17.5: Arsenic. (Public Domain; Aram Dulyan (Wikimedia: Aramgutang) via Wikipedia)

Antimony is a brittle, bluish-white metallic material that is a poor conductor of electricity (see figure below). Used with lead, antimony increases the hardness and strength of the mixture. This material plays an important role in the fabrication of electronic and semiconductor devices. About half of the antimony used industrially is employed in the production of batteries, bullets, and alloys.



Figure 2.17.6: Antimony. (Public Domain; Aram Dulyan (User:Aramgutang/Wikimedia Commons) via Wikipedia)

Summary

- Metalloids are elements with properties intermediate between those of metals and non-metals
- Silicon is a metalloid because it has luster, but is brittle.
- Boron, arsenic, and antimony are metalloids with a variety of uses.

Review

1. Define “metalloid.”
2. Why would it be difficult to decide whether or not an element was a metalloid based on its properties?

3. Why is silicon used extensively in electronics?
4. What are borosilicates used for?
5. Why is the use of arsenic as an insecticide decreasing?
6. What is a main application of antimony?

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2.18: Blocks of the Periodic Table



Figure 2.18.1 (Public Domain; User:Szalax/Wikimedia Commons via Wikipedia)

What makes these music notes unique?

We all enjoy music of some sort. Some people like classical music, others like jazz or country. Music styles change from one period of time to the next, and from one region to another. Each type of music has its language that describes it. Classical music has a certain structure, style, and content. There are different expressions of classical music – the symphony, concerto, sonata. We have ballet and opera as well as choral music. Jazz has a different set of characteristics from classical and different styles of performance. Each type of music can be described and compared to other types on the basis of certain common qualities like notes, chords, and melodic styles.

The elements in the periodic table could be considered to be similar to types of music. Each set of elements has its unique set of properties, with different sets of elements having some common characteristics in terms of electron arrangements. We can see patterns of electronic structure and reactivity in the periodic table that allow us to understand better the behavior of individual elements.

Periods and Blocks

There are seven horizontal rows of the periodic table, called **periods**. The length of each period is determined by the number of electrons that are capable of occupying the **sublevels** that fill during that period, as seen in the table below.

Table 2.18.1: Period Length and Sublevels in the Periodic Table

Period	Number of Elements in Period	Sublevels in Order of Fill
1	2	$1s$
2	8	$2s\ 2p$
3	8	$3s\ 3p$
4	18	$4s\ 3d\ 4p$
5	18	$5s\ 4d\ 5p$
6	32	$6s\ 4f\ 5d\ 6p$
7	32	$7s\ 5f\ 6d\ 7s$

Recall that the four different sublevels each consist of a different number of orbitals. The s sublevel has one orbital, the p sublevel has three orbitals, the d sublevel has five orbitals, and the f sublevel has seven orbitals. In the first period, only the $1s$ sublevel is being filled. Since all orbitals can hold two electrons, the entire first period consists of just two elements. In the second period, the $2s$ sublevel, with two electrons, and the $2p$ sublevel, with six electrons, are being filled. Consequently, the second period contains eight elements. The third period is similar to the second, filling the $3s$ and $3p$ sublevels. Notice that the $3d$ sublevel does not actually fill until after the $4s$ sublevel. This results in the fourth period containing 18 elements due to the additional 10 electrons that are contributed by the d sublevel. The fifth period is similar to the fourth. After the $6s$ sublevel fills, the $4f$ sublevel with its 14 electrons fills. This is followed by the $5d$ and the $6p$. The total number of elements in the sixth period is 32. The later elements in the seventh period are still being created. So while there is a possible number of 32 elements in the period, the current number is slightly less.

The period to which a given element belongs can be easily determined by its electron configuration. For example, consider the element nickel (Ni). Its electron configuration is $[\mathrm{Ar}]\ 3d^8\ 4s^2$. The highest occupied principal energy level is the fourth, indicated by the 4 in the $4s^2$ portion of the configuration. Therefore, nickel can be found in the fourth period of the periodic table.

Based on electron configurations, the periodic table can be divided into **blocks** denoting which sublevel is in the process of being filled. The s, p, d, and f blocks are illustrated below.

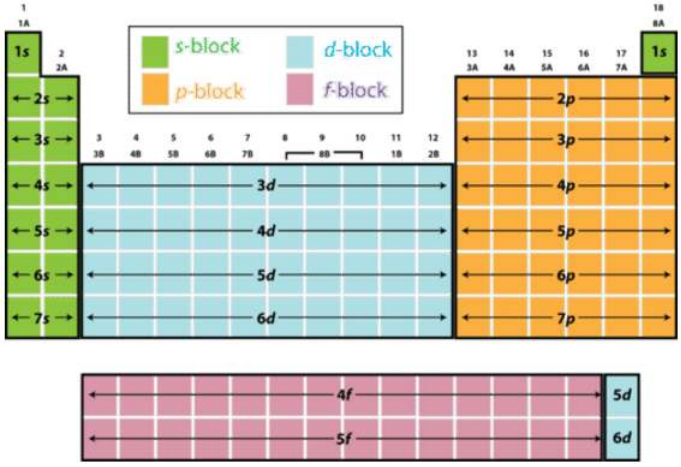


Figure 2.18.2 (CC BY-NC 3.0; Christopher Auyeung and Joy Sheng via CK-12 Foundation)

The figure also illustrates how the d sublevel is always one principal level behind the period in which that sublevel occurs. In other words, the $3d$ sublevel fills during the fourth period. The f sublevel is always two levels behind. The $4f$ sublevel belongs to the sixth period.





Summary

- The horizontal rows of the periodic table are called periods.
- The length of a period depends on how many electrons are needed to occupy the sublevels that fill the period.
- Blocks indicate which sublevel is being filled.

Review

1. What are the horizontal rows of the periodic table called?
2. Which sublevel is being filled in period 1?
3. Which sublevel is being filled in period 7?
4. How does the electron configuration of an element give information about the period it is in?
5. What block of elements has the d sublevels being filled?

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2.19: Hydrogen and Alkali Metals



Figure 2.19.1 (Public Domain; User:Ajhalls/Wikimedia Commons via Commons Wikimedia, Large Sodium Explosion [commons.wikimedia.org])

Can you guess what kind of reaction is taking place in this picture?

Some chemistry students just enjoy learning about the science, while others are intrigued by the violent reactions that sometimes can occur. Many chemistry classes have been enlivened by the demonstration of how reactive sodium is with water. In some instances, the demonstration has gone off safely. Unfortunately, in other situations students and instructors have incurred serious injury due to their failure to observe proper safety precautions.

One value of the periodic table is the ability to make predictions about the behavior of individual elements. By knowing which group an element is in, we can determine the number of reactive electrons and say something about how that element will behave.

Hydrogen and Alkali Metals

The periodic table is arranged on the basis of atomic numbers (number of protons in the nucleus). One of the valuable consequences of this arrangement is that we can learn a lot about the electron distribution in these atoms. The colors in the table below indicate the different groupings of atoms based on the location and number of electrons in the atom.

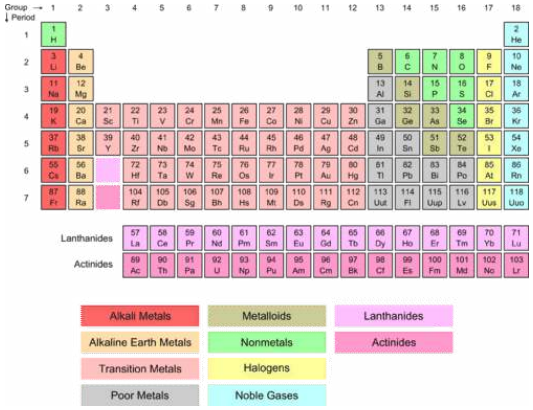


Figure 2.19.2 (Public Domain; User:Cepheus/Wikimedia Commons, modified by CK-12 Foundation via Commons Wikimedia, Periodic Table [commons.wikimedia.org])

If we look at Group I (red column), we see that it is labeled alkali metals. Also note the green H above the alkali metals. All of these elements have a similar configuration of outer-shell electrons (see table below). In each case, there is one electron in the outer orbital and that is an s-orbital electron. Hydrogen is not an alkali metal itself, but has some similar properties due to its simple one proton (located in the nucleus), one electron arrangement. The lone electron exists in a s-orbital around the nucleus. For lithium, there are two 1s electrons in an inner orbit and one 2s electron in the outer orbit. The same pattern holds for sodium and potassium.

Element, Symbol, Electron Configuration

Element	Symbol	Electron Configuration
hydrogen	H	$\backslash 1s^1$
lithium	Li	$[\mathrm{He}]\, 2s^1$

Element	Symbol	Electron Configuration
sodium	Na	$[\mathrm{Ne}]\ 3s^1$
potassium	K	$[\mathrm{Ar}]\ 4s^1$
rubidium	Rb	$[\mathrm{Kr}]\ 5s^1$
cesium	Cs	$[\mathrm{Xe}]\ 6s^1$
francium	Fr	$[\mathrm{Rn}]\ 7s^1$

Even an atom with a very complex electron composition such as cesium still has the single s electron in its outer orbital (see figure below).

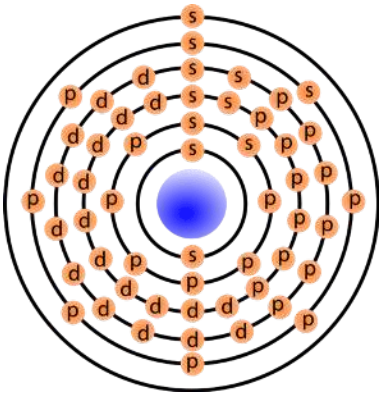


Figure 2.19.3: Celsium Orbitals. (CC BY-NC-SA 3.0; Joy Sheng via CK-12 Foundation)

This one electron is very easily removed during chemical reactions. The group I elements react rapidly with oxygen to produce metal oxides. They are very soft metals, which become liquid just above room temperature.

Li reacts with water to produce hydrogen gas. Sodium also reacts the same way, just more rapidly. Potassium reacts rapidly with water producing hydrogen gas and heat which ignites the hydrogen gas. Rubidium and cesium react yet more vigorously and explode on contact with water.



Summary

- Group I (alkali metals and hydrogen) elements all have one electron in their outer shell. This electron is in a s orbital.
- The Group I metals are all very reactive with water.

Review

1. What group are the alkali metals and hydrogen in?
2. What is the outer shell electron configuration in this group?
3. How reactive are the alkali metals with oxygen?
4. How reactive are these metals with water?

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2.20: Alkaline Earth Metals



Figure 2.20.1 (Public Domain; U.S. Marine Corps via Wikipedia)

How are oyster shells and chemistry related?

We take a lot of chemistry for granted. Very few of us think about the chemistry of bone or oyster shells. Both of these materials have large amounts of calcium compounds in them and play important roles in maintaining the structure of the organism. The shell provides a solid surrounding for the oyster. Bones give support to the body so the person can move around and not just be a soft mass of tissue.



Figure 2.20.2 (Public Domain; Jossifresco via Wikipedia)

Alkaline Earth Metals

Group 2 elements are referred to as "**alkaline earth**" metals (tan column below). The name "**alkaline**" comes from the fact that compounds of these elements form **basic** (pH greater than 7) or alkaline solutions when dissolved in water. If the Group 1 elements all have one s electron in their outer orbital, we can predict that the Group 2 elements will have two electrons in that outer shell.

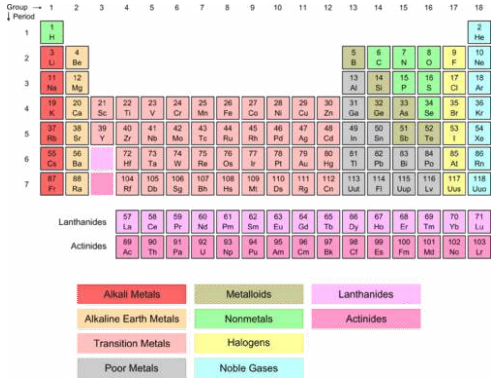


Figure 2.20.3 (Public Domain; User:Cepheus/Wikimedia Commons, modified by CK-12 Foundation via Wikipedia)

The beryllium atom, the first element of Group 2, has an atomic number of four. The atom has the 1s shell filled as well as the 2s shell, giving a total of four electrons ($1s^2 2s^2$). Note that there are two s electrons in the outer shell, a structure that is characteristic of the Group 2 elements. Barium (atomic number 56) has the same outer shell structure of two electrons in the s orbital, even though the internal electron structure for barium is quite complicated.

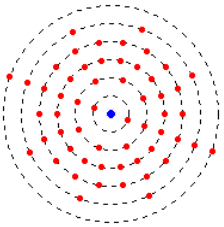


Figure 2.20.4 (Public Domain; Ingmar Runge via Wikipedia)

Radium (atomic number 88) has similar properties to barium and is also in the Group 2 category. However, radium is a radioactive element and is generally under the category of radioisotopes in addition to being an alkaline earth metal, because it is not a stable element.

The Group 2 elements tend to be less reactive than their Group 1 counterparts. The need to remove two electrons in order for the material to react means more energy is needed for electron removal. However, these elements are reactive enough that they do not exist in their elemental forms in nature, but are present as compounds.



Uses of Alkaline Earth Compounds

Since magnesium burns brightly, it is used in flares and fireworks. Magnesium alloys with aluminum provide light weight and sturdy materials for airplanes, missiles, and rockets. Several antacids use magnesium hydroxide to neutralize excess stomach acid.

Calcium compounds are widely found in limestone, marble, and chalk. Calcium is an important constituent of cement. Other uses include calcium chloride as a deicer and limestone as a white pigment in paints and toothpaste.

Strontium is widely used in fireworks and magnets. Barium compounds can be used in paints, filler for rubber, plastic, and resins, and as a contrast medium for X-rays. Many beryllium compounds are toxic, but these materials have been employed in metal alloys.

Summary

- The alkaline earth elements are in Group 2 of the periodic table.
- These elements each have two s electrons in their outer shell.
- The alkaline earth elements are less reactive than the alkali metals.

Review

1. Why are these elements known as “alkaline earth” elements?
2. How many electrons are in the outer shell of the alkaline earth elements?

3. Are the alkaline earth elements more or less reactive than the alkali metals? Explain your answer.
4. Is radium usually considered as part of the alkaline earth category in terms of chemistry? Explain your answer.

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2.21: Noble Gases



Figure 2.21.1 (Public Domain; User:Ingolfson/Wikimedia Commons via Wikipedia)

What gives these lights their color?

Cities at night would be rather boring without all the bright lights. They provide colorful Illuminations and help make things much more visible. We call these lights “neon lights,” but they use several gases to make the different colors.

Noble Gases

The reactivity of an element can give us important clues as to the electron configuration of that material. If an element is extremely unreactive, this suggests that the electron configuration is such that adding or removing electrons is very unlikely. There must be a stable electron configuration that resists further reaction.

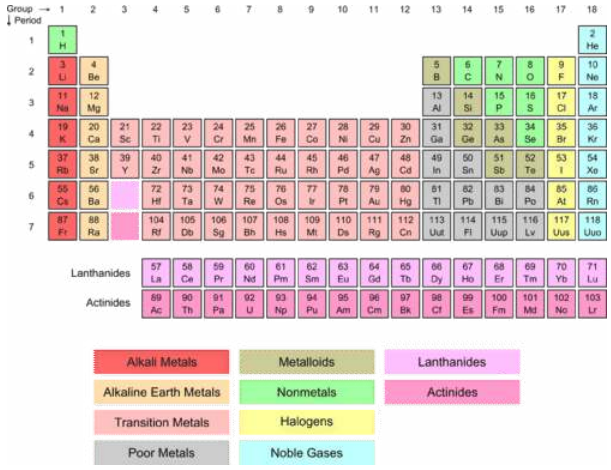


Figure 2.21.2 (Public Domain; User:Cepheus/Wikimedia Commons, modified by CK-12 Foundation via Wikipedia)

The Group 18 (once known as group VIII) elements are essentially chemically **inert** (light blue column on the right). All these elements exist as **monatomic** gases at room temperature. If we look at the electron configurations, we see that helium (atomic number 2) has a full shell of two s electrons. Since there are no electrons shielding this shell from the nucleus, these two electrons will be very difficult to remove, making helium unreactive.

The remaining elements in the group have full outer shells consisting of two s electrons and six p electrons for an outer shell content of eight electrons. This particular arrangement renders the atoms fairly unreactive. This group has been referred to as the “inert” gases, indicating that they are chemically inert, or unreactive. Another popular term is “**noble gases**,” suggesting that these gases do not like to have much to do with the other, more common materials (or that they don’t do a lot of work).

Noble Gas Compounds

In more recent years, a number of reactions using the noble gas elements have been discovered. Although the conventional wisdom was that the complete outer shells of these elements would not allow them to react, some scientists believed that the outer electrons of the larger elements (such as Rn, Xe, and Kr) were far enough away from the nucleus that they should be able to be displaced under the right set of conditions. The first compound ($XePtF_6$) was made with xenon in 1962. Since then, several compounds have been made with radon, xenon, krypton, and argon. Only helium and neon have not formed compounds at this time.

Colors of Noble Gases

The different gases glow when an electric current is passed through them. Many of these gases are used in displays because of their chemical inertness. They are stable and will not react with other materials in the system. Radon also will give a reddish glow, but is not used because it is radioactive and will not retain its structure as radon for any significant length of time.



Figure 2.21.3 (CC BY 3.0; User:Jurii/Wikimedia Commons via Wikipedia)

Royal Society of Chemistry - Colors of the Noble Gases



Summary

- The noble gases are in Group VIII of the periodic table.
- Helium has a full outer shell of two s electrons.
- The other gases have full outer shells of two s and six p electrons.
- Compounds have been formed with Rn, Xe, Kr, and Ar.

Review

1. What elements comprise the noble elements?
2. What state are they in at room temperature?
3. Why is helium non-reactive?
4. Why were the other noble gases believed to be non-reactive?
5. When was the first compound formed from xenon?
6. What happens when an electric current is passed through these gases?

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2.22: Halogens

How do you study a gas that does not exist as such in nature?

It's not as easy as you think. Fluorine is so reactive that we cannot find it free in nature. None of the halogens exist free in nature (unlike some of the metals such as gold and silver) because they are very reactive. The video below shows how violently elemental fluorine reacts with other materials.



Halogens

Some elements are much more reactive than others. The Group I (red) and Group II (tan) elements can easily lose electrons during a reaction. Elements of other groups are much more likely to accept electrons as they react.

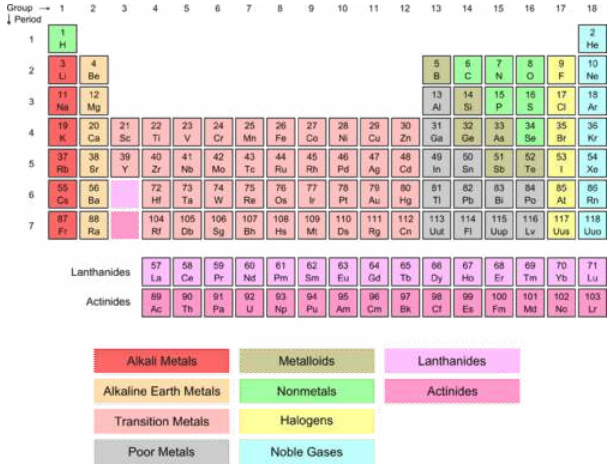


Figure 2.22.1 (Public Domain; User:Cepheus/Wikimedia Commons, modified by CK-12 Foundation via Wikipedia)

The elements of Group VIIA (new Group 17 - fluorine, chlorine, bromine, iodine, and astatine) are called the **halogens** (yellow column). The term "halogen" means "salt-former" because these elements will readily react with alkali metal and alkaline earth metals to form halide salts. The halogens all have the general electron configuration ns^2np^5, giving them seven valence electrons. They are one electron short of having the full outer s and p sublevel, which makes them very reactive.

Physical Properties of Halogens

As elements, chlorine and fluorine are gases at room temperature, bromine is a dark orange liquid, and iodine is a dark purple-gray solid. Astatine is so rare that its properties are mostly unknown. In the picture below we see chlorine gas on the left (green), bromine solid and vapor in the middle (orange), and solid iodine (grey) on the right. Fluorine is not shown in the picture below because it is too corrosive and will destroy the glass container.



Figure 2.22.2 (Chlorine and iodine: Public Domain; Bromine: The copyright holder of this work allows anyone to use it for any purpose including unrestricted redistribution, commercial use, and modification; Chlorine: User:Greenhorn1/Wikimedia Commons Bromine: User:Tomihahndorf/De.Wikipedia; Iodine: Ben Mills (Wikimedia: Benjah-bmm27) via Chlorine: http://commons.wikimedia.org/wiki/File:Chlorinegas.jpg; Bromine: http://commons.wikimedia.org/wiki/File:Brom_amp.jpg; Iodine: http://commons.wikimedia.org/wiki/File:Iodine-sample.jpg)

None of these elements are found free in nature because of their reactivity. Fluorine is found in combination with cations in several minerals. Chlorine is found in table salt, in the oceans (which are about 2% chloride ion by weight) and in lakes such as the Great Salt Lake in Utah. Small amounts of bromide and iodide salts can be found in the oceans and in brine wells in several states.



Figure 2.22.3 (Public Domain; NASA via Wikipedia)

Watch the following two video experiments of *p* block elements:

This first video is of bromine reacting with aluminum.



This second video discusses the properties of halogens and shows a few more reactions they can participate in.



Summary

- The halogens all have seven electrons in their outer shells.
- The electron configuration in the outer shell is ns^2np^5.
- As the atomic number increases, the reactivity of the halogens decreases.
- Fluorine and chlorine exist as gases at room temperature, while bromine is a liquid, and iodine is a solid.

Review

1. Pick two elements that are halogens. For each, write the name, chemical symbol, and atomic weight.
2. What does the term “halogen” mean?
3. What is the outer shell electron configuration for the halogens?
4. What is the physical state of each halogen at room temperature?
5. Where are the halogens found?

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2.23: Lanthanides and Actinides



Figure 2.23.1 (Public Domain; Adrian Pingstone (User:Arpingstone/Wikimedia Commons) via Commons Wikimedia, Russian Dolls Huge Set [commons.wikimedia.org])

How many dolls are in this picture?

Russian "nesting dolls" (often known as matryoshka dolls) have a long history in Russia. These dolls are designed to nest inside of one another. When we open the largest doll, we find a slightly smaller doll inside it. These dolls can often go down seven or eight layers, and some have over thirty-five layers.

Lanthanides and Actinides

We see some hidden "layers" in chemistry. Examining the periodic table below, visible are two pink boxes—one between Ba (element 56) and Hf (element 72) and the other between Ra (88) and Rf (104). These elements all have unfilled f-sublevels. Because of the uniqueness of the electron configurations, these elements fit into the two boxes in the larger periodic table.

As the number of electrons in an atom increases, we begin to see some strange behaviors. Due to the way the electron energy levels work, some inner levels fill after one or more outer layers do. We see this in two similar groups of elements—the **lanthanides** and the **actinides**.

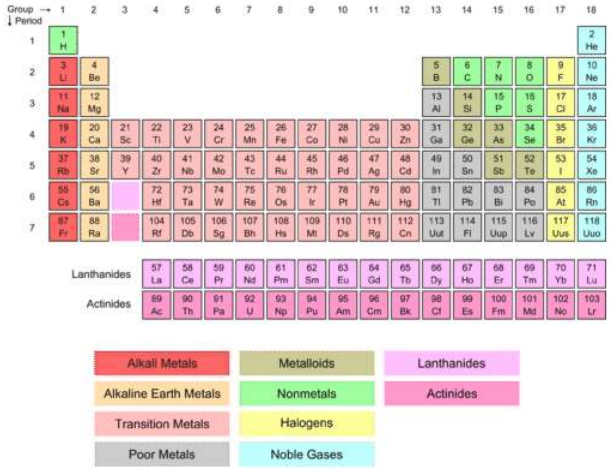


Figure 2.23.2: (Public Domain; Cepheus, modified by CK-12 Foundation via Commons Wikimedia, Periodic Table [commons.wikimedia.org])

The f-Block

The first of the f sublevels to begin filling is the $4f$ sublevel. It fills after the $6s$ sublevel, meaning that f sublevels are two principal energy levels behind. The general electron configuration for elements in the **f-block** is $(n-2)\,f^{1-14}ns^2$. The seven orbitals of the f sublevel accommodate 14 electrons, so the f block is 14 elements in length. It is pulled out of the main body of the periodic table and is shown at the very bottom. Because of that, the elements of the f block do not belong to a group, being wedged in between Groups 3 and 4. The lanthanides are the 14 elements from cerium (atomic number 58) to lutetium (atomic number 71). The word comes from the Greek "$\lambda\alpha\nu\theta\alpha\nu\epsilon\iota\nu$" meaning "to be hidden". The name probably arose because these elements all hide behind one another in the periodic table. The $4f$ sublevel is in the process of being filled for the lanthanides. They are all metals and are similar in reactivity to the Group 2 alkaline earth metals.

The actinides are the 14 elements from thorium (atomic number 90) to lawrencium (atomic number 103). The $5f$ sublevel is in the process of being filled. The actinides are all radioactive elements and only the first four have been found naturally on Earth. All of

the others have only been artificially made in the laboratory. The lanthanides and actinides together are sometimes called the inner transition elements.

Uses of Lanthanides

Lanthanides have been widely used as alloys to impart strength and hardness to metals. The main lanthanide used for this purpose is cerium, mixed with small amounts of lanthanum, neodymium, and praseodymium. These metals are also widely used in the petroleum industry for refining crude oil into gasoline products.



Figure 2.23.3: Oil refinery. (CC BY 2.0; Walter Siegmund via Commons Wikimedia, Anacortes Refinery [commons.wikimedia.org])

Erbium and other lanthanides are widely used in some optical devices, such as night vision goggles, laser beams, and phosphorescent materials.



Figure 2.23.4: Night vision goggles. (Public Domain; the U.S. Army via Commons Wikimedia, File:PEO ANAVS-6 NVG.jpg [commons.wikimedia.org])

Uses of Actinides

The actinides are valuable primarily because they are radioactive. These elements can be used as energy sources for applications as varied as cardiac pacemakers, to the generation of electrical energy for instruments on the moon. Uranium and plutonium have been employed in nuclear weapons and in nuclear power plants.



Figure 2.23.5: Pacemaker. (CC BY 3.0; Steven Fruitsmaak via Commons Wikimedia, St. Jude Medical Pacemaker with Ruler [commons.wikimedia.org])

Summary

- Lanthanides and actinides are elements with unfilled f orbitals.
- Lanthanides are all metals with reactivity similar to group 2 elements.
- Actinides are all radioactive elements.
- Lanthanides are used in optical devices (night vision goggles), petroleum refining, and alloys.
- Actinides are found primarily in applications where their radioactivity can be used to power devices such as cardiac pacemakers.

Review

1. What electron sublevel is being filled in the lanthanides?
2. What electron sublevel is being filled in the actinides?
3. What sublevel is filled just prior to the filling of this sublevel?
4. Which actinides are found naturally on earth?
5. List some uses for lanthanides.
6. List some uses for actinides.

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2.24: Transition Elements



Figure 2.24.1 (Public Domain; Stock model: Bull-Doser; Race model: Dana60Cummins via Stock model: Commons Wikimedia, Ford Focus ZX5 [commons.wikimedia.org]; Race model: Commons Wikimedia, Ford Focus Ecoboost Race Car [commons.wikimedia.org])

What are the similarities and differences between these two cars?

From the outside, the two cars below look the same (except for the flashy paint job on the racing model). They are the same model of the car, but one is a stock edition for regular driving, while the other one is built for high-speed racing. We really can't tell much from the external view. To see the differences, we need to go under the hood, take the engines apart, and look at the braking and suspension systems in order to see how the two cars differ.

Many electron configurations of elements are simple and straightforward. We can look at the outer shell and easily understand how that set of elements will react in terms of electron gain or loss. However, there are sets of elements that are more complex in their behavior. One such group is the **transition elements**.

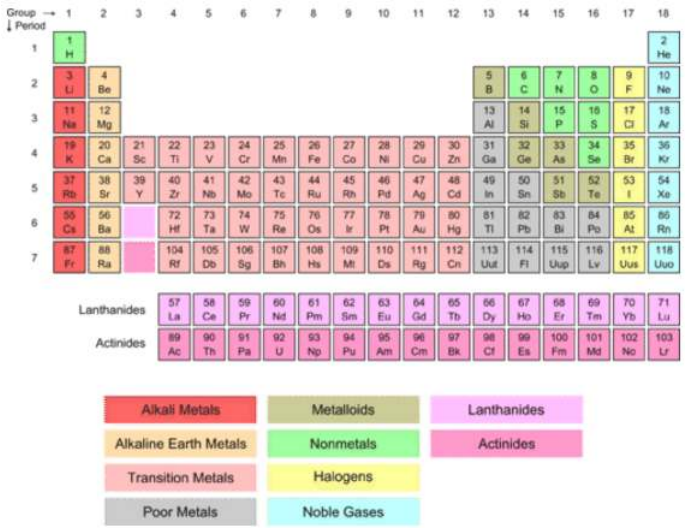


Figure 2.24.2 (Public Domain; User:Cepheus/Wikimedia Commons, modified by CK-12 Foundation via Commons Wikimedia, Periodic Table [commons.wikimedia.org])

The Transition Elements

Transition elements are the elements that are found in Groups 3-12 (old groups IIA-IIB) on the periodic table (salmon-colored block in the middle of the table). The term refers to the fact that the d **sublevel**, which is in the process of being filled, is in a lower principal energy level than the s sublevel filled before it. For example, the electron configuration of scandium, the first transition element, is $[\mathrm{Ar}]\ 3d^1\ 4s^2$. Remember that the configuration is reversed from the fill order—the $4s$ fills before the $3d$ begins. Because they are all metals, the transition elements are often called the transition metals. As a group, they display typical metallic properties and are less reactive than the metals in Groups 1 and 2. Some of the more familiar ones are so unreactive that they can be found in nature in their free, or uncombined, state. These include platinum, gold, and silver. Because of this unique filling order, the transition elements are often referred to as "d-block" elements.



Figure 2.24.3: Piece of silver. (Public Domain; US Geological Survey via Commons Wikimedia, Silver [commons.wikimedia.org])

Compounds of many transition elements are distinctive for being widely and vividly colored. As visible light passes through a transition metal compound dissolved in water, the d-orbitals absorb light of various energies. The visible light of a given energy level that is not absorbed produces a distinctly colored solution.



Figure 2.24.4: Transition metal compounds dissolved in water exhibit a wide variety of bright colors. From left to right are shown solutions of cobalt (II) nitrate, potassium dichromate, potassium chromate, nickel (II) chloride, copper (II) sulfate, and potassium permanganate. (Public Domain; Ben Mills (Wikimedia: Benjah-bmm27) via Commons Wikimedia, Coloured Transition Metal Solutions [commons.wikimedia.org])



Summary

- The transition elements are found in groups IIA-IIB (new groups 3-12).
- These elements are characterized by having unfilled d sublevels.
- In general, the next higher s sublevel is already filled or has one electron missing.
- Many transition element compounds are brightly colored due to the inner-level d electron transitions.

Review

1. List five different transition elements, giving their name, chemical symbol, and atomic number.
2. What is unique about the transition elements in terms of electron configurations?
3. Why are these elements often referred to as "d-block" elements?
4. Why do many transition element compounds have bright colors?

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2.25: Periodic Trends- Atomic Radius



Figure 2.25.1 (CC by 2.0; James Cridland via Flickr)

How can all of these people fit in such a small space?

Events draw large numbers of people to them. Even an outdoor event can fill up so that there is no room for more people. The crowd capacity depends on the amount of space in the venue, and the amount of space depends on the size of the objects filling it. We can get more people into a given space than can elephants, because elephants are larger than people. We can get more squirrels into that same space than we can people for the same reason. Knowing the sizes of objects to be dealt with can be important in deciding how much space is needed.

Atomic Radius

The size of atoms is important to explanations of the behavior of atoms or compounds. One way to express the size of atoms is by use of **atomic radius**. This data helps us understand why some molecules fit together and why other molecules have parts that get too crowded under certain conditions.

The size of an atom is defined by the edge of its orbital. However, orbital boundaries are fuzzy, and variable under different conditions. In order to standardize the measurement of atomic radii, the distance between the nuclei of two identical atoms bonded together is measured. The atomic radius is defined as one-half the distance between the nuclei of identical atoms that are bonded together.

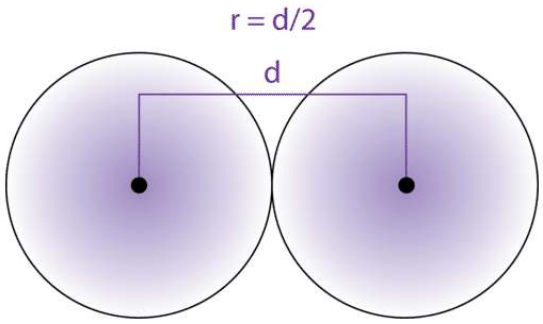


Figure 2.25.2: The atomic radius (r) of an atom can be defined as one half the distance (d) between two nuclei in a diatomic molecule. (CC BY-NC 3.0; Christopher Auyeung via CK-12 Foundation)

Atomic radii have been measured for elements. The units for atomic radii are picometers, equal to 10^{-12} meters. As an example, the internuclear distance between the two hydrogen atoms in an H_2 molecule is measured to be 74 pm. Therefore, the atomic radius of a hydrogen atom is $\frac{74}{2} = 37$ pm.

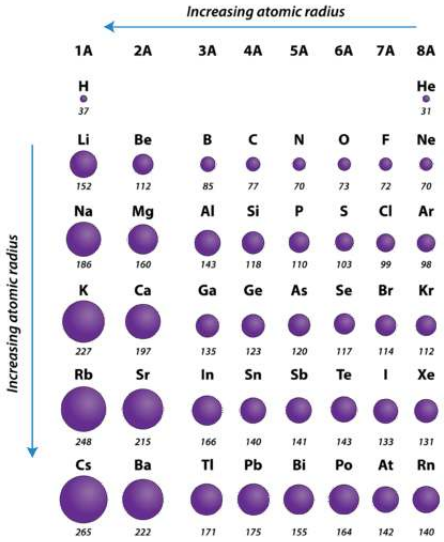


Figure 2.25.3: Atomic radii of the representative elements measured in picometers. (CC BY-NC 3.0; Christopher Auyeung via CK-12 Foundation)

Periodic Trend

The atomic radius of atoms generally decreases from left to right across a period. There are some small exceptions, such as the oxygen radius being slightly greater than the nitrogen radius. Within a period, protons are added to the nucleus as electrons are being added to the same principal energy level. These electrons are gradually pulled closer to the nucleus because of its increased positive charge. Since the force of attraction between nuclei and electrons increases, the size of the atoms decreases. The effect lessens as one moves further to the right in a period, because of electron-electron repulsions that would otherwise cause the atom's size to increase.

Group Trend

The atomic radius of atoms generally increases from top to bottom within a group. As the atomic number increases down a group, there is again an increase in the positive nuclear charge. However, there is also an increase in the number of occupied principal energy levels. Higher principal energy levels consist of orbitals which are larger in size than the orbitals from lower energy levels. The effect of the greater number of principal energy levels outweighs the increase in nuclear charge, and so atomic radius increases down a group.

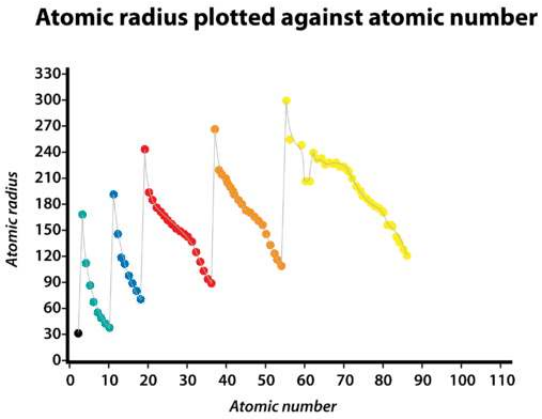
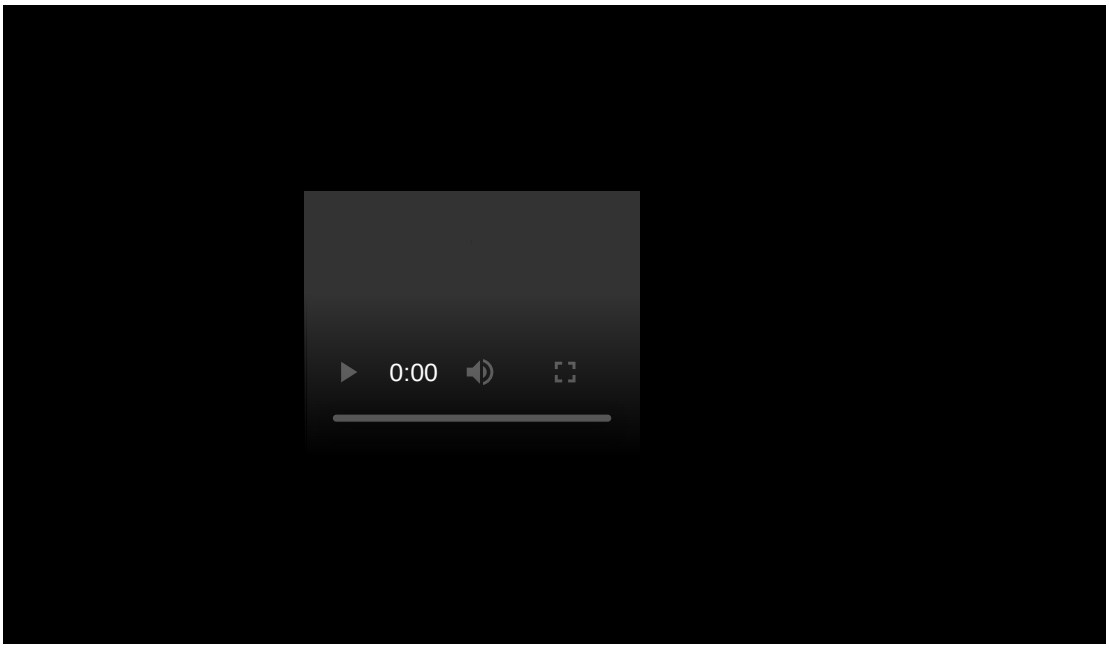


Figure 2.25.4: A graph of atomic radius plotted versus atomic number. Each successive period is shown in a different color. As the atomic number increases within a period, the atomic radius decreases. (CC BY-NC 3.0; Christopher Auyeung via CK-12 Foundation)



Summary

- Atomic radius is determined as half the distance between the nuclei of two identical atoms bonded together.
- The atomic radius of atoms generally decreases from left to right across a period.
- The atomic radius of atoms generally increases from top to bottom within a group.

Review

1. Define “atomic radius.”
2. What are the units of measurement for atomic radius?
3. How does the atomic radius of different elements change across a period?
4. How does atomic radius change from top to bottom within a group?
5. Explain why the atomic radius of hydrogen is so much smaller than the atomic radius of potassium.

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2.26: Ionic Radii



Figure 2.26.1 (Public Domain; the US Department of Agriculture via Commons Wikimedia, Peanuts [commons.wikimedia.org])

How are peanuts sold?

Peanuts can be sold two ways. The bare peanut without the shell (brown inner portion of peanut) can be purchased in jars and packages for casual munching or for cooking. The size of the peanut in this situation is smaller than the peanut plus shell since the outer portion is missing. If we add the shell to the peanut, we have a larger size for the combination.

Electrons and protons are strongly attracted to one another. The strength of that attraction and the relative numbers of the two particles in a given atom or ion have a significant influence on the size of that species. When an atom loses one or more electrons, the resulting ion becomes smaller. If electrons are added to the atom, the ion becomes larger.

Ionic Radius

The **ionic radius** for an atom is measured in a **crystal lattice**, requiring a solid form for the compound. These radii will differ somewhat depending upon the technique used. Usually, x-ray crystallography is employed to determine the radius for an ion.

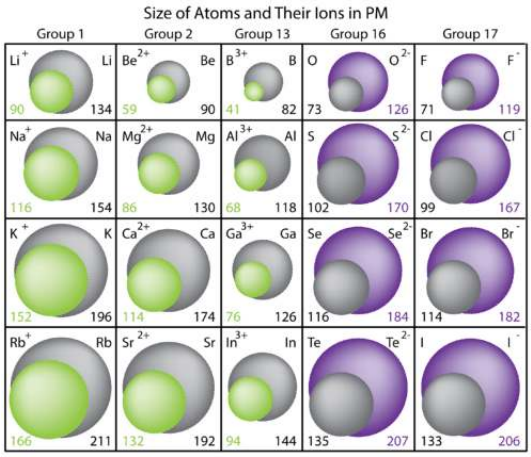
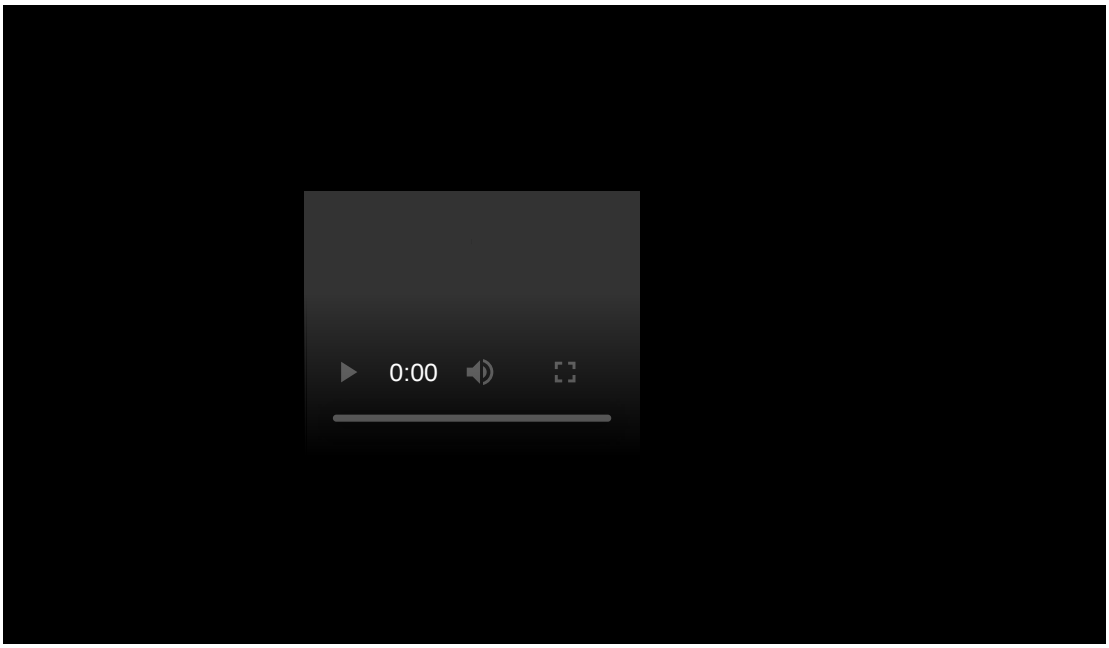


Figure 2.26.2: Comparison of ion sizes for Groups 1, 2, 13, 16, and 17. The atoms are shown in gray. Groups 1, 2, and 13 are metals and form cations, shown in green. Groups 16 and 17 are nonmetals and form anions, shown in purple. (CC BY-NC 3.0; Zachary Wilson via CK-12 Foundation)

The removal of electrons always results in a cation that is considerably smaller than the parent atom. When the valence electron(s) are removed, the resulting ion has one fewer occupied principal energy level, so the electron cloud that remains is smaller. Another reason is that the remaining electrons are drawn closer to the nucleus because the protons now outnumber the electrons. One other factor is the number of electrons removed. The potassium atom has one electron removed to form the corresponding ion, while calcium loses two electrons.

The addition of electrons always results in an anion that is larger than the parent atom. When the electrons outnumber the protons, the overall attractive force that the protons have for the electrons is decreased. The electron cloud also spreads out because more electrons results in greater electron-electron repulsion. Notice that the group 16 ions are larger than the group 17 ions. The group 16 elements each add two electrons, while the group 17 elements add one electron per atom, to form the anions.



Summary

- Ionic radius is determined by measuring the atom in a crystal lattice.
- Removal of electrons results in an ion that is smaller than the parent element.
- Addition of electrons results in an ion that is larger than the parent atom.

Review

1. How are ionic radii measured?
2. Explain why the radius of the rubidium ion is smaller than the radius of the rubidium atom.
3. Explain why the radius of the tellurium ion is larger than the radius of the tellurium atom.
4. Why is the oxygen anion larger than the fluoride anion?
5. Why is the sodium cation larger than the magnesium cation?

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2.27: Periodic Trends- Ionization Energy



Figure 2.27.1 (CC by 2.0; Nick Russill via Flickr, Northern Lights, Greenland [www.flickr.com])

The incredible green lights in this cold northern sky consist of charged particles known as ions. Their swirling pattern is caused by the pull of Earth's magnetic field. Called the northern lights, this phenomenon of nature shows that ions respond to a magnetic field. Do you know what ions are? Read on to find out.

Atoms Are Neutral

The northern lights aren't caused by atoms, because atoms are not charged particles. An atom always has the same number of electrons as protons. Electrons have an electric charge of -1 and protons have an electric charge of +1. Therefore, the charges of an atom's electrons and protons "cancel out." This explains why atoms are neutral in electric charge.

Q: What would happen to an atom's charge if it were to gain extra electrons?

A: If an atom were to gain extra electrons, it would have more electrons than protons. This would give it a negative charge, so it would no longer be neutral.

Atoms to Ions

Atoms cannot only gain extra electrons. They can also lose electrons. In either case, they become **ions**. Ions are atoms that have a positive or negative charge because they have unequal numbers of protons and electrons. If atoms lose electrons, they become positive ions, or cations. If atoms gain electrons, they become negative ions, or anions. Consider the example of fluorine (see figure below). A fluorine atom has nine protons and nine electrons, so it is electrically neutral. If a fluorine atom gains an electron, it becomes a fluoride ion with an electric charge of -1.

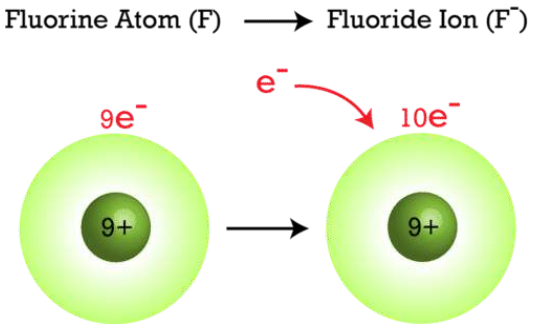


Figure 2.27.2 (CC BY-NC 3.0; Christopher AuYeung via CK-12 Foundation)

Names and Symbols

Like fluoride, other negative ions usually have names ending in *–ide*. Positive ions, on the other hand, are just given the element name followed by the word *ion*. For example, when a sodium atom loses an electron, it becomes a positive sodium ion. The charge of an ion is indicated by a plus (+) or minus sign (-), which is written to the right of and just above the ion's chemical symbol. For example, the fluoride ion is represented by the symbol F^-, and the sodium ion is represented by the symbol Na^+. If the charge is greater than one, a number is used to indicate it. For example, iron (Fe) may lose two electrons to form an ion with a charge of plus two. This ion would be represented by the symbol Fe^{2+}. This and some other common ions are listed with their symbols in the table below.

Table $PageIndex1$: Some Common Ions

Cations		Anions	
Name of Ion	Chemical Symbol	Name of Ion	Chemical Symbol
Calcium ion	Ca^{2+}	Chloride	Cl^-
Hydrogen ion	H^+	Fluoride	F^-
Iron(II) ion	Fe^{2+}	Bromide	Br^-
Iron(III) ion	Fe^{3+}	Oxide	O^{2-}

Q: How does the iron(III) ion differ from the iron(II) ion?

A: The iron(III) ion has a charge of +3, so it has one less electron than the iron(II) ion, which has a charge of +2.

Q: What is the charge of an oxide ion? How does its number of electrons compare to its number of protons?

A: An oxide ion has a charge of -2. It has two more electrons than protons.

How Ions Form

The process in which an atom becomes an ion is called ionization. It may occur when atoms are exposed to high levels of radiation. The radiation may give their outer electrons enough energy to escape from the attraction of the positive nucleus. However, most ions form when atoms transfer electrons to or from other atoms or molecules. For example, sodium atoms may transfer electrons to chlorine atoms. This forms positive sodium ions (Na^+) and negative chloride ions (Cl^-).



Q: Why do you think atoms lose electrons to, or gain electrons from, other atoms?

A: Atoms form ions by losing or gaining electrons because it makes them more stable and this state takes less energy to maintain. The most stable state for an atom is to have its outermost energy level filled with the maximum possible number of electrons. In the case of metals such as lithium, with just one electron in the outermost energy level, a more stable state can be achieved by losing that one outer electron. In the case of nonmetals such as fluorine, which has seven electrons in the outermost energy level, a more stable state can be achieved by gaining one electron and filling up the outer energy level.



Properties of Ions

Ions are highly reactive, especially as gases. They usually react with ions of opposite charge to form neutral compounds. For example, positive sodium ions and negative chloride ions react to form the neutral compound sodium chloride, commonly known as table salt. This occurs because oppositely charged ions attract each other. Ions with the same charge, on the other hand, repel each other. Ions are also deflected by a magnetic field, as you saw in the opening image of the northern lights.

Summary

- Atoms have equal numbers of positive protons and negative electrons, so they are neutral in electric charge.
- Atoms can gain or lose electrons and become ions, which are atoms that have a positive or negative charge because they have unequal numbers of protons and electrons.
- The process in which an atom becomes an ion is called ionization. It may occur when atoms are exposed to high levels of radiation or when atoms transfer electrons to or from other atoms.
- Ions are reactive, attracted or repulsed by other charged particles, and deflected by a magnetic field.

Review

1. Why are atoms neutral in electric charge?
2. Define ion.
3. Compare and contrast cations and anions, and give an example of each.
4. Describe how ions form.
5. List properties of ions.
6. The model in the illustration below represents an atom of lithium (Li). If the lithium atom becomes an ion, which type of ion will it be, a cation or an anion? What will be the electric charge of this ion? What will the ion be named? What symbol will be used to represent it?

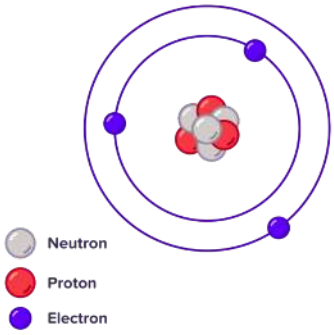


Figure 2.27.3 (CC BY-NC 3.0; CK-12 Foundation Employee via CK-12 Foundation)

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2.28: Periodic Trends- Electronegativity



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Is it easy or hard for you to make new friends?

Have you ever noticed how some people attract others to them? Whether it be their personality, attractiveness, or athletic skills—something pulls people toward them; while others have a smaller group of friends and acquaintances. Atoms do the same thing. One atom may pull electrons strongly to it, while a second type of atom has much less "pulling power".

Electronegativity

Valence electrons of both atoms are always involved when those two atoms come together to form a chemical bond. Chemical bonds are the basis for how elements combine with one another to form compounds. When these chemical bonds form, atoms of some elements have a greater ability to attract the valence electrons involved in the bond than other elements.

Electronegativity is a measure of the ability of an atom to attract the electrons when the atom is part of a compound. Electronegativity differs from electron affinity because electron affinity is the actual energy released when an atom gains an electron. Electronegativity is not measured in energy units, but instead a relative scale. All elements are compared to one another, with the most electronegative element, fluorine, being assigned an electronegativity value of 3.98. Fluorine attracts electrons better than any other element. The table below shows the electronegativity values for the elements.

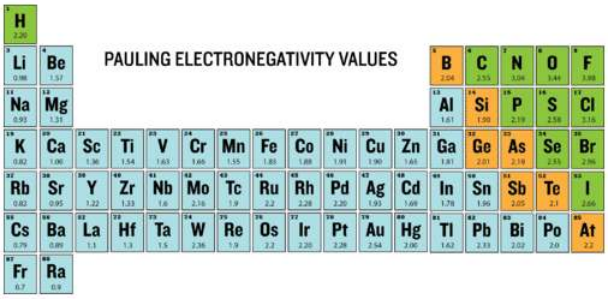


Figure 2.28.2: The electronegativity scale was developed by Nobel Prize winning American chemist Linus Pauling. The largest electronegativity (3.98) is assigned to fluorine and all other electronegativity measurements are on a relative scale. (CC BY-NC 3.0; Christopher Auyeung via CK-12 Foundation)

Since metals have few valence electrons, they tend to increase their stability by losing electrons to become cations. Consequently, the electronegativities of metals are generally low. Nonmetals have more valence electrons and increase their stability by gaining electrons to become anions. The electronegativities of nonmetals are generally high.

Trends

Electronegativities generally increase from left to right across a period. This is due to an increase in nuclear charge. Alkali metals have the lowest electronegativities, while halogens have the highest. Because most noble gases do not form compounds, they do not have electronegativities. Note that there is little variation among the transition metals. Electronegativities generally decrease from top to bottom within a group, due to the larger atomic size.

Of the main group elements, fluorine has the highest electronegativity (EN $= 4.0$) and cesium the lowest (EN $= 0.79$). This indicates that fluorine has a high tendency to gain electrons from other elements with lower electronegativities. We can use these values to predict what happens when certain elements combine.

When the difference between atom electronegativities is greater than ~1.7, then a complete exchange of electrons occurs. Typically this exchange is between a metal and a nonmetal. For instance, sodium and chlorine will typically combine to form a new

compound and each ion becomes isoelectronic with its nearest noble gas. When we compare the EN values, we see that the electronegativity for Na is 0.93 and the value for Cl is 3.2. The absolute difference between ENs is $|0.93 - 3.2| = 2.27$. This value is greater than 1.7, and therefore indicates the occurence of a complete electron exchange.

Summary

- Electronegativity is a measure of the ability of an atom to attract the electrons when the atom is part of a compound.
- Electronegativity values generally increase from left to right across the periodic table.
- Electronegativities generally decrease from the top to bottom of a group.
- The highest electronegativity value is for fluorine.

Review

1. Define “electronegativity.”
2. How does electronegativity differ from electron affinity?
3. Why are the electronegativity values of metals generally low?
4. Describe the trend in electronegativities across the periodic table.
5. Describe the trends in electronegativities in a group of the periodic table.

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CHAPTER OVERVIEW

3: Chemical Compounds

3.1: Molecular Formula
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3.3: Anions
3.4: Formulas for Binary Ionic Compounds
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3.7: Stock System Naming
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3.9: Names and Formulas of Ternary Ionic Compounds

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3.1: Molecular Formula



Figure 3.1.1 (Public Domain; J. S. Bach via Commons Wikimedia, Bach cello harmony [commons.wikimedia.org])

Why are music notes a unique "language"?

There are many "universal languages" in the world. Musicians of every culture recognize music embodied in a series of notes on a staff.

This passage from a Bach cello suite could be played by any trained musician from any country, because there is an agreement as to what the symbols on the page mean. In the same way, molecules are represented using symbols that all chemists agree upon.

Molecular Formula

A **molecule** is comprised of two or more atoms that have been chemically combined. A **molecular formula** is a chemical formula of a molecular compound that shows the kinds and numbers of atoms present in a molecule of the compound. Ammonia is a compound of nitrogen and hydrogen as shown below:

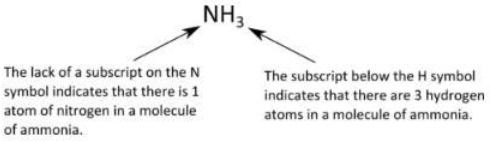


Figure 3.1.2: The molecular formula for ammonia. (CC BY-NC 3.0; Joy Sheng via CK-12 Foundation)

Note from the example that there are some standard rules to follow in writing molecular formulas. The arrangements of the elements depend on the particular structure, so we will not concern ourselves with that point right now. The number of atoms of each kind is indicated by a subscript following the atom. If there is only one atom, no number is written. If there is more than one atom of a specific kind, the number is written as a subscript following the atom. We would not write N_3H for ammonia, because that would mean that there are three nitrogen atoms and one hydrogen atom in the molecule, which is incorrect.

The molecular formula does not tell us anything about the shape of the molecule or where the different atoms are. The molecular formula for sucrose (table sugar) is $C_{12}H_{22}O_{11}$. This simply tells us the number of carbon, hydrogen, and oxygen atoms in the molecule. There is nothing said about where the individual atoms are located. We need a much more complicated formula (shown below) to communicate that information.

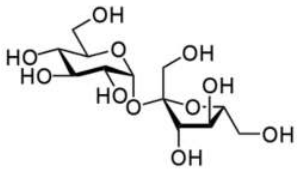


Figure 3.1.3: The molecular structure of sucrose, $C_{12}H_{22}O_{11}$. (Public Domain; User:Calvero/Wikimedia Commons via Commons Wikimedia, Sucrose [commons.wikimedia.org])



Summary

- A molecular formula tells us which atoms and how many of each type of atom are present in a molecule.
- If only one atom of a specific type is present, no subscript is used.
- For atoms that have two or more of a specific type of atom present, a subscript is written after the symbol for that atom.
- Molecular formulas do not indicate how the atoms are arranged in a molecule.

Review

1. What does a molecular formula tell us?
2. What does a molecular formula not tell us?
3. What do the subscripts mean in a molecular formula?
4. If you wrote $C_6H_{11}O_5C_6H_{11}O_6$ as the molecular formula for sucrose, would that be correct? Explain your answer.
5. Sometimes the formula for acetic acid is written CH_3COOH. Is this a true molecular formula?

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3.2: Cations



Figure 3.2.1 (Public Domain; User:Gold Guru/Wikipedia via Wikipedia)

Have you ever gone digging for gold?

When the prospectors during the California Gold Rush (1848-1855) searched for gold nuggets in the earth, they were able to find the nuggets because gold is an unreactive material that exists in its elemental state in many places. Not everyone was fortunate enough to find significantly large gold nuggets, but a number of miners did become very wealthy (of course, a large number of others went back home broke).

Many of the elements we know about do not exist in their native form. They are so reactive that they are found only in compounds. These non-elemental forms are known as ions. Their properties are very different from those of the elements they come from. The term comes from a Greek word meaning "move" and was first coined by Michael Faraday, who studied the movement of materials in an electrical field.

Cations

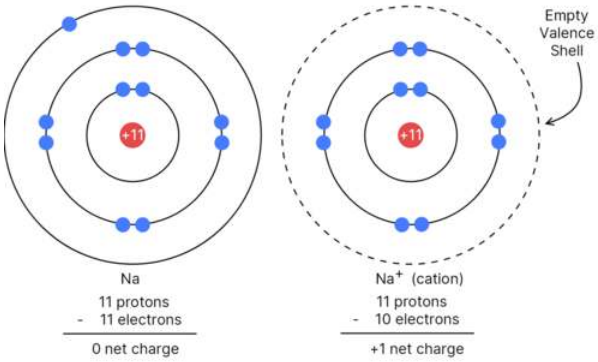


Figure 3.2.2: Sodium loses an electron to become a cation. (CK-12 Curriculum Materials License; CK-12 Foundation via CK-12 Foundation)

Some elements lose one or more electrons in forming ions. These ions are known as "**cations**" because they are positively charged and migrate toward the negative electrode (**cathode**) in an electrical field. Looking at the periodic table below, we know that the group 1 elements are all characterized by having one s electron in the outer orbit; group 2 elements have two s electrons in the outer orbit. These electrons are loosely attached to the atom and can easily be removed, leaving more protons in the atom than there are electrons, so that the resulting ion has a positive charge. Cations can also be formed from electron loss to many of the transition elements.

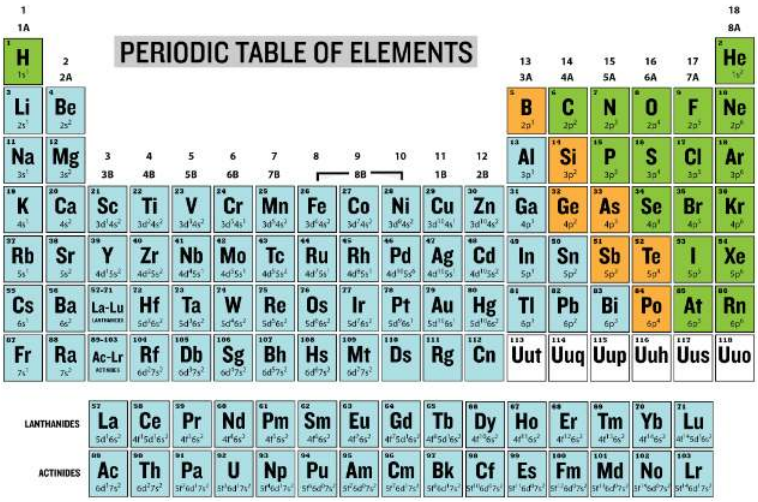
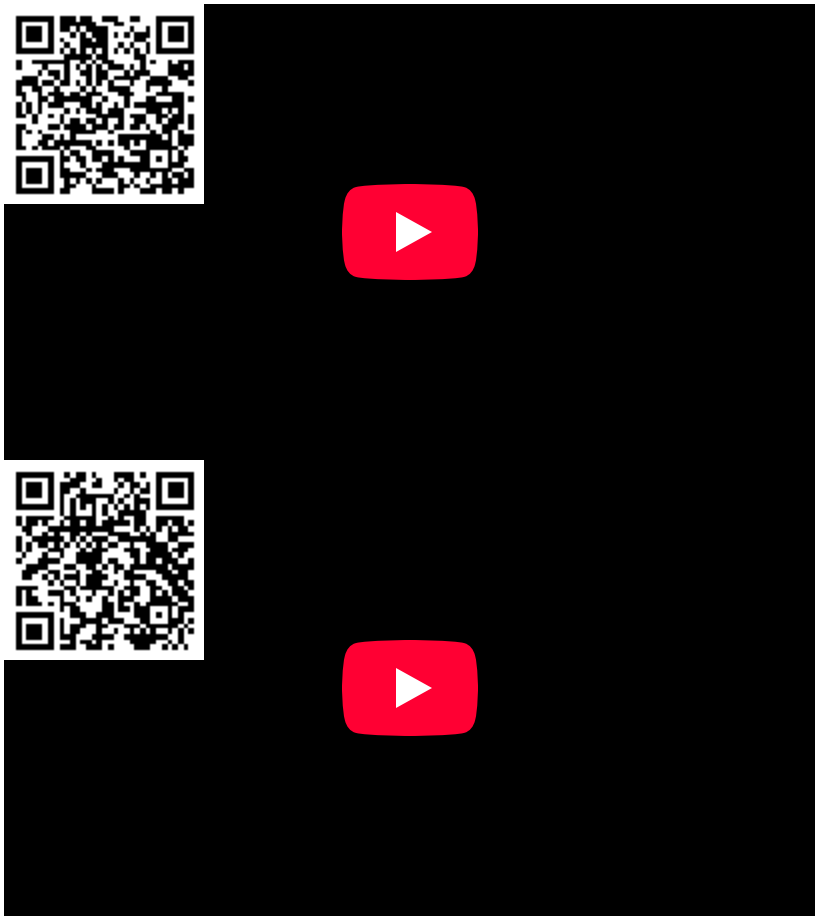


Figure 3.2.3: Periodic Table of Elements, notated with group numbers. (CC BY-NC 3.0; Christopher Auyeung via CK-12)

The cations are designated by the symbol for the parent element and a plus charge as a superscript after the element symbol—the potassium cation would be indicated as K^{+}. Note that the charge is placed after the symbol and not before it. The potassium ion is **monovalent**, meaning that it has lost one electron and has a $+1$ charge. The symbol for the magnesium cation would be Mg^{2+} or Mg^{++} to indicate that it has lost two electrons and has a $+2$ charge, so the magnesium cation would be referred to as a **divalent** cation.

The cations are simply named as the parent element. The sodium cation is still called "sodium". Often, the charge would be attached for clarity, so the sodium cation might be referred to as "sodium one plus".



Applications of Cations

Cations play important roles in our daily lives. Sodium, potassium, and magnesium ions are essential for such processes as blood pressure regulation and muscle contraction. Calcium ions are an important part of bone structure. Sodium ions can be used in water softeners to remove other harmful elements. We put sodium chloride (table salt) on our food and use it as a preservative.

Summary

- Cations are formed by the loss of one or two electrons from an element.
- Groups 1 and 2 elements form cations.
- Cations are named according to the parent element.
- Cation charges are indicated with a superscript following the chemical symbol.

Review

1. What is a cation?
2. Write the symbol for the barium cation.
3. Write the symbol for the cesium cation.
4. List three ways cations are useful.

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3.3: Anions



Figure 3.3.1 (Public Domain; Shane Anderson/NOAA via Commons Wikimedia, Kelp 300 [commons.wikimedia.org])

What does the amount of salt in seaweed tell us?

Before iodized salt was developed, some people experienced a number of developmental difficulties, including problems with thyroid gland function and intellectual disabilities. In the 1920s, we learned that these conditions could usually be treated easily with the addition of iodide anion to the diet. One easy way to increase iodide intake was to add the anion to table salt. This simple step greatly enhanced health and development. Large amounts of iodide ion are also found in seaweed such as kelp (see picture above) and saltwater fish.

When a metal loses an electron, energy is needed to remove that electron. The other part of this process involves the addition of the electron to another element. The electron adds to the outer shell of the new element. Just as the loss of the electron from the metal produces a full shell, when the electron or electrons are added to the new element, it also results in a full shell.

Anions

Anions are negative ions that are formed when a **nonmetal** atom gains one or more electrons. Anions are so named because they are attracted to the **anode** (positive field) in an electrical field. Atoms typically gain electrons so that they will have the electron configuration of a noble gas. All the elements in Group 17 have seven valence electrons due to the outer $ns^2\ np^5$ configuration. Therefore, each of these elements would gain one electron and become an anion with a -1 charge. Likewise, Group 16 elements form ions with a -2 charge, and the Group 15 nonmetals form ions with a -3 charge.

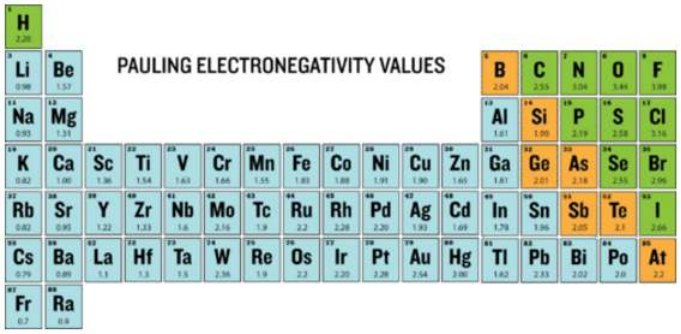


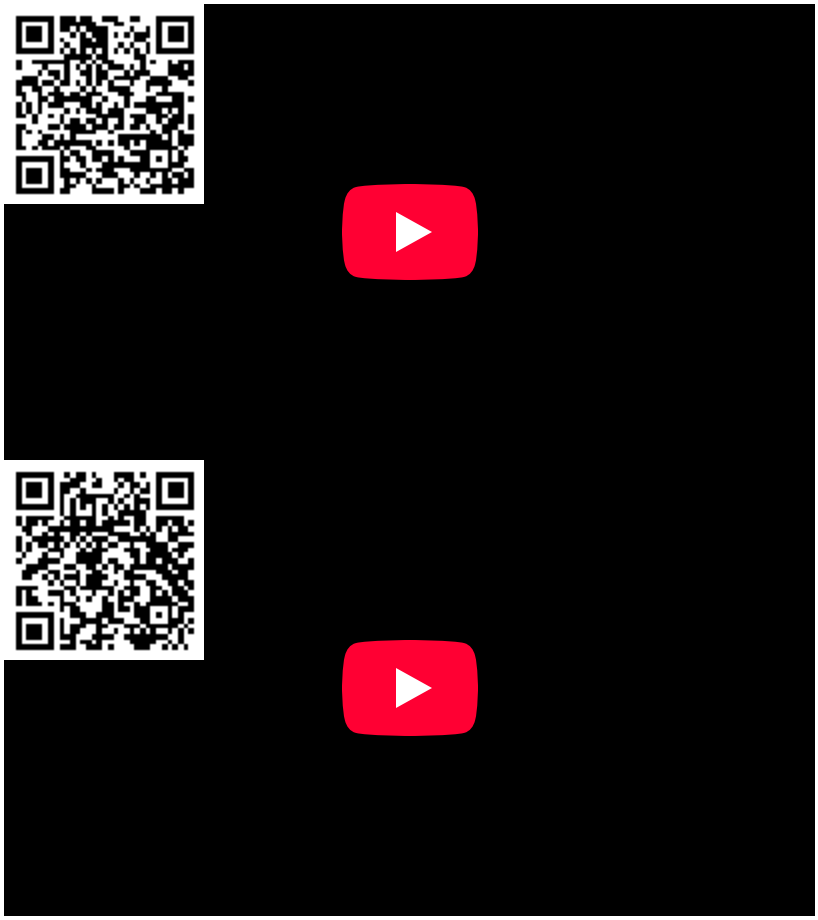
Figure 3.3.2 (CC BY-NC 3.0; Christopher Auyeung via CK-12 Foundation)

Naming anions is slightly different than naming cations. The ending of the element's name is dropped and replaced with the *-ide* suffix. For example, F^- is the fluoride ion, while O^{2-} is the oxide ion. As is the case with cations, the charge on the anion is indicated by a superscript following the symbol. Common anions are listed in the table below:

Table 3.3.1

Anion Name	Symbol and Charge
fluoride	F^-
chloride	Cl^-
bromide	Br^-

Anion Name	Symbol and Charge
iodide	I^-
oxide	O^{2-}
sulfide	S^{2-}
nitride	N^{3-}



Uses for Anions

Fluoride ion is widely used in water supplies to help prevent tooth decay. Chloride is an important component in ion balance in blood. Iodide ion is needed by the thyroid gland to make the hormone thyroxine.

Summary

- Anions are formed by the addition of one or more electrons to the outer shell of an atom.
- Group 17 elements add one electron to the outer shell, group 16 elements add two electrons, and group 15 elements add three electrons.
- Anions are named by dropping the ending of the element's name and adding *-ide*.

Review

1. What is an anion?
2. How are anions formed?
3. Why do anions form?
4. How are anions named?
5. List three examples of anions with names, charges, and chemical symbols.

6. List three ways anions are used.

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3.4: Formulas for Binary Ionic Compounds

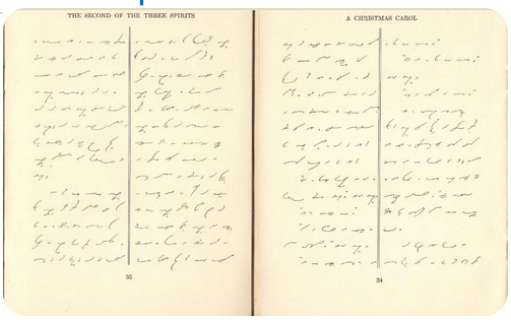


Figure 3.4.1 (Public Domain; Winifred Kenna via Commons Wikimedia, Gregg shorthand A Christmas Carol [commons.wikimedia.org])

How does shorthand work?

Shorthand was a very popular way of recording speech, especially in dictating letters and in court testimony. Instead of trying to write out all the words, the person taking the dictation would use a set of symbols that represented syllables or words. The pages above show a shorthand version of "A Christmas Carol" written by Charles Dickens. Unless you know shorthand, the passage is meaningless. But knowing shorthand allows you to read this classic story. Different professions also use a type of shorthand in communication to save time. Chemists use chemical symbols in combination to indicate specific compounds. There are two advantages to this approach:

1. The compound under discussion is clearly described so that there can be no confusion about its identity.
2. Chemical symbols represent a universal language that all chemists can understand, no matter what their native language is.

Writing Formulas for Binary Ionic Compounds

If you know the name of a binary ionic compound, you can write its **chemical formula**. Start by writing the metal ion with its charge, followed by the nonmetal ion with its charge. Because the overall compound must be electrically neutral, decide how many of each ion is needed in order for the positive and negative charge to cancel each other out. Consider the compound aluminum nitride. The ions are:

$$\mathrm{Al}^{3+} \quad \mathrm{N}^{3-}$$

Since the ions have charges that are equal in magnitude, one of each will be the lowest ratio of ions in the formula. The formula for aluminum nitride is AlN.

The ions for the compound lithium oxide are:

$$\mathrm{Li}^{+} \quad \mathrm{O}^{2-}$$

In this case, two lithium ions are required to balance out the charge of one oxide ion. The formula of lithium oxide is $\mathrm{Li_2O}$.

An alternative way to write a correct formula for an ionic compound is to use the crisscross method. In this method, the numerical value of each of the ion charges is crossed over to become the subscript of the other ion. Signs of the charges are dropped. Shown below is the crisscross method for aluminum oxide.



Figure 3.4.2 (CC BY-NC 3.0; Joy Sheng via CK-12 Foundation)

The red arrows indicate that the 3 from the $3+$ charge will cross over to become the subscript of the O. The 2 from the $2-$ charge will cross over to become the subscript of the Al. The formula for aluminum oxide is $\mathrm{Al_2O_3}$.

Be aware that ionic compounds are empirical formulas and so must be written as the lowest ratio of the ions. In the case of aluminum nitride, the crisscross method would yield a formula of $\mathrm{Al_3N_3}$, which is not correct. It must be reduced to AlN. Following the crisscross method to write the formula for lead (IV) oxide would involve the following steps:

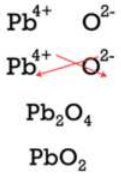
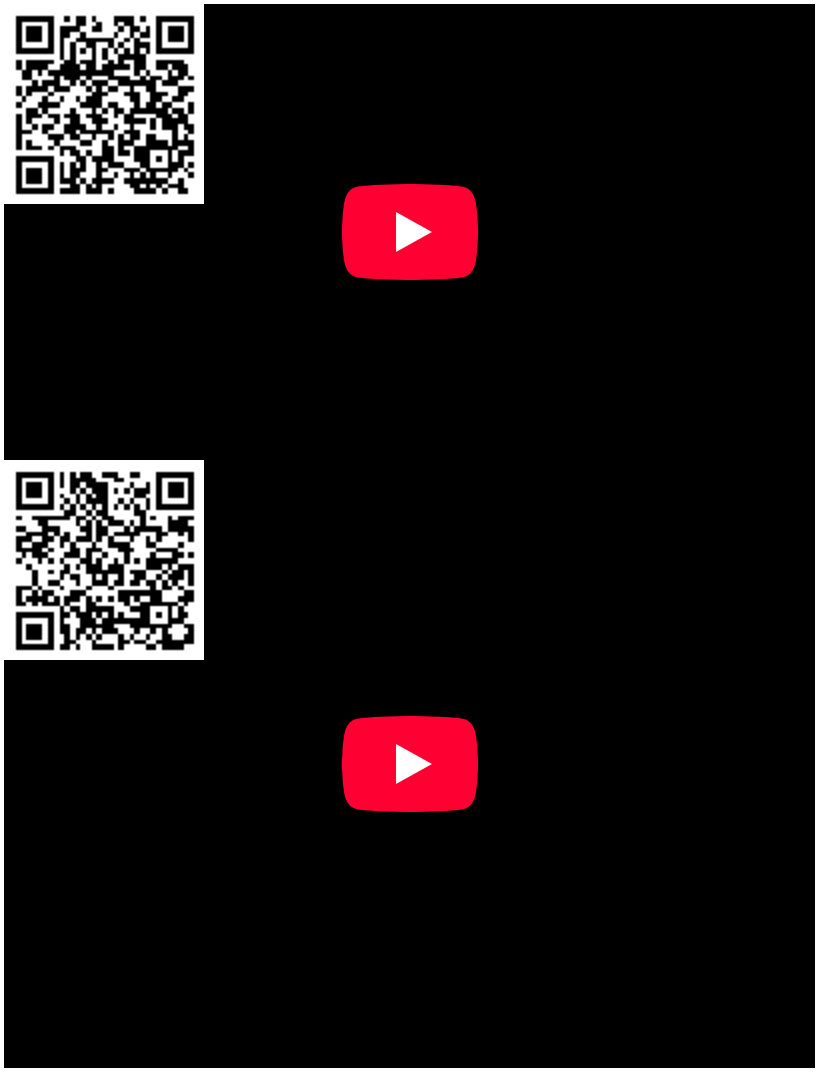


Figure 3.4.3 (CC BY-NC 3.0; Joy Sheng via CK-12 Foundation)

The crisscross first yields Pb_2O_4 for the formula, but that must be reduced to the lower ratio, and PbO_2 is the correct formula.



Summary

- Formulas for binary compounds begin with the metal followed by the nonmetal.
- Positive and negative charges must cancel each other out.
- Ionic compound formulas are written using the lowest ratio of ions.

Review

1. Write formulas for the binary ionic compounds formed between the following pairs of elements:
    a. cesium and fluorine
    b. calcium and sulfur
    c. aluminum and chlorine
    d. zinc and nitrogen

2. Write the formula and give the name for the compound formed by the following ions:
    a. Fe^{3+} and O^{2-}
    b. Ni^{2+} and S^{2-}
    c. Au^{+} and Cl^{-}
    d. Sn^{4+} and I^{-}
3. Give names for the following compounds:
    a. Ag_2S
    b. PdO
    c. $PtCl_4$
    d. V_2O_5

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3.5: Naming Binary Molecular Compounds



Figure 3.5.1 (Public Domain; Anonymous via Wikipedia)

Why do so many relatives in royalty share the same name?

Some families name a son (usually the first born) after his father. So, it is somewhat common to meet a John Smith, Jr. named after John Smith the father. Certain families may name a grandson John Smith III. Countries with long histories of royalty take the naming even further. One line of kings named Henry goes up to Henry the Eighth (not the nicest guy in the world—he had six wives and two of them met untimely ends). The use of numbering for names adds clarity to a system—it's easily discernible which Henry is being spoken of.

Inorganic chemical compounds can be broadly classified into two groups: ionic compounds and molecular compounds. The structure of all ionic compounds is an extended three-dimensional array of alternating positive and negative ions. Since ionic compounds do not take the form of individual molecules, they are represented by empirical formulas. Now we will begin to examine the formulas and nomenclature of molecular compounds.

Molecular Compounds

Molecular compounds are inorganic compounds that take the form of discrete **molecules**. Examples include such familiar substances as water (H_2O) and carbon dioxide (CO_2). These compounds are very different from ionic compounds like sodium chloride $(NaCl)$. Ionic compounds are formed when metal atoms lose one or more of their electrons to nonmetal atoms. The resulting cations and anions are electrostatically attracted to each other.

So what holds the atoms of a molecule together? Rather than forming ions, the atoms of a molecule share their **valence electrons** in such a way that a **bond** forms between pairs of atoms. In a carbon dioxide molecule, there are two of these bonds, each occurring between the carbon atom and one of the two oxygen atoms.

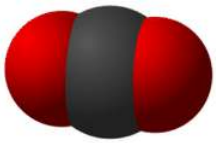


Figure 3.5.2: Carbon dioxide molecules consist of a central carbon atom bonded to two oxygen atoms. (Public Domain; Ben Mills (Wikimedia: Benjah-bmm27) via Wikipedia)

Larger molecules can have many, many bonds that serve to keep the molecule together. In a large sample of a given molecular compound, all of the individual molecules are identical.

Naming Binary Molecular Compounds

Recall that a molecular formula shows the number of atoms of each element that a molecule contains. A molecule of water contains two hydrogen atoms and one oxygen atom, so its formula is H_2O. A molecule of octane, which is a component of gasoline, contains 8 atoms of carbon and 18 atoms of hydrogen. The molecular formula of octane is C_8H_{18}.



Figure 3.5.3: Nitrogen dioxide (NO_2) is a reddish-brown toxic gas that is a prominent air pollutant produced by internal combustion engines. (Public Domain; User:Greenhorn1/Wikimedia Commons via Wikipedia)

A binary molecular compound is a molecular compound that is composed of two elements. The elements that combine to form binary molecular compounds are both nonmetal atoms. This contrasts with ionic compounds, which are formed from a metal ion and a nonmetal ion. Therefore, binary molecular compounds are different because ionic charges cannot be used to name them or to write their formulas. Another difference is that two nonmetal atoms will frequently combine with one another in a variety of ratios. Consider the elements nitrogen and oxygen. They combine to make several compounds including NO, NO_2, and N_2O. They cannot all be called nitrogen oxide. How would someone know which one you were talking about? Each of the three compounds has very different properties and reactivities. A system to distinguish between compounds such as these is necessary.

Prefixes are used in the names of binary molecular compounds to identify the number of atoms of each element. The table below shows the prefixes up to ten.

Table 3.5.1: Numerical Prefixes

Number of Atoms	Prefix
1	*mono-*
2	*di-*
3	*tri-*
4	*tetra-*
5	*penta-*
6	*hexa-*
7	*hepta-*
8	*octa-*
9	*nona-*
10	*deca-*

The rules for using the prefix system of nomenclature of binary compounds can be summarized as follows:

1. Generally, the less electronegative element is written first in the formula, though there are a few exceptions. Carbon is always first in a formula and hydrogen is after nitrogen in a formula such as NH_3. The order of common nonmetals in binary compound formulas is C, P, N, H, S, I, Br, Cl, O, F.
2. When naming, the appropriate prefix is used only if there are more than one atom of that element in the formula.
3. The second element is named after the first, but with the ending of the element's name changed to *-ide*. The appropriate prefix is always used for the second element.
4. The *a* or *o* at the end of a prefix is usually dropped from the name when the name of the element begins with a vowel. As an example, four oxygen atoms are tetroxide instead of tetraoxide.

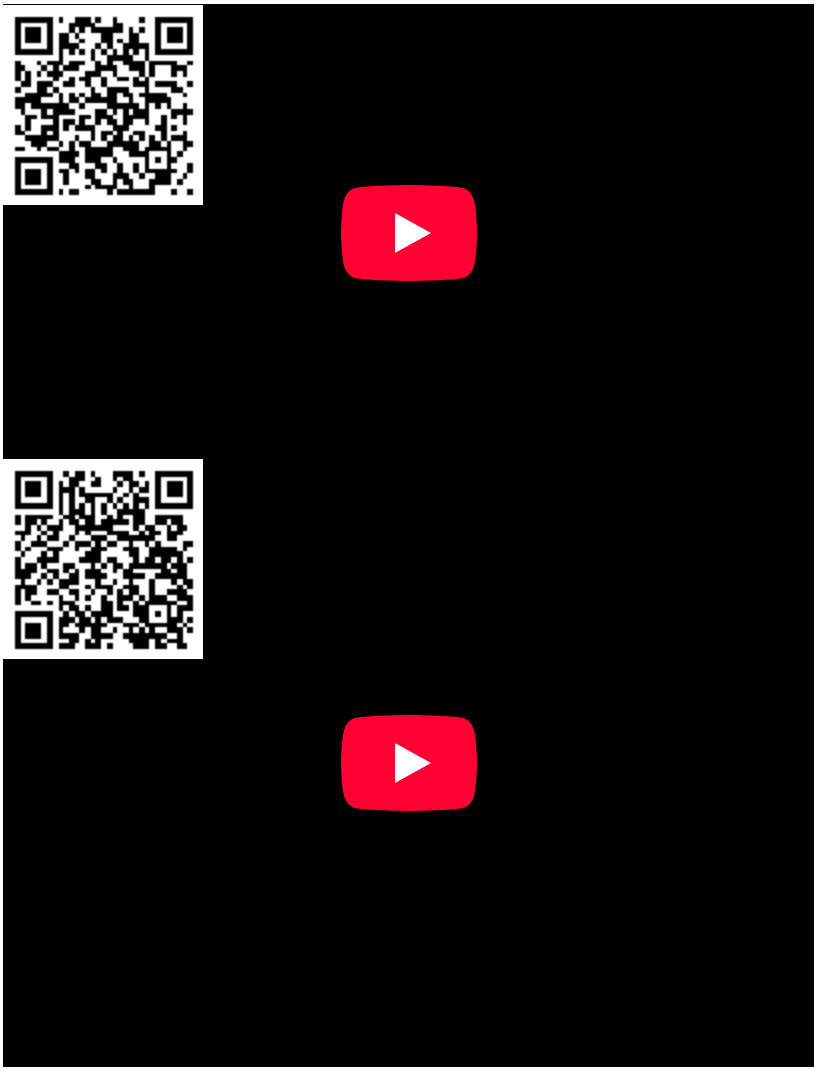
Some examples of molecular compounds are listed in Table 3.5.2.

Table 3.5.2

Formula	Name
NO	nitrogen monoxide

Formula	Name
N_2O	dinitrogen monoxide
S_2Cl_2	disulfur dichloride
Cl_2O_7	dichlorine heptoxide

Notice that the *mono-* prefix is not used with the nitrogen in the first compound, but is used with the oxygen in both of the first two examples. The S_2Cl_2 emphasizes that the formulas for molecular compounds are not reduced to their lowest ratios. The *o* of the *mono-* and the *a* of *hepta-* are dropped from the name when paired with oxide.



Summary

- Molecular compounds are inorganic compounds that take the form of discrete molecules.
- The atoms of these compounds are held together by covalent bonds.
- Prefixes are used to indicate the number of atoms of an element that are in the compound.

Review

1. What are molecular compounds?
2. How do they differ from ionic compounds?
3. What holds the atoms of a molecule together?
4. Are the elements of molecular compounds metals or non-metals?

5. What is the prefix for the number of atoms of an element when there are four atoms of that element in the compound?
6. What is the prefix for the number of atoms of an element when there are 7 atoms of that element in the compound?
7. Name the following compounds:
    a. ClF_3
    b. As_2O_5
    c. B_4H_{10}

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3.6: Transition Metal Ions



Figure 3.6.1 (Public Domain; the US Mint via Commons Wikimedia, Platinium eagle 101 [commons.wikimedia.org])

What kind of coin is this?

Most of us are familiar with the common coins: penny, nickel, dime, quarter. In some areas (such as Las Vegas), you might see large amounts of silver dollars (these get a little heavy in your pocket). But most of us have probably never seen a platinum eagle—an eagle-depicting coin that is held primarily by collectors. If you were to take a one-ounce platinum eagle into a store to buy one hundred dollars worth of items, the store owner will most likely not believe you when you claim that the coin is worth one hundred dollars. It would also be awkward and annoying if you lost one of these coins out of your pocket. Platinum is just one of several transition metals that is worth a lot of money (gold is another one).

The group 1 and 2 elements form cations through a simple process that involves the loss of one or more outer shell electrons. These electrons come from the s orbital and are removed very readily.

Transition Metal Ions

Most **transition metals** differ from the metals of Groups 1, 2, and 13 in that they are capable of forming more than one cation with different ionic charges. As an example, iron commonly forms two different ions. It can sometimes lose two electrons to form the Fe^{2+} ion, while at other times it loses three electrons to form the Fe^{3+} ion. Tin and lead, though members of the p block rather than the ***d* block**, also are capable of forming multiple ions.

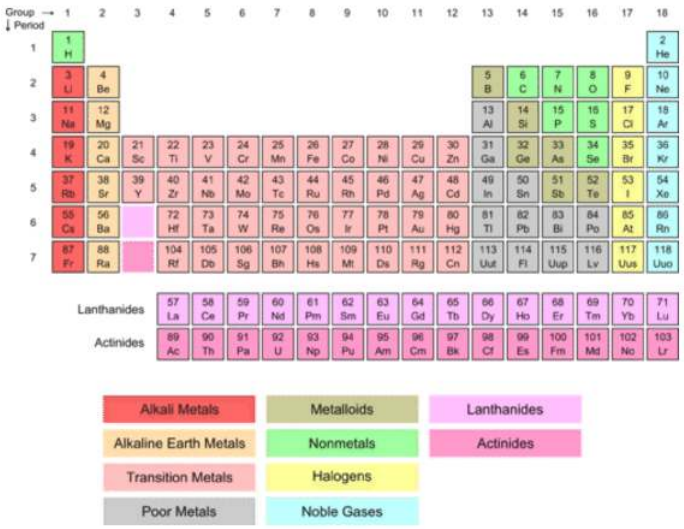


Figure 3.6.2: (Public Domain; Cepheus, modified by CK-12 Foundation via Commons Wikimedia, Periodic Table [commons.wikimedia.org])

Ionic formation for transition metals is complicated by the fact that these elements have unfilled inner d shells. Although the next higher s orbitals are actually at a lower energy level than the d level, these s electrons are the ones that are removed during ionization.

The table below lists the names and formulas of some of the common transition metal ions:

Common Transition Metal Ions

Table 3.6.1 : Common Transition Metal Ions

1+	2+	3+	4+
copper (I), Cu^{+}	cadmium, Cd^{2+}	chromium (III), Cr^{3+}	lead (IV), Pb^{4+}
gold (I), Au^{+}	chromium (II), Cr^{2+}	cobalt (III), Co^{3+}	tin (IV), Sn^{4+}
mercury (I), Hg_2^{2+}	cobalt (II), Co^{2+}	gold (III), Au^{3+}	
silver, Ag^{+}	copper (II), Cu^{2+}	iron (III), Fe^{3+}	
	iron (II), Fe^{2+}		
	lead (II), Pb^{2+}		
	manganese (II), Mn^{2+}		
	mercury (II), Hg^{2+}		
	nickel (II), Ni^{2+}		
	platinum (II), Pt^{2+}		
	tin (II), Sn^{2+}		
	zinc, Zn^{2+}		



Uses for Transition Metals

Because there are so many metals in this group, there are a wide variety of uses. Many of the metals are used in electronics, while others (such as gold and silver) are used in monetary systems. Iron is a versatile structural material. Cobalt, nickel, platinum, and other metals are employed as catalysts in a number of chemical reactions. Zinc is a significant component of batteries.

Summary

- Transition metals have unfilled inner d electron shells.
- Ions form primarily through loss of s electrons.
- Many transition metals can form more than one ion.
- Transition metals have a wide variety of applications.

Review

1. What is unique about the electron configurations of transition metals?
2. Which electrons of transition metal elements are most likely to be lost during ion formation?
3. How many ions can iron form?
4. Which transition metal forms only one ion?
5. List several uses for transition metals.

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3.7: Stock System Naming



Figure 3.7.1 (Public Domain; XAVeRY via Wikipedia)

How is an mp3 player designed?

In describing many technological items, it's not enough to simply say what brand or model we have. We talk about details such as how much horsepower is “under the hood” for a car or how fast the chip is for our computer. Even a simple device like an mp3 player has more than one size. We can get an 8 MB player, or a 16 MB player. Designation of the item often is incomplete without other information as to its capabilities.

Transition metals have more than one possibility for ion formation. In order to name these compounds correctly, we need to be able to indicate which ion is involved in any given compound.

Naming Compounds Using the Stock System

Naming compounds that involve transition metal cations necessitates use of the **Stock system**. Consider the binary ionic compound $\mathrm{FeCl_3}$. To simply name this compound "iron chloride" would be incomplete, because iron is capable of forming two ions with different charges. The name of any iron-containing compound must reflect which iron ion is in the compound. In this case, the subscript in the formula indicates that there are three chloride ions, each with a $1-$ charge. Therefore, the charge of the single iron ion must be $3+$. The correct name of $\mathrm{FeCl_3}$ is iron (III) chloride, with the cation charge written as the Roman numeral. Here are several other examples:

Table 3.7.1

Formula	Name
$\mathrm{Cu_2O}$	copper (I) oxide
CuO	copper (II) oxide
$\mathrm{SnO_2}$	tin (IV) oxide

The first two examples are both oxides of copper (shown in the figure below). The ratio of copper ions to oxide ions determines the name. Since the oxide ion is $\mathrm{O^{2-}}$, the charges of the copper ion must be $1+$ in the first formula and $2+$ in the second formula. In the third formula, there is one tin ion for every two oxide ions. This means that the tin must carry a $4+$ charge, making the name tin (IV) oxide.



Figure 3.7.2: Copper (I) oxide, a red solid, and copper (II) oxide, a black solid, are different compounds because of the charge of the copper ion. (Public Domain; Ondřej Mangl via Copper(I) oxide: http://commons.wikimedia.org/wiki/File:Cu2O.png; Copper(II) oxide: http://commons.wikimedia.org/wiki/File:Oxid_m%25C4%259B%25C4%258Fnat%25C3%25BD.PNG)



Summary

- The Stock system allows for the specification of transition metal ionic charge when naming ionic compounds.
- Roman numerals are used to indicate the amount of positive charge on the cation.

Review

1. What is the Stock system?
2. For which group of metal ions would we use the Stock system?
3. What does the Roman numeral stand for?
4. Assign a Roman numeral to each of the following cations:
   a. Sn^{4+}
   b. Fe^{3+}
   c. Co^{2+}
   d. Pb^{4+}

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3.8: Polyatomic Ions



Figure 3.8.1 (Public Domain; Huhu via Wikipedia)

Have you ever read the story of Romeo and Juliet?

Shakespeare wrote, "A rose by any other name would smell as sweet" as part of the romantic balcony scene between Romeo and Juliet in the famous play. The two families were bitter rivals, but Juliet meant this statement to mean that she loved Romeo no matter what his name was. Some names are simple—we know Romeo mainly as Romeo. Most of us have a first name, middle name (often not used), and last name. In some cultures, names will be much more complex. The full name of the famous 20th century artist Pablo Picasso is Pablo Diego José Francisco de Paula Juan Neponuceno María de los Remedios Cipriano de la Santísima Trinidad Martyr Patricio Clito Ruíz y Picasso.

Many materials exist as simply binary compounds composed of a metal cation and a nonmetal anion, with each ion consisting of only one type of atom. Other combinations of atoms also exist, either as larger ionic complexes or complete molecules. Some of the most useful materials we work with contain polyatomic ions.

Polyatomic Ions

A **polyatomic** ion is an ion composed of more than one atom. The ammonium ion consists of one nitrogen atom and four hydrogen atoms. Together, they comprise a single ion with a $1+$ charge and a formula of NH_4^+. The carbonate ion consists of one carbon atom and three oxygen atoms, and carries an overall charge of $2-$. The formula of the carbonate ion is CO_3^{2-}. The atoms of a polyatomic ion are tightly bonded together, and so the entire ion behaves as a single unit. The figures below show several models.

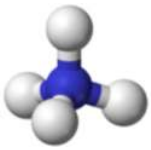


Figure 3.8.2: The ammonium ion $\left(\text{NH}_4^+\right)$ is a nitrogen atom (blue) bonded to four hydrogen atoms (white). (Public Domain; Ben Mills (Wikimedia: Benjah-bmm27) via Wikipedia)



Figure 3.8.3: The hydroxide ion $\left(\text{OH}^-\right)$ is an oxygen atom (red) bonded to a hydrogen atom. (Public Domain; Ben Mills (Wikimedia: Benjah-bmm27) via Wikipedia)

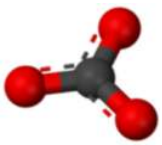


Figure 3.8.4: The carbonate ion $\left(\text{CO}_3^{2-}\right)$ is a carbon atom (black) bonded to three oxygen atoms. (Public Domain; Ben Mills (Wikimedia: Benjah-bmm27) via Wikipedia)

The table below lists a number of polyatomic ions by name and by formula. The heading for each column indicates the charge on the polyatomic ions in that group. Note that the vast majority of the ions listed are anions—there are very few polyatomic cations.

Table 3.8.1: Common Polyatomic Ions

1−	2−	3−	1+	2+
acetate, CH_3COO^-	carbonate, CO_3^{2-}	arsenate, AsO_3^{3-}	ammonium, NH_4^+	dimercury, Hg_2^{2+}
bromate, BrO_3^-	chromate, CrO_4^{2-}	phosphite, PO_3^{3-}		
chlorate, ClO_3^-	dichromate, $Cr_2O_7^{2-}$	phosphate, PO_4^{3-}		
chlorite, ClO_2^-	hydrogen phosphate, HPO_4^{2-}			
cyanide, CN^-	oxalate, $C_2O_4^{2-}$			
dihydrogen phosphate, $H_2PO_4^-$	peroxide, O_2^{2-}			
hydrogen carbonate, HCO_3^-	silicate, SiO_3^{2-}			
hydrogen sulfate, HSO_4^-	sulfate, SO_4^{2-}			
hydrogen sulfide, HS^-	sulfite, SO_3^{2-}			
hydroxide, OH^-				
hypochlorite, ClO^-				
nitrate, NO_3^-				
nitrite, NO_2^-				
perchlorate, ClO_4^-				
permanganate, MnO_4^-				

The vast majority of polyatomic ions are anions, many of which end in *-ate* or *-ite*. Notice that in some cases, such as nitrate $\left(NO_3^-\right)$ and nitrite $\left(NO_2^-\right)$, there are multiple anions that consist of the same two elements. In these cases, the difference between the ions is in the number of oxygen atoms present, while the overall charge is the same. As a class, these are called oxoanions. When there are two oxoanions for a particular element, the one with the greater number of oxygen atoms gets the *-ate* suffix, while the one with the fewer number of oxygen atoms gets the *-ite* suffix. The four oxoanions of chlorine are as follows:

- ClO^-, hypochlorite
- ClO_2^-, chlorite
- ClO_3^-, chlorate
- ClO_4^-, perchlorate

In cases such as this, the ion with one more oxygen atom than the *-ate* anion is given a *per-* prefix. The ion with one fewer oxygen atom than the *-ite* anion is given a *hypo-* prefix.



Summary

- Polyatomic ions contain more than one type of atom in the ion.
- The majority of polyatomic ions are anions that are named ending in *-ate* or *-ite*.
- Some anions have multiple forms and are named accordingly.

Review

1. Write the formulas for the following ions:
    a. ammonium
    b. carbonate
    c. sulfate
    d. phosphate
2. Name the following ions:
    1. PO_3^{3-}
    2. SiO_3^{2-}
    3. OH^-
    4. MnO_4^-

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3.9: Names and Formulas of Ternary Ionic Compounds



Figure 3.9.1 (Public Domain; Jon Sullivan via Commons Wikimedia, Pepperoni Pizza [commons.wikimedia.org])

How many varieties of pizza can you think of?

Many people enjoy eating pizza. When someone orders a pizza (either by phone, online, or in a restaurant), they don't just order "pizza". Even the simplest "binary" pizza will have a topping and cheese—maybe pepperoni, maybe something else. However, many pizzas quickly become more complex. One person may want pepperoni and sausage, another may wish to order Canadian bacon and pineapple; then you have the folks that can't decide, so they order half-this and half-that. The combinations may be more complex, but the same basic ideas about pizza are valid.

Ternary Ionic Compounds

Not all ionic compounds are composed of only monatomic ions. A **ternary ionic compound** is an ionic compound composed of three elements. In a typical ternary ionic compound, there is still one type of cation and one type of anion involved. The cation, the anion, or both, are polyatomic ions.

Naming Ternary Ionic Compounds

The process of naming ternary ionic compounds is the same as naming binary ionic compounds. The cation is named first, followed by the anion. Some examples are shown in the table below:

Table 3.9.1: Examples of Ternary Ionic Compounds

Formula	Name
$\mathrm{NaNO_3}$	sodium nitrate
$\mathrm{NH_4Cl}$	ammonium chloride
$\mathrm{Fe(OH)_3}$	iron (III) hydroxide

When more than one polyatomic ion is present in a compound, the formula of the ion is placed in parentheses with a subscript outside of the parentheses that indicates how many of those ions are in the compound. In the last example above, there is one $\mathrm{Fe^{3+}}$ cation and three $\mathrm{OH^-}$ anions.

Writing Formulas for Ternary Ionic Compounds

Writing a formula for a ternary ionic compound also involves the same steps as for a binary ionic compound. Write the symbol and charge of the cation followed by the symbol and charge of the anion. Use the crisscross method to ensure that the final formula is neutral. Calcium nitrate is composed of a calcium cation and a nitrate anion.

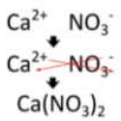


Figure 3.9.2 (CC BY-NC 3.0; Joy Sheng via CK-12 Foundation)

The charge is balanced by the presence of two nitrate ions and one calcium ion. Parentheses are used around the nitrate ion because more than one of the polyatomic ion is needed. If only one polyatomic ion is in a formula, parentheses are not used. As an example, the formula for calcium carbonate is $\mathrm{CaCO_3}$. The carbonate ion carries a $2-$ charge and so exactly balances the $2+$ charge of the calcium ion.

There are two polyatomic ions that produce unusual formulas. The Hg_2^{2+} ion is called either the dimercury ion or, preferably, the mercury (I) ion. When bonded with an anion with a $1-$ charge, such as chloride, the formula is Hg_2Cl_2. Because the cation consists of two Hg atoms bonded together, this formula is <u>not</u> reduced to HgCl. Likewise, the peroxide ion, O_2^{2-}, is also a unit that must stay together in its formulas. For example, the formula for potassium peroxide is K_2O_2.

Summary

- Ternary compounds are composed of three or more elements.
- Ternary compounds are named by stating the cation first, followed by the anion.
- Positive and negative charges must balance.

Review

1. What is a ternary compound?
2. What is the basic rule for naming ternary compounds?
3. Write the formulas for the following compounds:
    a. mercury(II) nitrate
    b. ammonium phosphate
    c. calcium silicate
    d. lead(II) chromate
4. Name the following compounds:
    a. $KClO_3$
    b. Rb_2SO_4
    c. $Cd(NO_3)_2$
    d. NaCN

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CHAPTER OVERVIEW

4: Organic Compounds

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4.5: Covalent Bonding in Polyatomic Ions
4.6: Straight-Chain Alkanes
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4.8: Alkenes and Alkynes
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4.13: Carboxylic Acids
4.14: Alkyl Halides

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4.1: Organic Chemistry

How many carbon-containing molecules are there? The current estimate is around 20 million different known organic compounds. Why the uncertainty? Every day, scientists are coming up with new compounds. Some of these materials are of interest for a research project, while others are destined to be developed for a commercial market. As soon as we think we know how many organic compounds exist, more are discovered and our number quickly becomes out of date.

Organic Chemistry

At one time in history, it was thought that only living things were capable of synthesizing the carbon-containing compounds present in cells. For that reason, the term organic was applied to those compounds. Eventually it was proved that carbon-containing compounds could be synthesized from inorganic substances, but the term "organic" has remained. Currently, **organic compounds** are defined as covalently bonded compounds containing carbon, excluding carbonates and oxides. By this definition, compounds such as carbon dioxide $\left(CO_2\right)$ and sodium carbonate $\left(Na_2CO_3\right)$ are considered to be inorganic. **Organic chemistry** is the study of all organic compounds.

Organic chemistry is a very vast and complex subject. There are millions of known organic compounds—far more than the number of inorganic compounds. The reason lies within the uniqueness of carbon's structure and bonding capabilities. Carbon has four valence electrons, and therefore makes four separate covalent bonds in compounds. Carbon has the ability to bond to itself repeatedly, making long chains of carbon atoms, as well as ringed structures. These bonds can be single, double, or triple covalent bonds. Carbon readily makes covalent bonds with other elements—primarily hydrogen, oxygen, nitrogen, halogens, and several other nonmetals. The figures below show ball-and-stick models of two of the many organic compounds.



Figure 4.1.1: Stearic acid is composed of many carbon (black) and hydrogen (white) atoms, along with two oxygen (red) atoms.

The related field of biochemistry overlaps to some extent with organic chemistry. **Biochemistry** is the study of the chemistry of living systems. Many biochemical compounds are considered to be organic chemicals. Both of the molecules shown above are biochemical materials in terms of their use in the body, but organic chemicals in terms of their structure and chemical reactivity.

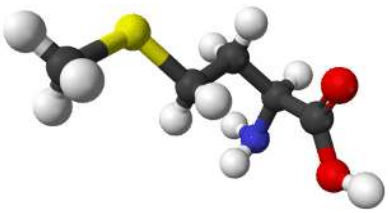


Figure 4.1.2: Methionine is composed of carbon, hydrogen, oxygen, nitrogen (blue), and sulfur (yellow) atoms.

Summary

- Organic compounds are defined as covalently bonded compounds containing carbon, excluding carbonates and oxides. (By this definition, compounds such as carbon dioxide $\left(CO_2\right)$ and sodium carbonate $\left(Na_2CO_3\right)$ are considered to be inorganic.)
- Organic chemistry is the study of all organic compounds.
- Biochemistry is the study of the chemistry of living systems.

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4.2: Lewis Electron-Dot Structures

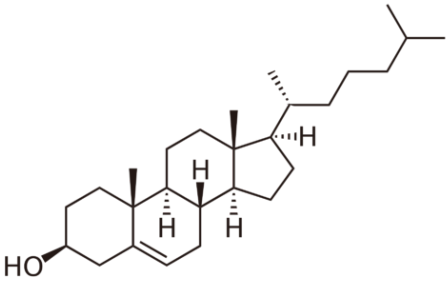


Figure 4.2.1 (Public Domain; User:BorisTM/Wikimedia Commons via Wikipedia).

What does cholesterol really look like?

We can write the structure of the cholesterol molecule a couple of different ways. The simplest approach is to simply write $C_{27}H_{46}O$. This "structure" is not very useful because it does not tell us how the carbons, hydrogens, and oxygen are connected to one another. The structure in the figure above is much more helpful—we see how the different atoms are connected together to form the molecule.

Lewis Electron-Dot Structures

In a previous chapter, you learned that the valence electrons of an atom can be shown in a simple way with an electron dot diagram. A hydrogen atom is shown as $H\cdot$ because of its one valence electron. The structures of molecules that are held together by covalent bonds can be diagrammed by **Lewis electron-dot structures**. The hydrogen molecule is shown in the figure below.

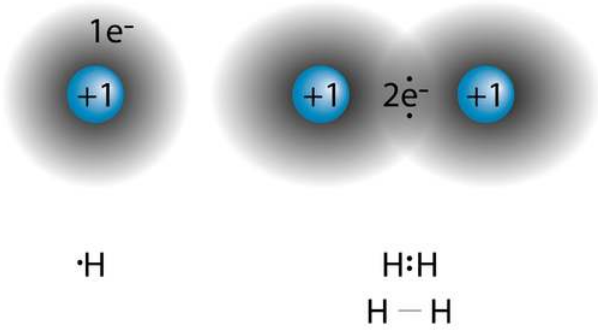
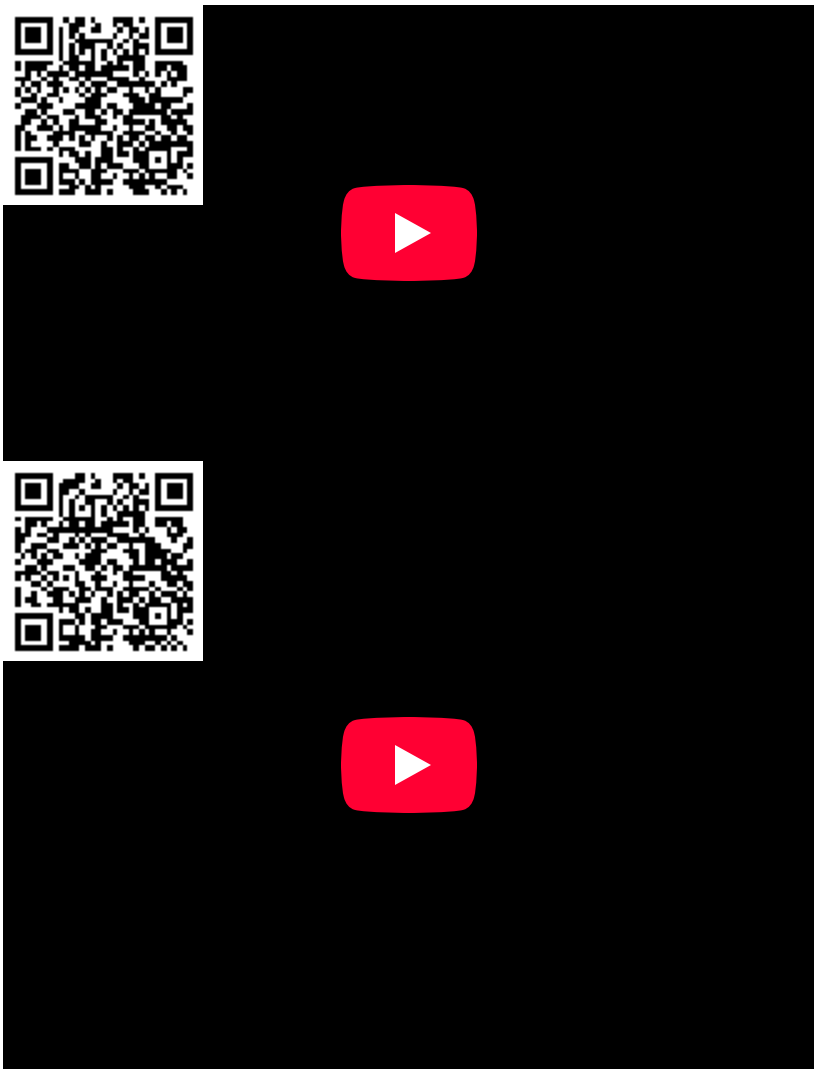


Figure 4.2.2: On the left is a single hydrogen atom with one electron. On the right is an H_2 molecule showing the electron cloud overlap. (CC BY-NC 3.0; Jodi So via CK-12 Foundation)

The shared pair of electrons is shown as two dots in between the two H symbols $(H:H)$. This is called a **single covalent bond**, when two atoms are joined by the sharing of one pair of electrons. The single covalent bond can also be shown by a dash in between the two symbols $(H{-}H)$. A **structural formula** is a formula that shows the arrangement of atoms in a molecule and represents covalent bonds between atoms by dashes.

The Octet Rule and Covalent Bonds

When ions form, they conform to the **octet rule** by either losing or gaining electrons in order to achieve the electron configuration of the nearest noble gas. In a similar way, nonmetal atoms share electrons in the formation of a covalent bond in such a way that each of the atoms involved in the bond can attain a noble-gas electron configuration. The shared electrons are "counted" for each of the atoms involved in the sharing. For hydrogen (H_2), the shared pair of electrons means that each of the atoms is able to attain the electron configuration of helium, the noble gas with two electrons. For atoms other than hydrogen, the sharing of electrons will usually provide each of the atoms with eight valence electrons.



Summary

- Lewis electron-dot structures show the bonding in covalent molecules.
- Covalent bonds between atoms can be indicated either with dots $(:)$ or a dash $(-)$.

Review

1. What is a single covalent bond?
2. How can covalently-bound atoms obey the octet rule?
3. Does the hydrogen molecule obey the octet rule?

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4.3: Single Covalent Bonds

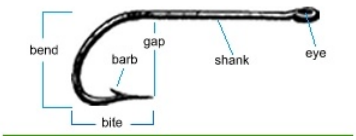


Figure 4.3.1 (Public Domain; the US Department of the Interior via Commons Wikimedia, Fishhook [commons.wikimedia.org])

What holds molecules together?

In one form or another, the idea of atoms connecting to form larger substances has been with us for a long time. The Greek philosopher Democritus (460-370 BCE) believed that atoms had hooks that allowed them to connect with one another. Today, we believe that atoms are held together by bonds formed when two atoms share a set of electrons—a much more complicated picture than the simple hooks that Democritus believed in.

Single Covalent Bonds

A covalent bond forms when two orbitals with one electron each overlap one another. For the hydrogen molecule, this can be shown as:

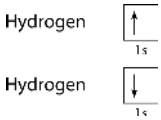


Figure 4.3.2 (CC BY-NC 3.0; Joy Sheng via CK-12 Foundation)

Upon formation of the H_2 molecule, the shared electrons must have opposite spin, so they are shown with opposite spin in the atomic $1s$ orbital.

The halogens also form single covalent bonds in their diatomic molecules. An atom of any halogen, such as fluorine, has seven valence electrons. Its unpaired electron is located in the $2p$ orbital.

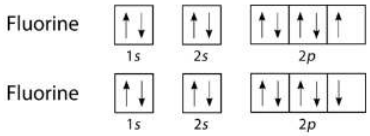


Figure 4.3.3 (CC BY-NC 3.0; Joy Sheng via CK-12 Foundation)

The single electrons in the third $2p$ orbital combine to form the covalent bond:

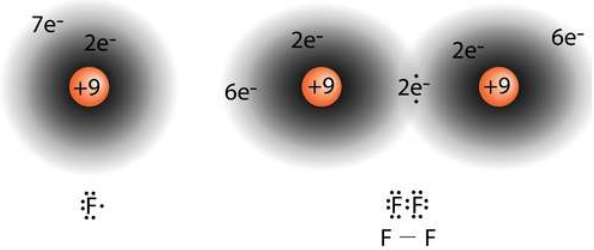


Figure 4.3.4: On the left is a fluorine atom with seven valence electrons. On the right is the F_2 molecule. (CC BY-NC 3.0; Jodi So via CK-12 Foundation)

The diatomic fluorine molecule (F_2) contains a single shared pair of electrons. Each F atom also has three pair of electrons that are not shared with the other atom. A **lone pair** is a pair of electrons in a Lewis electron-dot structure that is not shared between atoms. The oxygen atom in the water molecule shown below has two lone pair sets of electrons. Each F atom has three lone pairs. Combined with the two electrons in the covalent bond, each F atom follows the octet rule.



4.3.1 Example

Draw the Lewis electron dot structure for water.

Solution

Step 1: List the known quantities and plan the problem.

Known

- Molecular formula of water $= H_2O$
- 1 O atom $= 6$ valence electrons
- 2 H atoms $= 2 \times 1 = 2$ valence electrons
- Total number of valence electrons $= 8$

Use the periodic table to determine the number of valence electrons for each atom and the total number of valence electrons. Arrange the atoms and distribute the electrons so that each atom follows the octet rule. The oxygen atom will have 8 electrons, while the hydrogen atoms will each have 2.

Step 2: Solve.

Electron dot diagrams for each atom are:



Figure 4.3.5 (CC BY-NC 3.0; Joy Sheng via CK-12 Foundation)

Each hydrogen atom with its single electron will form a covalent bond with the oxygen atom where it has a single electron. The resulting Lewis electron dot structure is:



Figure 4.3.6 (CC BY-NC 3.0; Joy Sheng via CK-12 Foundation)

Step 3: Think about your result.

The oxygen atom follows the octet rule with two pairs of bonding electrons and two lone pairs. Each hydrogen atom follows the octet rule with one bonding pair of electrons.



Summary

- Covalent bonds form when electrons in two atoms form overlapping orbitals.
- Lone pair electrons in an atom are not shared with any other atom.

Review

1. How does a covalent bond form?
2. What relationship do the spins of shared electrons have with each other?
3. Do lone pair electrons form covalent bonds?

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4.4: Multiple Covalent Bonds

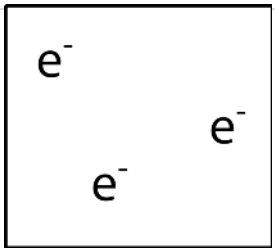


Figure 4.4.1 (CC BY-NC 3.0; Joy Sheng via CK-12 Foundation)

What do you do with your leftovers?

When working with covalent structures, it sometimes looks like there are leftover electrons. Maybe you have applied the rules you learned so far, but there are still some electrons hanging out there, unattached. You can't just leave them there...So, where do you put them?

Multiple Covalent Bonds

Some molecules are not able to satisfy the octet rule by making only single covalent bonds between the atoms. Consider the compound ethene, which has a molecular formula of C_2H_4. The carbon atoms are bonded together, with each carbon also bonded to two hydrogen atoms.

$$\text{two C atoms} = 2 \times 4 = 8 \text{ valence electrons}$$

$$\text{four H atoms} = 4 \times 1 = 4 \text{ valence electrons}$$

$$= \text{total of 12 valence electrons in the molecule}$$

If the Lewis electron dot structure was drawn with a single bond between the carbon atoms and with the octet rule followed, it would look like this:

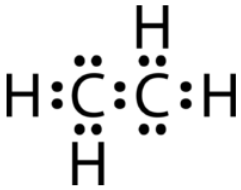


Figure 4.4.2: Incorrect dot structure of ethene. (CC BY-NC 3.0; Joy Sheng via CK-12 Foundation)

This Lewis structure is incorrect because it contains a total of 14 electrons. However, the Lewis structure can be changed by eliminating the lone pairs on the carbon atoms and having the carbon atoms share two pairs, instead of only one pair, of electrons.

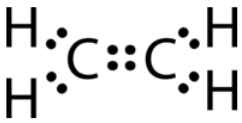


Figure 4.4.3: Correct dot structure for ethene. (CC BY-NC 3.0; Joy Sheng via CK-12 Foundation)

A **double covalent bond** is a covalent bond formed by atoms that share two pairs of electrons. The double covalent bond that occurs between the two carbon atoms in ethane can also be represented by a structural formula and with a molecular model, as shown in the figure below.

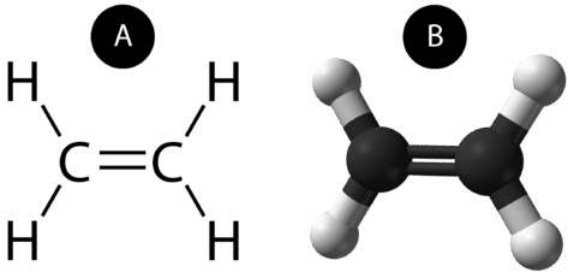


Figure 4.4.4: (A) The structural model for C_2H_4 consists of a double covalent bond between the two carbon atoms and single bonds to the hydrogen atoms. (B) Molecular model of C_2H_4. (Public Domain; Ben Mills (Wikimedia: Benjah-bmm27) via (A) http://commons.wikimedia.org/wiki/File:Ethylene-CRC-MW-dimensions-2D-Vector.svg; (B) http://commons.wikimedia.org/wiki/File:Ethylene-CRC-MW-3D-balls.png)

A **triple covalent bond** is a covalent bond formed by atoms that share three pairs of electrons. The element nitrogen is a gas that composes the majority of Earth's atmosphere. A nitrogen atom has five valence electrons, which can be shown as one pair and three single electrons. When combining with another nitrogen atom to form a diatomic molecule, the three single electrons on each atom combine to form three shared pairs of electrons.

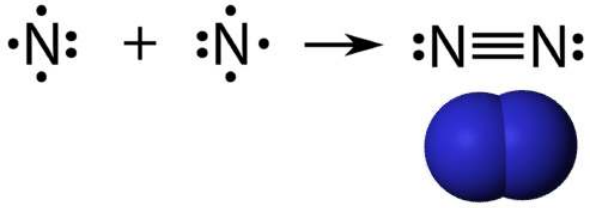


Figure 4.4.5: Triple bond in N_2. (CC BY-NC-SA 3.0; Molecule Public Domain; CK-12 Foundation - Joy Sheng, using 3D molecular structure by Ben Mills (Wikimedia: Benjah-bmm27) via Molecular structure: http://commons.wikimedia.org/wiki/File:Nitrogen-3D-vdW.png)

Each nitrogen atom follows the octet rule with one lone pair of electrons, and six electrons that are shared between the atoms.



Summary

- Lewis structures can be drawn for molecules that share multiple pairs of electrons.
- A double covalent bond is a covalent bond formed by atoms that share two pairs of electrons.
- A triple covalent bond is a covalent bond formed by atoms that share three pairs of electrons.

Review

1. Why is the first ethene Lewis structure incorrect?
2. What do the single electrons in nitrogen do to form a triple bond?
3. Draw the Lewis structure for ethyne C_2H_2.

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4.5: Covalent Bonding in Polyatomic Ions



Figure 4.5.1 (CC by 2.0; Jan Seifert via Flickr)

How do we extend basic principles?

The United States Supreme Court has the unenviable task of determining what the law dictates. This responsibility can be a major challenge when there is no clear principle involved, or when they face a situation not previously encountered. Chemistry faces the same challenge in extending basic concepts to fit a new situation. Drawing of Lewis structures for polyatomic ions uses the same approach, but tweaks the process a little to fit a somewhat different set of circumstances.

Polyatomic Ions

Recall that a **polyatomic ion** is a group of atoms that are covalently bonded together, and which carry an overall electrical charge. The ammonium ion, NH_4^+, is formed when a hydrogen ion $\left(H^+\right)$ attaches to the lone pair of an ammonia $\left(NH_3\right)$ molecule in a coordinate covalent bond.

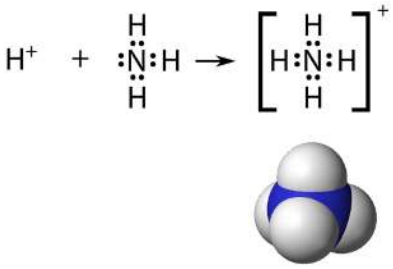


Figure 4.5.2: The ammonium ion. (CC BY-NC-SA 3.0; CK-12 Foundation - Joy Sheng, using 3D molecular structure by Ben Mills (Wikimedia: Benjah-bmm27) via Wikipedia; Molecule Public Domain)

When drawing the Lewis structure of a polyatomic ion, the charge of the ion is reflected in the number of total valence electrons in the structure. In the case of the ammonium ion:

$$1\ \text{N atom} = 5\ \text{valence electrons}$$

$$4\ \text{H atoms} = 4 \times 1 = 4\ \ \text{valence electrons}$$

$$\text{subtract 1 electron for the } 1+\text{charge of the ion}$$

$$\text{total of 8 valence electrons in the ion}$$

It is customary to put the Lewis structure of a polyatomic ion into a large set of brackets, with the charge of the ion as a superscript outside of the brackets.

4.5.1 Example

Draw the Lewis electron dot structure for the sulfate ion.

Solution

Step 1: List the known quantities and plan the problem.

Known

Molecular formula of sulfate ion: SO_4^{2-}

1 S atom $= 6$ valence electrons

4 O atoms $= 4 \times 6 = 24$ valence electrons

add 2 electrons for the $2-$ charge of the ion

= total of 32 valence electrons

The less electronegative sulfur atom is the central atom in the structure. Place the oxygen atoms around the sulfur atom, each with a single covalent bond. Distribute lone pairs to each oxygen atom in order to satisfy the octet rule. Count the total number of atoms. If there are too many electrons in the structure, make multiple bonds between the S and O.

Step 2: Solve.

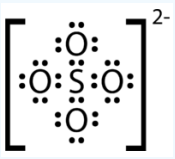


Figure 4.5.3: The sulfate ion. (CC BY-NC 3.0; Joy Sheng via CK-12 Foundation)

Step 3: Think about your result.

The Lewis structure for the sulfate ion consists of a central sulfur atom with four single bonds to oxygen atoms. This yields the expected total of 32 electrons. Since the sulfur atom started with six valence electrons, two of the S−O bonds are coordinate covalent.



Summary

- Lewis structures for polyatomic ions follow the same rules as those for other covalent compounds.

Review

1. What are two characteristics of polyatomic ions?
2. Which atom becomes the central atom in the structure?
3. Where is the charge on an ion placed in a lewis dot diagram?

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4.6: Straight-Chain Alkanes

As our country looks at the prospect of oil shortages in the future, we are searching for alternative transportation fuel sources. One very viable possibility is propane gas. Power and acceleration capacities for propane-powered vehicles are comparable to gasoline-powered vehicles, and fuel efficiency is greater. Propane has a higher octane rating than regular gasoline, leading to much longer engine life. When properly structured, propane engines can produce lower amounts of air pollution. We are seeing a growing use of propane in buses, trucks, and police cars. Maybe your next car will burn propane.

Straight-Chain Alkanes

Hydrocarbons

A **hydrocarbon** is an organic compound that is made up of only carbon and hydrogen. A hydrocarbon is the simplest kind of organic molecule, and is the basis for all other more complex organic compounds. Hydrocarbons can be divided into two broad categories: aliphatic and aromatic. **Aliphatic hydrocarbons** are hydrocarbons that do not contain the benzene group or a benzene ring. **Aromatic hydrocarbons** contain one or more benzene rings. In this section, we will focus on the aliphatic hydrocarbons.

Alkanes

An **alkane** is a hydrocarbon in which there are only single covalent bonds. The simplest alkane is methane, with the molecular formula CH_4. The carbon is the central atom and makes four single covalent bonds to hydrogen atoms.

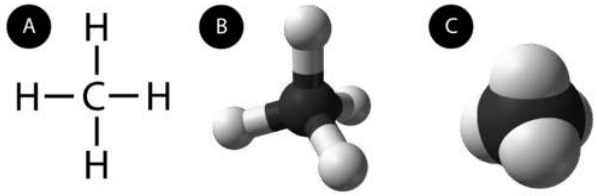
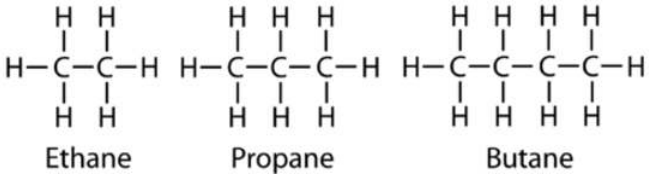


Figure 4.6.1: Methane is the simplest hydrocarbon and is shown with a structural formula, a ball-and-stick model, and a space-filling model.

The next simplest alkane is called ethane (C_2H_6), and consists of two carbon atoms with a single covalent bond between them. Each carbon is then able to bond to three hydrogen atoms. The alkane series progresses from there, increasing the length of the carbon chain by one carbon at a time. Structural formulas for ethane, propane (C_3H_8), and butane (H_4H_{10}) are shown below.



These alkanes are called straight-chain alkanes because the carbon atoms are connected in one continuous chain with no branches. Naming and writing structural and molecular formulas for the straight-chain alkanes is straightforward. The name of each alkane consists of a prefix that specifies the number of carbon atoms and the ending *-ane*. The molecular formula follows the pattern of $C_nH_{2\,n_2}$ where n is the number of carbons in the chain. The table below lists the first ten members of the alkane series.

Table 4.6.1: First Ten Members of the Alkane Series

Name	Molecular Formula	Condensed Structural Formula	Boiling Point (°C)
Methane	CH_4	CH_4	-161.0
Ethane	C_2H_6	CH_3CH_3	-88.5
Propane	C_3H_8	$CH_3CH_2CH_3$	-42.0
Butane	C_4H_{10}	$CH_3CH_2CH_2CH_3$	0.5
Pentane	C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	36.0
Hexane	C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$	68.7

Name	Molecular Formula	Condensed Structural Formula	Boiling Point (°C)
Heptane	C_7H_{16}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	98.5
Octane	C_8H_{18}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	125.6
Nonane	C_9H_{20}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	150.7
Decane	$C_{10}H_{22}$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	174.1

Note that the table shows a variation of a structural formula called a condensed structural formula. In this formula, the covalent bonds are understood to exist between each carbon and the hydrogens associated with it, as well as between carbon atoms. This table also shows that the boiling points of the alkanes steadily increase as the length of the carbon chain increases. This is due to an increase in the strength of the intermolecular attractive forces and is a general feature of other organic molecules as well.

Summary

- A hydrocarbon is an organic compound that is made up of only carbon and hydrogen; it is the simplest kind of organic molecule.
- Aliphatic hydrocarbons are hydrocarbons that do not contain the benzene group or a benzene ring.
- Aromatic hydrocarbons contain one or more benzene rings.
- An alkane is a hydrocarbon in which there are only single covalent bonds.

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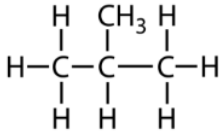
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4.7: Branched Alkanes

Tracing your family tree can be both fun and exciting. In order to do this correctly, it helps to know the exact names of your family members. Just a first, middle, or last name is not enough. A traceable family tree is one in which all relatives are carefully and precisely identified. After all, you would prefer that great-great-great-uncle to be royalty, and not a horse thief!

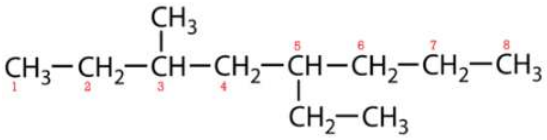
Branched Alkanes

Beginning with butane, there is an alternate structure possible that is not a straight chain. The structural formula below shows a structure with a three-carbon chain that has a $-CH_3$ group attached to the middle carbon.



The name of this molecule is 2-methylpropane. The molecular formula is still C_4H_{10}, which is the same formula as butane. A **structural isomer** is one of multiple molecules that have the same molecular formula, but different structural formulas. Butane and 2-methylpropane are structural isomers.

2-methylpropane is an example of a type of alkane called a branched alkane. The IUPAC system of nomenclature for branched alkanes follows a set of steps which will be applied to the example molecule below.



1. Find the longest continuous chain of carbon atoms in the molecule. This is called the parent chain. In the example, the longest chain is eight carbon atoms, and so the parent hydrocarbon is octane.
2. Number the carbon atoms in the parent chain. To do this, start at the end that will give the smallest numbers possible to the carbon atoms where the branches originate. In the example above, the branches are on carbons 3 and 5 when the chain is numbered left-to-right. If it were to be numbered right-to-left, the branches would be on carbons 4 and 6, so the left-to-right order is preferable.
3. The atoms attached to the parent chain (branches) are called substituents. A substituent that is a hydrocarbon is called an **alkyl group**. The names of alkyl groups use the same prefixes as the alkanes, but with a *-yl* suffix. So a 1-carbon alkyl group is a methyl group, a 2-carbon alkyl group is an ethyl group, and so on. The substituents are named by placing the number from the parent carbon chain in front of the name of the substituent. In the current example, we have 3-methyl and 4-ethyl substituents.
4. Use a prefix to indicate the appearance of more than one of the same substituent in the structural formula. Two of the same group is *di-*, three is *tri-*, four is *tetra-*, etc. For example, if methyl groups were attached to both carbons 2 and 3, that part of the name would be 2,3-dimethyl-. This rule does not apply to the structure pictured above.
5. Multiple different substituents are listed in alphabetical order. Ignore any of the prefixes from rule 4. In the current example, the 5-ethyl- comes before the 3-methyl-.
6. Commas are used to separate multiple numbers. Hyphens come between the number and the name of the substituent. The parent name comes immediately after the last substituent. There are no blank spaces in the name.

The correct name for the above structure, according to the IUPAC system, is 5-ethyl-3-methyloctane.

Summary

- A structural isomer is one of multiple molecules that have the same molecular formula, but different structural formulas.
- Nomenclature rules for branched hydrocarbons are given.

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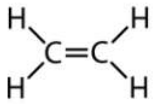
4.8: Alkenes and Alkynes

One of the most effective ways to cut metal is with an oxy-acetylene torch. Very high temperatures are obtained when acetylene burns in oxygen. Mixed 1:1 with oxygen, a temperature of over $3000^{\circ}\mathrm{C}$ can be achieved. The amount of energy released is high—the net heat of combustion is $1300\ \mathrm{kJ/mol}$ Safety precautions need to be observed, as the gas is very explosive. The oxy-acetylene torch is one of the top tools for welding and cutting.

Alkenes and Alkynes

Alkenes

An **alkene** is a hydrocarbon with one or more carbon-carbon double covalent bonds. The simplest alkene is composed of two carbon atoms and is called ethene (shown below). Each carbon is bonded to two hydrogen atoms, in addition to the double bond between them.

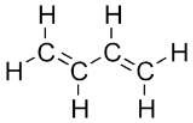


The hybridization of each carbon atom is sp^2 with trigonal planar geometry. All the atoms of the molecule lay in one plane. Like the alkane series, the names of alkenes are based on the number of atoms in the parent chain. Naming follows the same rules as for alkanes, with the addition of using a number to indicate the location of the double bond. Propene $\left(\mathrm{C_3H_6}\right)$ has three carbons total, while butene $\left(\mathrm{C_4H_8}\right)$ has four. The general formula for alkenes with one double bond is $\mathrm{C_nH_{2\,n}}$. Alkenes are called unsaturated hydrocarbons. An **unsaturated hydrocarbon** is a hydrocarbon that contains less than the maximum number of hydrogen atoms that can possibly bond with the number of carbon atoms present.

The location of the carbon-carbon double bond can vary. The 4-carbon alkene generic name is butene. Since the double bond can be located in more than one place, we have 1-butene and 2-butene:



Molecules with multiple double bonds are also quite common. The formula below shows a four-carbon chain with double bonds between carbons 1 and 2, and between carbons 3 and 4. This molecule is called 1,3-butadiene.



Alkynes

An **alkyne** is a hydrocarbon with one or more carbon-carbon triple covalent bonds. The simplest alkyne consists of two carbon atoms and is called ethyne (common name: acetylene).



The ethyne molecule is linear, with *sp* hybridization for each carbon atom. The general formula of alkynes with one triple bond is $\mathrm{C_nH_{2\,n-2}}$. Alkynes are also unsaturated hydrocarbons. Other alkynes exist, such as 2-pentyne:



Summary

- An alkene is a hydrocarbon with one or more carbon-carbon double covalent bonds.
- An alkyne is a hydrocarbon with one or more carbon-carbon triple covalent bonds.
- An unsaturated hydrocarbon is a hydrocarbon that contains less than the maximum number of hydrogen atoms that can possibly bond with the number of carbon atoms present.

- Structures of alkene and alkyne are given.

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4.9: Isomers

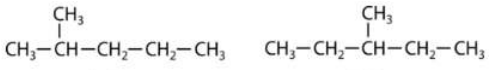
As we delve into the complexities of organic chemistry, we will see how molecular shape affects reactions. One common reaction for alkenes is the addition of hydrogen across the double bond to form the corresponding alkane. Because of the geometry of the reaction, the different 2-butene shapes have different heats of reaction. These differences are important, both from a theoretical standpoint, as well as from the point of view of industrial applications. Greater energy requirements mean a higher cost and a more expensive product.

Isomers

One of the interesting aspects of organic chemistry is that it is three-dimensional. A molecule can have a shape in space that may contribute to its properties. Molecules can differ in the way the atoms are arranged—the same combination of atoms can be assembled in more than one way. These compounds are known as **isomers**. Isomers are molecules with the same molecular formulas, but different arrangements of atoms. We will look at some isomer possibilities for alkanes and alkenes.

Structural Isomers

A **structural isomer** is one in which two or more organic compounds have the same molecular formulas, but different structures. The two pentane molecules below differ only in the location of the methyl group.



2-methylpentane 3-methylpentane

Alkenes can also demonstrate structural isomerism. In alkenes, there are multiple structural isomers based on where in the chain the double bond occurs. The condensed structural formulas of 1-butene and 2-butene show this.

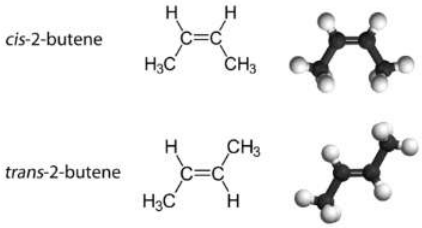


1-butene 2-butene

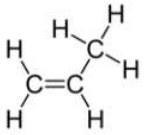
The number in the name of the alkene refers to the lowest numbered carbon in the chain that is part of the double bond.

Geometric Isomers

With a molecule such as 2-butene, a different type of isomerism called geometric isomerism can be observed. **Geometric isomers** are isomers in which the order of atom bonding is the same, but the arrangement of atoms in space is different. The double bond in an alkene is not free to rotate because of the nature of the pi bond. Therefore, there are two different ways to construct the 2-butene molecule. The image below shows the two geometric isomers, called *cis*-2-butene and *trans*-2-butene.



The *cis* isomer has the two single hydrogen atoms on the same side of the molecule, while the *trans* isomer has them on opposite sides of the molecule. In both molecules, the bonding order of the atoms is the same. In order for geometric isomers to exist, there must be a rigid structure in the molecule to prevent free rotation around a bond. If the double bond in an alkene was capable of rotating, the two geometric isomers above would not exist. In addition, the two carbon atoms must each have two different groups attached in order for there to be geometric isomers. Propene has no geometric isomers because one of the carbon atoms has two single hydrogens bonded to it.



Physical and chemical properties of geometric isomers are generally different. While *cis*-2-butene is a polar molecule, *trans*-2-butene is nonpolar. Heat or irradiation with light can be used to bring about the conversion of one geometric isomer to another. The input of energy must be large enough to break the pi bond between the two carbon atoms, which is weaker than the sigma bond. At that point, the now single bond is free to rotate, and the isomers can interconvert.

As with alkenes, alkynes display structural isomerism beginning with 1-butyne and 2-butyne. However, there are no geometric isomers with alkynes, because there is only one other group bonded to the carbon atoms that are involved in the triple bond.

Summary

- Isomers are molecules with the same molecular formulas, but different arrangements of atoms.
- A structural isomer is one in which two or more organic compounds have the same molecular formulas, but different structures.
- Geometric isomers are isomers in which the order of atom bonding is the same, but the arrangement of atoms in space is different.
- Examples of alkane and alkene isomers are given.

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4.10: Alcohols

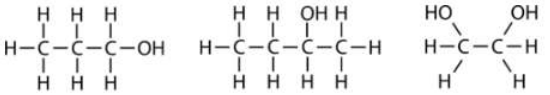
Water freezes at $0^{o}C$, which creates problems for cars in the winter. The water in the engine will freeze and crack the engine block. To prevent this, antifreeze is added to lower the freezing point of the liquid. The most common antifreeze is an alcohol known as propylene glycol. It has largely replaced the much more toxic ethylene glycol. Methanol can also be used as an antifreeze, mainly in windshield wiper fluid.

Alcohols

An **alcohol** is an organic compound that contains one or more hydroxyl $(-OH)$ groups. The general formula for alcohols is $R-OH$. Do not confuse alcohols with inorganic bases that contain the hydroxide ion (OH^{-}). The $-OH$ group in an alcohol is covalently bonded to a carbon atom and does not ionize in solution. The steps for naming alcohols are listed below.

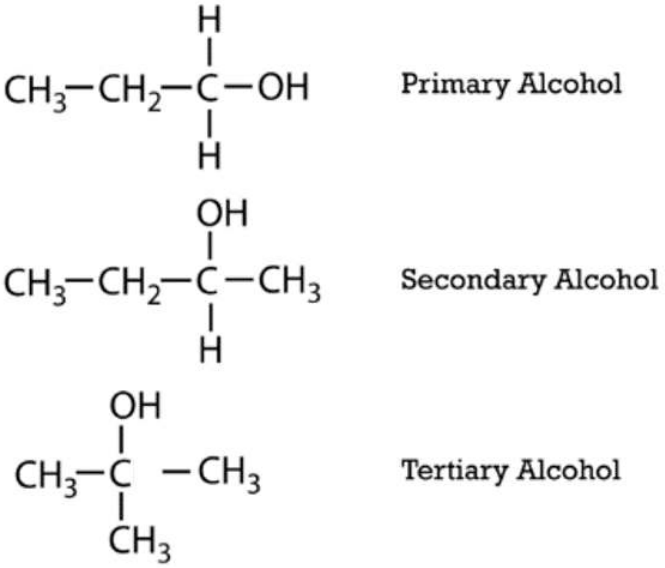
1. Name the parent compound by finding the longest continuous carbon atom chain that also contains the hydroxyl group. If there is one hydroxyl group in the molecule, change the final *-e* in the name of the alkane to *-ol*. If there is more than one hydroxyl group, use the full name of the alkane and add a suffix to indicate the number of hydroxyl groups. For example, two hydroxyl groups is *-diol*, three is *-triol*, etc.
2. Number the carbon chain in a way that makes the sum of the hydroxyl numbers as low as possible.
3. Add the numerical prefix into the name before the name of the alcohol.
4. Separate numbers with commas and separate numbers from names or prefixes with a hyphen. There are no spaces in the name.

Following are three examples of alcohols and their IUPAC names.



1-propanol 2-butanol 1,2-ethanediol

Aliphatic alcohols can be classified according to the number of R groups attached to the carbon with the hydroxyl group. If one R group is attached to that carbon, the alcohol is a primary alcohol. If two R groups are attached, the alcohol is a secondary alcohol. If three R groups are attached, the alcohol is a tertiary alcohol. Shown below is an example of each. The primary alcohol is 1-propanol, the secondary alcohol is 2-butanol, and the tertiary alcohol is 2-methyl-2-propanol.



Properties of Alcohols

The smallest and lightest alcohols (methanol, ethanol, propanol) are completely soluble in water in all proportions. In a solution, the hydroxyl groups of alcohol molecules and the water molecules form hydrogen bonds with each other, resulting in complete miscibility. However, as the length of the carbon chain increases, the solubility decreases. The solubility of 1-butanol is $7.4\ g$ per

100 g of water, while that of 1-pentanol is 2.7 g per 100 g of water, and 1-octanol is 0.06 g per 100 g of water. The carbon chain portion of the larger alcohol molecule is nonpolar, and leads to the decreased solubility of the overall compound.

The presence of hydrogen bonds in alcohols also explains the relatively high boiling points of alcohols compared to alkanes of similar molar mass (see table below).

Table 4.10.1: Boiling Point Comparison of Alkanes and Alcohols

Compound	Formula	Molar Mass $(\mathrm{g/mol})$	Boiling Point $(^{\circ}\mathrm{C})$
ethane	CH_3CH_3	32	-88
methanol	CH_3OH	30	64.7
propane	$CH_3CH_2CH_3$	44	-42.1
ethanol	CH_3CH_2OH	46	78.3

Only weak London dispersion forces hold molecules of nonpolar alkanes together in the liquid phase. Consequently, less energy is required to break these molecules away from the surface of the liquid and turn them into a vapor. The stronger hydrogen bonding between alcohol molecules means that more energy is required to convert the liquid to vapor, and boiling points are therefore high.

Summary

- An alcohol is an organic compound that contains one or more hydroxyl $(-OH)$ groups.
- The lightest alcohols (methanol, ethanol, propanol) are completely soluble in water in all proportions; as the length of the carbon chain increases, the solubility decreases.
- The presence of hydrogen bonds in alcohols also explains the relatively high boiling points of alcohols compared to alkanes of similar molar mass.

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4.11: Ethers

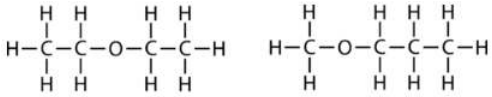
Race car drivers are always looking for that "edge" that will make their car (legally) faster than their competitors' cars. One way to get more speed is to burn the gasoline in the car engine more efficiently. Methyl-t-butyl ether (MTBE) has been used for this purpose, but is being discontinued due to concerns about the contamination of drinking water by leaking fuel tanks that contain this compound.

Ethers

An **ether** is an organic compound in which two hydrocarbon groups are bonded to the same atom of oxygen. An ether is represented by the general formula $\mathrm{R{-}O{-}R'}$. The $\mathrm{R'}$ in the formula means that the hydrocarbon group can be the same as R, or it can be different. The steps for naming ethers are listed below.

1. The parent compound is given by the word *ether*, which appears at the end of the name.
2. The names of each alkyl group come before the word *ether*. If the two alkyl groups are the same, the prefix *di-* is used. If the two alkyl groups are different, they are listed in alphabetical order.
3. Spaces are left between the names of the alkyl groups (if different) and before the word *ether*.

Shown below are two examples of ethers with their IUPAC names.



diethyl ether

methyl propyl ether

Properties of Ethers

Like alcohols, ethers are also quite soluble in water. The lone-pair electrons on the oxygen atom of the ether can form a hydrogen bond with the hydrogen atoms of water molecules. As with alcohols, the solubility is greater for ethers that have shorter length R groups. The boiling points of ethers are much lower than the boiling points of alcohols. Ether molecules do not have hydrogen atoms that are covalently bonded to a highly electronegative atom, and so ether molecules cannot form hydrogen bonds with each other. The weaker intermolecular force acting between ether molecules results in boiling points which are much closer to alkanes of similar molar mass than to alcohols.

The anesthetic effects of ethers were first discovered in the 1840s. Diethyl ether was used as a general anesthetic for patients undergoing surgery for many years. However, ethers are very flammable and have undesirable side effects, such as nausea and vomiting. Safer alternatives to ethers are now used in anesthesia, and the primary use of ethers today is as a solvent for other organic compounds.

Summary

- An ether is an organic compound in which two hydrocarbon groups are bonded to the same atom of oxygen.
- IUPAC naming rules for ethers are dictated.
- Ethers are quite soluble in water.
- The primary use of ethers today is as a solvent for other organic compounds.

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4.12: Aldehydes and Ketones

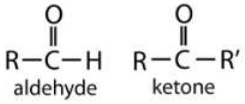
There's nothing like the smell of a fresh cinnamon roll; the taste is even better. What is that delicious taste owed to? This flavoring comes from the bark of a tree (actually, several different kinds of trees). One of the major compounds responsible for the taste and odor of cinnamon is cinnamaldehyde. Cinnamon has been widely used through centuries to treat a number of different disorders. In ancient times, doctors believed it could cure snakebite poisoning, freckles, and the common cold. Today, there are several research studies being carried out on the health benefits of cinnamon. So, enjoy that cinnamon roll—it just might have a health benefit or two.

Aldehydes and Ketones

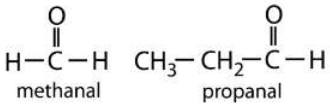
Aldehydes and ketones are two related categories of organic compounds that both contain the **carbonyl group**, shown below.



The difference between aldehydes and ketones is the placement of the carbonyl group within the molecule. An **aldehyde** is an organic compound in which the carbonyl group is attached to a carbon atom at the end of a carbon chain. A **ketone** is an organic compound in which the carbonyl group is attached to a carbon atom within the carbon chain. The general formulas for each are shown below.

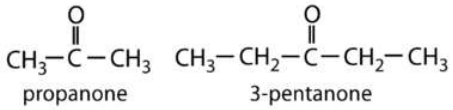


For aldehydes, the R group may be a hydrogen atom or any length carbon chain. Aldehydes are named by finding the longest continuous chain that contains the carbonyl group. Change the *-e* at the end of the name of the alkane to *-al*.



For ketones, R and R' must be carbon chains, of either the same or different lengths. The steps for naming ketones, followed by two examples, are shown below.

1. Name the parent compound by finding the longest continuous chain that contains the carbonyl group. Change the *-e* at the end of the name of the alkane to *-one*.
2. Number the carbon atoms in the chain in a way so that the carbonyl group has the lowest possible number.
3. Add the numerical prefix into the name before the name of the ketone.
4. Use a hyphen between the number and the name of the ketone.



Properties of Aldehydes and Ketones

Aldehydes and ketones can work weak hydrogen bonds with water through the carbonyl oxygen atom. The lower members of both series (3 carbons or fewer) are soluble in water in all proportions. As the length of the carbon chain increases, water solubility decreases. Similar to ethers, neither aldehydes nor ketones can hydrogen bond with themselves. As a result, their boiling points are generally lower than those of alcohols. Unlike alkanes however, aldehydes and ketones are polar molecules due to the more electronegative oxygen atom. The dipole-dipole interactions are stronger than the dispersion forces present in alkanes. The boiling points of aldehydes and ketones are intermediate between those of alkanes and alcohols. For example, the boiling point of ethane is $-89^{\circ}\mathrm{C}$, ethanal is $20^{\circ}\mathrm{C}$, and ethanol is $78^{\circ}\mathrm{C}$.

Methanal, commonly known as formaldehyde, was once commonly used as a biological preservative for dead animals. In recent years, formaldehyde has been shown to be a carcinogen, and so has been replaced by safer alternatives for preservation purposes.

Aldehydes are currently used in the production of resins and plastics. The simplest ketone, propanone, is commonly called acetone. Acetone is a common organic solvent that was once used in most nail polish removers, but has largely been replaced by other solvents.

Summary

- Aldehydes and ketones are two related categories of organic compounds that both contain the carbonyl group.
- An aldehyde is an organic compound in which the carbonyl group is attached to a carbon atom at the end of a carbon chain.
- A ketone is an organic compound in which the carbonyl group is attached to a carbon atom within the carbon chain.
- Aldehydes and ketones generally have lower boiling points than those of alcohols.

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4.13: Carboxylic Acids

Vinegar (dilute acetic acid) is available in every grocery store in the country. The large one-gallon jugs can be found in households everywhere. One magazine published an article listing 150 ways to use vinegar, from getting dirt off of your computer to cleaning window blinds. A mixture of vinegar and baking soda is an excellent way to clean sink drains. You can also clean your carpets and your piano keys. Not bad for something that may have struck you as merely an ingredient in salad dressing!

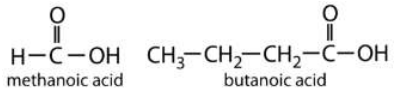
Carboxylic Acids

Organic acids such as acetic acid all contain a functional group called a **carboxyl group**.



The carboxyl group contains the $C{=}O$ of the carbonyl group, with the carbon atom also being bonded to a hydroxyl $(-OH)$ group. A **carboxylic acid** is an organic compound that contains the carboxyl functional group. The general formula for a carboxylic acid can be abbreviated as $R{-}COOH$. The carbon atom of the carboxyl group may be attached to a hydrogen atom or to a carbon chain. The naming of a carboxylic acid is as follows:

1. Name the parent compound by finding the longest continuous chain that contains the carboxyl group.
2. Change the *-e* at the end of the name of the alkane to *-oic acid*.



Properties of Carboxylic Acids

Carboxylic acids are all weak acids. In aqueous solution, the $O{-}H$ bond of the hydroxyl group can break, yielding a negative carboxylate ion and the hydrogen ion.

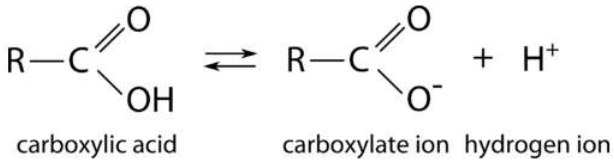


Figure 4.13.1: Equilibrium between carboxyl group and carboxylate ion.

The smaller members of the aliphatic carboxylic acid series are colorless, volatile liquids with strong odors. Ethanoic acid is commonly known as acetic acid; common household vinegar is a 5% solution of acetic acid. Larger carboxylic acids are solids with low melting points. There are numerous aromatic carboxylic acids, which are all crystalline solids. Carboxylic acids can form intermolecular hydrogen bonds, and thus have relatively high melting and boiling points compared to other organic compounds that cannot hydrogen bond. Carboxylic acids with shorter carbon chains are very soluble in water, while those with longer carbon chains are less soluble.

Many carboxylic acids occur naturally in plants and animals. Citrus fruits such as oranges and lemons contain citric acid.

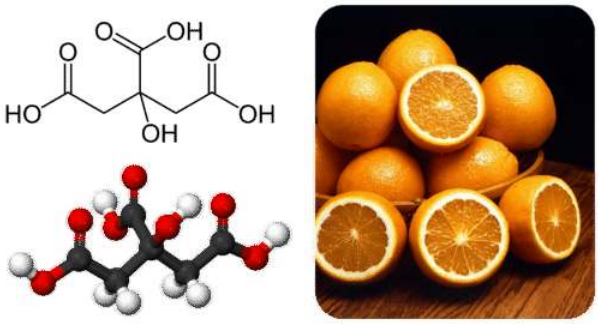


Figure 4.13.2: Citric acid is a large carboxylic acid with three ionizable hydrogen atoms. It is found in citrus fruits and gives them their sour or tart flavor.

Ethanoic and citric acids are frequently added to foods to give them a tart flavor. Benzoic, propanoic, and sorbic acids are used as food preservatives because of their ability to kill microorganisms that can lead to spoilage. Methanoic and ethanoic acids are widely used in industry as starting points for the manufacture of paints, adhesives, and coatings.

Summary

- Organic acids, such as acetic acid, all contain a functional group called a carboxyl group.
- The carboxyl group contains the $C{=}O$ of the carbonyl group, with the carbon atom also being bonded to a hydroxyl $(-OH)$ group.
- A carboxylic acid is an organic compound that contains the carboxyl functional group.

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4.14: Alkyl Halides

A class of simple alkyl halides called chlorofluorocarbons (CFCs) was once very widely used in aerosol sprays and as refrigerants. One such example is CCl_3F, or trichlorofluoromethane. Unfortunately, CFCs are harmful to the ozone layer of our upper atmosphere. Ozone is critical in limiting the amount of damaging ultraviolet radiation that reaches the Earth. CFCs react with the ozone and damage it, leaving the earth less protected.

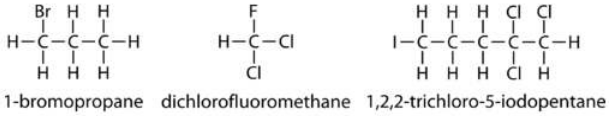
Beginning in the late 1970s, ozone depletion was recognized as a significant environmental issue. The most dramatic decrease in ozone occurs seasonally over the continent of Antarctica. The size and duration of the ozone hole steadily increased, with the largest hole recorded in 2006. Fortunately, most countries have recognized the danger of CFCs and dramatically curtailed their use in recent years. It is hoped that ozone depletion will slow, and that the ozone layer may eventually be restored to its earlier levels.

Alkyl Halides

An **alkyl halide** is an organic compound in which one or more halogen atoms are substituted for one or more hydrogen atoms in a hydrocarbon. The general formulas for organic molecules with functional groups use the letter R to stand for the rest of the molecule outside of the functional group. Because there are four possible halogen atoms (fluorine, chlorine, bromine, or iodine) that can act as the functional group, we use the general formula $R-X$ to represent an alkyl halide. The rules for naming simple alkyl halides are listed below.

1. Name the parent compound by finding the longest continuous carbon atom chain that also contains the halogen. Add a prefix for the particular halogen atom. The prefixes for each of the four halogens are *fluoro-*, *chloro-*, *bromo-*, and *iodo-*. If more than one kind of halogen atom is present, put them in alphabetical order. If there is more than one of the same halogen on a given carbon atom, use the prefixes *di-*, *tri-*, or *tetra-* before the prefix for the halogen.
2. As with hydrocarbons, number the carbon chain in a way that makes the sum of halogen numbers as low as possible. If different halogens are in equivalent positions, give the lower number to the one that comes first in alphabetical order.
3. Add the numerical prefix into the name before the halogen prefix.
4. Separate numbers with commas, and separate numbers from names or prefixes with a hyphen. There are no spaces in the name.

Listed below are some examples of names and structural formulas of a few alkyl halides.



Note that for the structure based on methane, no number needs to be used, since there is only one carbon atom. In the third example, the *chloro-* is listed first alphabetically and the chain is numbered so that the sum of the numbers is as low as possible.

Uses of Alkyl Halides

Alkyl halides are often used as synthetic intermediates in the laboratory. Although these compounds were once widely used as dry cleaning solvents, coolants in refrigerators and air conditioners, and propellants in hairsprays and deodorants, increasing awareness of their toxicity has led to a widespread decrease in applications for these materials. Some specific compounds are still used. Halothane (2-bromo-2-chloro-1,1,1-trifluoroethane) is still used in some situations as an inhalation anesthetic. The compound DDT is a very effective pesticide, but is only used when nothing else works, because of its harmful effects on the environment.

Summary

- An alkyl halide is an organic compound in which one or more halogen atoms are substituted for one or more hydrogen atoms in a hydrocarbon.
- Alkyl halides are often used as synthetic intermediates in the laboratory.

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CHAPTER OVERVIEW

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5.1: Word Equations



Figure 5.1.1 (Public Domain; User:Daderot/Wikimedia Commons via Wikipedia)

What's for Dinner?

Various ways of recording recipes have developed over the centuries. The cookbook shown above was written by a woman who probably collected all her own recipes. Later, printed cookbooks became available (even guys had no excuse for not being able to cook). Today we can find recipes on a number of internet sites and can quickly search for information on how to cook anything we want. Reading a recipe sometimes requires we understand a few codes and symbols (what's the difference between a tsp and a Tsp?), but the information on what we start with and what we end up with is there.

Writing Chemical Equations

Chemical reactions are occurring all around us. Plants use sunlight to drive their photosynthetic process and produce energy. Cars and other vehicles burn gasoline in order to power their engines. Batteries use electrochemical reactions to produce energy and power many everyday devices. Many chemical reactions are going on within the human body as well, particularly during the digestion of food.

In math class, you have written and solved many mathematical equations. Chemists keep track of chemical reactions by writing equations as well. In any chemical reaction, one or more substances—called **reactants**—are converted into one or more new substances—called **products**. The general form of the equation for such a process looks like this:

$$\text{Reactants} \rightarrow \text{Products}$$

Unlike a math equation, a chemical equation does not use an equal sign. Instead, the arrow is called a yield sign and so the equation is described as "reactants yield products".

Word Equations

You can describe a chemical reaction by writing a **word equation**. When silver metal is exposed to sulfur, it reacts to form silver sulfide. Silver sulfide is commonly known as tarnish and turns the surface of silver objects dark and streaky black (see figure below). The sulfur that contributes to tarnish can come from traces of sulfur in the air, or from foods such as eggs. The word equation for the process is:

$$\text{Silver} + \text{sulfur} \rightarrow \text{Silver sulfide}$$

The silver and the sulfur are the reactants in the equation, while the silver sulfide is the product.



Figure 5.1.2: You can see dark spots of tarnished (silver sulfide) forming on this ring as it reacts with sulfur compounds in the air. (CK-12 Curriculum Materials license; CK-12 Foundation via CK-12 Foundation)

Another common chemical reaction is the burning of methane gas. Methane is the major component of natural gas and is commonly burned on a gas stove or in a Bunsen burner (figure below). Burning is a chemical reaction in which some type of fuel is

reacted with oxygen gas. The products of the reaction in the burning of methane, as well as other fuels, are carbon dioxide and water. The word equation for this reaction is:

$$\text{Methane} + \text{oxygen} \rightarrow \text{carbon dioxide} + \text{water}$$

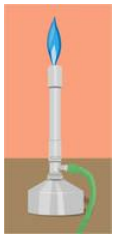


Figure 5.1.3: A Bunsen burner is commonly used to heat substances in a chemistry lab. Methane is reacted with oxygen to form carbon dioxide and water. (CK-12 Curriculum Materials license; CK-12 Foundation via CK-12 Foundation)

Word equations can be very useful, but do have one major drawback—they cannot be used for any quantitative work. A word equation does not tell how many moles of each material are needed, or how many moles of product are formed.



Summary

- Word equations are used to describe the conversion of reactants to products.

Review

1. Write the generic form of a chemical reaction.
2. What are reactants?
3. What are products?

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5.2: Chemical Equations



Figure 5.2.1 (Public Domain; jons2 at pdphoto.org via Wikipedia)

How do you make shrimp gumbo?

Shrimp gumbo is one of many dishes that are part of the Cajun culture in Louisiana. It's a spicy dish that needs careful control of all the ingredients so that it has a "kick", but is not overwhelming. Recipes convey not only what the preparation entails, but also describe how much of each ingredient is needed, and the details of how to cook the meal. Similarly, we need this type of information in order to carry out chemical reactions successfully and safely.

Chemical Equations

Word equations are time-consuming to write and do not prove to be convenient for many of the things that chemists need to do with equations. A **chemical equation** is a representation of a chemical reaction that displays the reactants and products with chemical formulas. The chemical equation for the reaction of methane with oxygen is shown:

$$\mathrm{CH_4 + O_2 \rightarrow CO_2 + H_2O}$$

The equation above, called a **skeleton equation**, is an equation that shows only the formulas of the reactants and products with nothing to indicate the relative amounts. The first step in writing an accurate chemical equation is to write the skeleton equation, making sure that the formulas of all substances involved are written correctly. All reactants are written to the left of the yield arrow, separated from one another by a plus sign. Likewise, products are written to the right of the yield arrow, also separated with a plus sign.

It is often important to know the physical states of the reactants and products taking part in a reaction. To do this, put the appropriate symbol in parentheses after each formula: (s) for solid, (l) for liquid, (g) for gas, and (aq) for an aqueous (water-based) solution. The previous reaction becomes:

$$\mathrm{CH_4\,(g) + O_2\,(g) \rightarrow CO_2\,(g) + H_2O\,(l)}$$

The table below shows a listing of symbols used in chemical equations. Some, such as the double arrow which represents equilibrium, and the use of a catalyst in a reaction, will be detailed in other concepts.

Table 5.2.1: Symbols Used in Chemical Equations

Symbols	Description
$+$	Used to separate multiple reactants or products.
$\rightarrow$	Yield sign; separates reactants from products.
$\rightleftharpoons$	Replaces the yield sign for reversible reactions that reach equilibrium.
(s)	Reactant or product in the solid state.
(l)	Reactant or product in the liquid state.
(g)	Reactant or product in the gaseous state.
(aq)	Reactant or product in an aqueous solution (dissolved in water).

Symbols	Description
$\xrightarrow{Pt}$	Formula written above the arrow is used as a catalyst in the reaction.
$\xrightarrow{\Delta}$	Triangle indicates that the reaction is being heated.



Summary

- A chemical equation is representation a chemical reaction using chemical formulas reactants and products, as well as symbols.
- Symbols used in chemical equations are described and explained.

Review

1. What does a skeleton equation tell you?
2. Why would you want to know the physical state of materials in a chemical reaction?
3. In a chemical reaction what does symbol → mean?
4. If I see Δ over the arrow, what does this indicate?

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5.3: Balancing Equations



Figure 5.3.1 (Public Domain; Joseph Allen via Wikipedia)

Any leftovers?

When you cook a meal, quite often there are leftovers because you prepared more than people would eat at one sitting. Sometimes when you repair a piece of equipment, you end up with what are called "pocket parts"—small pieces you put in your pocket because you're not sure where they belong. Chemistry tries to avoid leftovers and pocket parts. In normal chemical processes, we cannot create or destroy matter (law of conservation of mass). If we start out with ten carbon atoms, we need to end up with ten carbon atoms. John Dalton's atomic theory said that chemical reactions basically involve the rearrangement of atoms. Chemical equations need to follow these principles in order to be correct.

Balancing Chemical Equations

A **balanced equation** is a chemical equation in which mass is conserved and there are equal numbers of atoms of each element on both sides of the equation. We can write a chemical equation for the reaction of carbon with hydrogen gas to form methane $\left(\mathrm{CH_4}\right)$:

$$\begin{array}{ccccc} \mathrm{C}\,(s) & + & \mathrm{H_2}\,(g) & \rightarrow & \mathrm{CH_4}\,(g) \\ 2\ \mathrm{C\ atoms} & & 2\ \mathrm{H\ atoms} & & 1\ \mathrm{C\ atom},\ 4\ \mathrm{H\ atoms} \end{array}$$

In order to write a correct equation, you must first write the correct skeleton equation with the correct chemical formulas. Recall that hydrogen is a diatomic molecule and so is written as $\mathrm{H_2}$.

When we count the number of atoms of both elements, shown under the equation, we see that the equation is not balanced. There are only 2 atoms of hydrogen on the reactant side of the equation, while there are 4 atoms of hydrogen on the product side. We can balance the above equation by adding a coefficient of 2 in front of the formula for hydrogen.

$$\mathrm{C}\,(s) + 2\mathrm{H_2}\,(g) \rightarrow \mathrm{CH_4}\,(g)$$

A **coefficient** is a small whole number placed in front of a formula in an equation in order to balance it. The 2 in front of the $\mathrm{H_2}$ means that there are a total of $2 \times 2 = 4$ atoms of hydrogen as reactants. Visually, the reaction looks like the figure below.

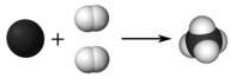


Figure 5.3.2: Reaction between carbon and hydrogen to form methane. (Public Domain; Ben Mills (Wikimedia: Benjah-bmm27 via Wikipedia and http://commons.wikimedia.org/wiki/File:Methane-3D-space-filling.png)

In the balanced equation, there is one atom of carbon and four atoms of hydrogen on both sides of the arrow. Below are guidelines for writing and balancing chemical equations.

1. Determine the correct chemical formulas for each reactant and product.
2. Write the skeleton equation.
3. Count the number of atoms of each element that appears as a reactant and as a product. If a polyatomic ion is unchanged on both sides of the equation, count it as a unit.
4. Balance each element one at a time by placing coefficients in front of the formulas.
    a. It is best to begin by balancing elements that only appear in one chemical formula on each side of the equation.
    b. No coefficient is written for a 1.
    c. NEVER change the subscripts in a chemical formula—you can only balance equations by using coefficients.

5. Check each atom or polyatomic ion to be sure that they are equal on both sides of the equation.
6. Make sure that all coefficients are in the lowest possible ratio. If necessary, reduce to the lowest ratio.

5.3.1 Example : Balancing Chemical Equations

Aqueous solutions of lead (II) nitrate and sodium chloride are mixed. The products of the reaction are an aqueous solution of sodium nitrate and a solid precipitate of lead (II) chloride. Write the balanced chemical equation for this reaction.

Solution

Step 1: Plan the problem.

Follow the steps for writing and balancing a chemical equation listed in the text.

Step 2: Solve.

Write the skeleton equation with the correct formulas.

$$\mathrm{Pb(NO_3)_2}\,(aq) + \mathrm{NaCl}\,(aq) \rightarrow \mathrm{NaNO_3}\,(aq) + \mathrm{PbCl_2}\,(s)$$

Count the number of each atom or polyatomic ion on both sides of the equation.

Reactants	**Products**
1 Pb atom	1 Pb atom
2 $\mathrm{NO_3^-}$ ions	1 $\mathrm{NO_3^-}$ ions
1 Na atom	1 Na atom
1 Cl atom	2 Cl atoms

The nitrate ions and the chlorine atoms are unbalanced. Start by placing a 2 in front of the NaCl. This increases the reactant counts to 2 Na atoms and 2 Cl atoms. Then place a 2 in front of the $\mathrm{NaNO_3}$. The result is:

$$\mathrm{Pb(NO_3)_2}\,(aq) + 2\mathrm{NaCl}\,(aq) \rightarrow 2\mathrm{NaNO_3}\,(aq) + \mathrm{PbCl_2}\,(s)$$

The new count for each atom and polyatomic ion becomes:

Reactants	**Products**
1 Pb atom	1 Pb atom
2 $\mathrm{NO_3^-}$ ions	2 $\mathrm{NO_3^-}$ ions
2 Na atom	2 Na atom
2 Cl atom	2 Cl atoms

Step 3: Think about your result.

The equation is now balanced since there are equal numbers of atoms of each element on both sides of the equation.



Summary

- The process of balancing chemical equations is described.

Review

1. What is the law of conservation of mass?
2. How did Dalton describe the process of a chemical reaction?
3. Why don’t we change the subscripts in order to balance an equation?

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5.4: Oxygen in Reactions

People worry a lot about their smiles. Over the years, teeth do discolor some, so the procedure of teeth bleaching has become more and more popular. Best done in a dentist's office, various chemical preparations containing peroxides are used to whiten teeth. Less effective, but easier to use are "teeth-whitening" toothpastes (also containing peroxides) that promise to give you a brighter smile.

Oxygen in Reactions

Many elements simply combine with oxygen to form the oxide of that element. The heating of magnesium in air allows it to combine with oxygen from the air to form magnesium oxide:

$$2\text{Mg}\,(s) + \text{O}_2\,(g) \rightarrow 2\text{MgO}\,(s)$$

Compounds can also react with oxygen, possibly creating oxides of more than one element. When methane burns, carbon dioxide and water are produced:

$$\text{CH}_4\,(g) + 2\text{O}_2\,(g) \rightarrow \text{CO}_2\,(g) + 2\text{H}_2\text{O}\,(g)$$

Carbon dioxide is an oxide of carbon, while water is an oxide of hydrogen. Early scientists viewed **oxidation** as a process in which a substance was reacted with oxygen to produce one or more oxides. In the previous examples, magnesium and methane are oxidized.

Oxidation is also defined as a loss of hydrogen atoms. In the following equation, ethanol is oxidized to acetaldehyde by the loss of two hydrogen atoms:

$$\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CHO} + 2\text{H atoms}$$

Oxidation does not necessarily require heating. Iron that is exposed to air and water slowly oxidizes in a process commonly known as rusting. Bleaches contain various compounds such as sodium hypochlorite (NaClO), which releases oxygen that oxidizes stains. Hydrogen peroxide (H_2O_2) releases oxygen as it spontaneously decomposes. It acts as a bleach and an antiseptic that kills bacteria by oxidizing them.

The chemical reaction that is the opposite of oxidation is called reduction. Following from the notion that oxidation was originally thought to mean only the addition of oxygen, **reduction** was thought to be only the removal of oxygen from a substance. Many naturally occurring metal ores are present as oxides. The pure metals can be extracted by reduction. Iron is obtained from iron (III) oxide by reacting with carbon at high temperatures:

$$2\text{Fe}_2\text{O}_3\,(s) + 3\text{C}\,(s) \rightarrow 4\text{Fe}\,(s) + 3\text{CO}_2\,(g)$$

The removal of oxygen from the Fe_2O_3 means that it is being reduced to Fe. Note that an oxidation process is simultaneously occurring. The carbon reactant is being oxidized to CO_2. This is an important concept. Oxidation and reduction must happen together. Neither can happen alone in a reaction.

Reduction can also be considered as a gain of hydrogen. The reverse of the ethanol $\rightarrow$ acetaldehyde reaction shown above is a reduction reaction:

$$\text{CH}_3\text{CHO} + 2\text{H atoms} \rightarrow \text{CH}_3\text{CH}_2\text{OH}$$

Summary

- Oxidation is a process in which a substance is reacted with oxygen to produce one or more oxides; it is also defined as a loss of hydrogen atoms.
- Reduction is the removal of oxygen from a substance, or the gain of hydrogen atoms.
- Oxidation and reduction reactions must occur together; neither can happen alone in a reaction.

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5.5: Redox Reactions and Ionic Compounds

Nitric acid has many uses in the manufacture of fertilizers and explosives. Most nitric acid is manufactured from ammonia using a three-step process. The ammonia is oxidized to HNO_3 through the formation of several nitrogen oxides, finally resulting in the acid.

Redox Reactions and Ionic Compounds

In the course of a chemical reaction between a metal and a nonmetal, electrons are transferred from the metal atoms to the nonmetal atoms. For example, when zinc metal is mixed with sulfur and heated, the compound zinc sulfide is produced. Two valence electrons from each zinc atom are transferred to each sulfur atom.

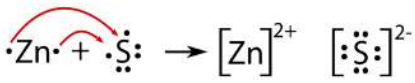


Figure 5.5.1: Reaction between zinc and sulfur.

Since the zinc is losing electrons in the reaction, it is being oxidized. The sulfur is gaining electrons and is thus being reduced. An **oxidation-reduction reaction** is a reaction that involves the full or partial transfer of electrons from one reactant to another. **Oxidation** is the full or partial loss of electrons or the gain of oxygen. **Reduction** is the full or partial gain of electrons or the loss of oxygen. A **redox reaction** is another term for an oxidation-reduction reaction.

Each of these processes can be shown in a separate equation called a half-reaction. A **half-reaction** is an equation that shows either the oxidation or the reduction reaction that occurs during a redox reaction.

$$\text{Oxidation: } \text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$$
$$\text{Reduction: } \text{S} + 2\text{e}^- \rightarrow \text{S}^{2-}$$

It is important to remember that the two half-reactions occur simultaneously. The resulting ions that are formed are then attracted to one another in an ionic bond.

Another example of an oxidation-reduction reaction involving electron transfer is the well-known combination of metallic sodium and chlorine gas to form sodium chloride:

$$2\text{Na} + \text{Cl}_2 \rightarrow 2\text{NaCl}$$

The half reactions are as follows:

$$\text{Oxidation: } \text{Na} \rightarrow \text{Na}^+ + \text{e}^-$$
$$\text{Reduction: } \text{Cl} + \text{e}^- \rightarrow \text{Cl}^-$$

We will concern ourselves with the balancing of these equations at another time.

Summary

- An oxidation-reduction reaction, or redox reaction, is a reaction that involves the full or partial transfer of electrons from one reactant to another.
- Oxidation is the full or partial loss of electrons or the gain of oxygen.
- Reduction is the full or partial gain of electrons or the loss of oxygen.
- A half-reaction is an equation that shows either the oxidation or the reduction reaction that occurs during a redox reaction.
- Examples of oxidation-reduction reactions are shown.

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5.6: Oxidizing and Reducing Agents

Life on planet Earth is a complicated and well-organized set of processes. Animals are designed to breathe oxygen, and plants are designed to produce oxygen. Photosynthesis is the means by which plants produce the oxygen that animals need for life. Light striking a plant pigment known as chlorophyll initiates a complex series of reactions, many of which involve redox processes complete with the movement of electrons. In this series of reactions, water is converted to oxygen gas, and we have something to sustain our lives.

Oxidizing and Reducing Agents

The reaction below is a redox reaction that produces zinc sulfide:

$$\mathrm{Zn} + \mathrm{S} \rightarrow \mathrm{ZnS}$$

The half-reactions can be written:

$$\text{Oxidation: } \mathrm{Zn} \rightarrow \mathrm{Zn}^{2+} + 2\mathrm{e}^-$$
$$\text{Reduction: } \mathrm{S} + 2\mathrm{e}^- \rightarrow \mathrm{S}^{2-}$$

In the reaction above, zinc is being oxidized by losing electrons. However, there must be another substance present that gains those electrons and in this case that is the sulfur. In other words, the sulfur is causing the zinc to be oxidized. Sulfur is called the oxidizing agent. The zinc causes the sulfur to gain electrons and become reduced and so the zinc is called the reducing agent. The **oxidizing agent** is a substance that causes oxidation by accepting electrons. The **reducing agent** is a substance that causes reduction by losing electrons. The simplest way to think of this is that the oxidizing agent is the substance that is reduced, while the reducing agent is the substance that is oxidized. The example below shows how to analyze a redox reaction.

5.6.1 Example

When chlorine gas is bubbled into a solution of sodium bromide, a reaction occurs which produces aqueous sodium chloride and bromine. Determine what is being oxidized and what is being reduced. Identify the oxidizing and reducing agents.

$$\mathrm{Cl_2}\,(g) + 2\mathrm{NaBr}\,(aq) \rightarrow 2\mathrm{NaCl}\,(aq) + \mathrm{Br_2}\,(l)$$

Solution:

Step 1: Plan the problem.

Break the reaction down into a net ionic equation and then into half-reactions. The substance that loses electrons is being oxidized and is the reducing agent. The substance that gains electrons is being reduced and is the oxidizing agent.

Step 2: Solve.

$$\mathrm{Cl_2}\,(g) + \cancel{2\mathrm{Na^+}\,(aq)} + 2\mathrm{Br^-}\,(aq) \rightarrow \cancel{2\mathrm{Na^+}\,(aq)} + 2\mathrm{Cl^-}\,(aq) + \mathrm{Br_2}\,(l)$$
$$\mathrm{Cl_2}\,(g) + 2\mathrm{Br^-}\,(aq) \rightarrow 2\mathrm{Cl^-}\,(aq) + \mathrm{Br_2}\,(l) \quad \text{(net ionic equation)}$$
$$\text{Oxidation: } \mathrm{Cl_2}\,(g) + 2\mathrm{e}^- \rightarrow 2\mathrm{Cl^-}\,(aq)$$
$$\text{Reduction: } 2\mathrm{Br^-}\,(aq) \rightarrow \mathrm{Br_2}\,(l) + 2\mathrm{e}^-$$

The $\mathrm{Cl_2}$ is being reduced and is the oxidizing agent. The $\mathrm{Br^-}$ is being oxidized and is the reducing agent.

Summary

- The oxidizing agent is a substance that causes oxidation by accepting electrons.
- The reducing agent is a substance that causes reduction by losing electrons.
- Examples of oxidizing and reducing agents are shown.

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5.7: Molecular Redox Reactions

Acetone is a versatile chemical used both in manufacture of plastics and as a solvent. It is a major constituent of such products as nail polish remover, paints, and cleaning fluids. The manufacture of acetone involves formation of an intermediate peroxide compound by oxidation, followed by formation of the final product.

Molecular Redox Reactions

The electron loss and gain is easy to see in a reaction in which ions are formed. However, in many reactions, no such electron transfer occurs. In a molecular compound, electrons are shared between atoms in a type of bond called a covalent bond. Yet, it is still common for reactions involving molecular compounds to be classified as redox reactions.

When hydrogen gas is reacted with oxygen gas, water is formed as the product.

$$2\mathrm{H}_2\,(g) + \mathrm{O}_2\,(g) \rightarrow 2\mathrm{H}_2\mathrm{O}\,(l)$$

In the individual hydrogen molecules, a pair of bonding electrons is shared equally between the hydrogen atoms (a nonpolar covalent bond). Likewise, the bonding electrons in the oxygen molecule are also shared equally between the two oxygen atoms. However, when the atoms are rearranged to form the water molecule, the electron sharing is no longer equal. In each hydrogen-oxygen bond in the water molecule, the bonding electrons are more attracted to the oxygen atom than they are to the hydrogen atom. We know this because oxygen has a higher electronegativity than hydrogen.

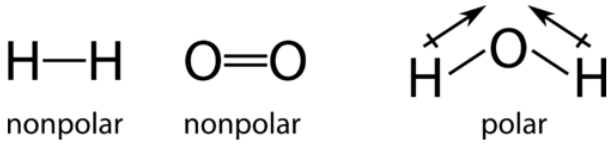


Figure 5.7.1: Bonding electrons in hydrogen, oxygen, and water.

In the course of this reaction, electrons are shifted away from each hydrogen atom and towards the oxygen atom. The hydrogen is oxidized because it undergoes a partial loss of electrons. Even though the loss is not complete enough to form ions, the hydrogen atoms in water have less electron density near them than they did in the H_2 molecule. The oxygen is reduced because it undergoes a partial gain of electrons. The oxygen atom in water has greater electron density here than it did in the O_2 molecule.

Another approach to this type of problem is to go back to our earlier definitions of oxidation being the gain of oxygen or loss of hydrogen, and reduction being the gain of hydrogen or loss of oxygen. This makes the decision about redox reactions much easier. The hydrogen is oxidized because it added oxygen to form water. Conversely, the oxygen is reduced because it added hydrogen to form water.

Summary

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5.8: Corrosion

The tractor was once a very useful piece of farm equipment. But tractors got old, likely broke down a lot, and were eventually difficult to find parts for. Farmers bought new, more efficient tractors with all the latest gadgets. There is not much of a market for old tractors, so they often sit parked out of the way, exposed to the weather, and quietly left to rust.

Corrosion

Rust is a combination of several different oxides of iron. The equations below show the steps involved in one of the many processes of rust formation.

$$2\mathrm{Fe}\,(s) + \mathrm{O_2}\,(g) + 4\mathrm{H^+}\,(aq) \rightarrow 2\mathrm{Fe^{2+}}\,(aq) + 2\mathrm{H_2O}\,(l)$$
$$4\mathrm{Fe^{2+}}\,(aq) + \mathrm{O_2}\,(g) + 6\mathrm{H_2O}\,(l) \rightarrow 2\mathrm{Fe_2O_3 \cdot H_2O}\,(s) + 8\mathrm{H^+}\,(aq)$$

Iron is first oxidized to iron (II) ions by oxygen. In the second step, the iron (II) ions are further oxidized and combine with water and oxygen gas to produce a hydrated form of iron (III) oxide known as rust. Rusting is one of many examples of corrosion. **Corrosion** is the deterioration of metals by redox processes. Corrosion causes enormous amounts of damage to buildings, bridges, ships, cars, and other objects. It has been estimated that corrosion costs the U.S. economy over $100 billion each year. A great amount of time and effort is spent to try to limit or prevent corrosion.

Corrosion Resistance

Some metals, such as gold and platinum, do not corrode easily because they are very resistant to oxidation by common substances. Some other metals begin to be oxidized, but are further protected from additional corrosion by a coating formed on the surface. Aluminum reacts with oxygen to form aluminum oxide, which remains tightly packed on the surface. The aluminum oxide prevents the interior of the aluminum from corroding. Not all corrosion is a result of reaction with oxygen. Copper corrodes by reaction with carbon dioxide to form copper (II) carbonate. This distinctive green compound is also called patina and prevents the copper underneath from further corrosion (see Statue of Liberty in the figure below).



Figure 5.8.1: Statue of Liberty.

Conversely, the iron oxides that form during the corrosion of iron form a layer that flakes off easily, rather than remaining tight to the surface. This allows the iron to corrode completely through until the iron object is destroyed.

One way to prevent corrosion is to protect the surface of metal. Covering the surface of a metal object with paint or oil will prevent corrosion by not allowing oxygen to contact it. Unfortunately, scratches in the paint or wearing off of the oil will allow the corrosion to begin. Corrosion-sensitive metals can also be coated with another metal that is resistant to corrosion. A "tin can" is actually made of iron coated with a thin layer of tin, which protects the iron.

Corrosion can also be controlled by connecting the object to be protected to another object made of a metal that is corroded even more easily. When an iron nail is wrapped with a strip of zinc and exposed to water, the zinc (being a more active metal than iron) is oxidized while the iron remains intact. This technique, called cathodic protection, is commonly used to prevent the hulls of steel ships from rusting. Blocks of zinc are attached to the underside of the hull (see figure below). The zinc blocks preferentially corrode, keeping the hull intact. The zinc blocks must be periodically replaced to maintain the protection of the iron.



Figure 5.8.2: Small blocks of zinc are attached to the steel hull of this ship.

Summary

- Corrosion is the deterioration of metals by redox processes.
- Examples of corrosion are given.

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5.9: Assigning Oxidation Numbers

Moving from studying the element iron to iron compounds, we need to be able to clearly designate the form of the iron ion. An example of this is iron that has been oxidized to form iron oxide during the process of rusting. Although Antoine Lavoisier first began the idea of oxidation as a concept, it was Wendell Latimer (1893-1955) who gave us the modern concept of oxidation numbers. His 1938 book *The Oxidation States of the Elements and Their Potentials in Aqueous Solution* laid out the concept in detail. Latimer was a well-known chemist who later became a member of the National Academy of Sciences. Not bad for a gentleman who started college planning on being a lawyer.

Assigning Oxidation Numbers

The **oxidation number** is a positive or negative number that is assigned to an atom to indicate its degree of oxidation or reduction. In oxidation-reduction processes, the driving force for chemical change is in the exchange of electrons between chemical species. A series of rules have been developed to determine oxidation numbers:

1. For free elements (uncombined state), each atom has an oxidation number of zero. H_2, Br_2, Na, Be, K, O_2, P_4, all have an oxidation number of 0.
2. Monatomic ions have oxidation numbers equal to their charge. $Li^+ = +1$, $Ba^{2+} = +2$, $Fe^{3+} = +3$, $I^- = -1$, $O^{2-} = -2$, etc. Alkali metal oxidation numbers $= +1$. Alkaline earth oxidation numbers $= +2$. Aluminum $= +3$ in all of its compounds. Oxygen's oxidation number $= -2$ *except* when in hydrogen peroxide (H_2O_2), or a peroxide ion $\left(O_2^{2-}\right)$ where it is -1.
3. Hydrogen's oxidation number is $+1$, except for when bonded to metals as the hydride ion forming binary compounds. In LiH, NaH, and CaH_2, the oxidation number is -1.
4. Fluorine has an oxidation number of -1 in all of its compounds.
5. Halogens (Cl, Br, I) have negative oxidation numbers when they form halide compounds. When combined with oxygen, they have positive numbers. In the chlorate ion $\left(ClO_3^-\right)$, the oxidation number of Cl is $+5$, and the oxidation number of O is -2.
6. In a neutral atom or molecule, the sum of the oxidation numbers must be 0. In a polyatomic ion, the sum of the oxidation numbers of all the atoms in the ion must be equal to the charge on the ion.

5.9.1 Example

What is the oxidation number for manganese in the compound potassium permanganate $\left(KMnO_4\right)$?

Solution

The oxidation number for K is $+1$ (rule 2).

The oxidation number for O is -2 (rule 2).

Since this is a compound (there is no charge indicated on the molecule), the net charge on the molecule is zero (rule 6).

So we have:

$$\begin{aligned} +1 + Mn + 4(-2) &= 0 \\ Mn - 7 &= 0 \\ Mn &= +7 \end{aligned}$$

When dealing with oxidation numbers, we must always include the charge on the atom.

Another way to determine the oxidation number of Mn in this compound is to recall that the permanganate anion $\left(MnO_4^-\right)$ has a charge of -1. In this case:

$$\begin{aligned} Mn + 4(-2) &= -1 \\ Mn - 8 &= -1 \\ Mn &= +7 \end{aligned}$$

5.9.2 Example

What is the oxidation number for iron in Fe_2O_3?

Solution

$$\begin{aligned} \text{O is } -2 \text{ (rule 2)} \\ 2\text{Fe} + 3(-2) &= 0 \\ 2\text{Fe} &= 6 \\ \text{Fe} &= 3 \end{aligned}$$

If we have the compound FeO, then $\text{Fe} + (-2) = 0$ and $\text{Fe} = 2$. Iron is one of those materials that can have more than one oxidation number.

The halogens (except for fluorine) can also have more than one number. In the compound NaCl, we know that Na is $+1$, so Cl must be -1. But what about Cl in NaClO_3?

$$\begin{aligned} \text{Na} &= 1 \\ \text{O} &= -2 \\ 1 + \text{Cl} + 3(-2) &= 0 \\ 1 + \text{Cl} - 6 &= 0 \\ \text{Cl} - 5 &= 0 \\ \text{Cl} &= +5 \end{aligned}$$

Not quite what we expected, but Cl, Br, and I will exhibit multiple oxidation numbers in compounds.

Summary

- The oxidation number is a positive or negative number that is assigned to an atom to indicate its degree of oxidation or reduction.
- In oxidation-reduction processes, the driving force for chemical change is in the exchange of electrons between chemical species.
- Six rules for determining oxidation numbers are listed.
- Examples of oxidation number determinations are provided.

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5.10: Changes in Oxidation Number in Redox Reactions

Zinc is an important component of many kinds of batteries. This metal is mined as zinc compounds, one of which is zinc carbonate. To obtain the pure metal, the ore must go through the following chemical processes:

1. High temperatures and hot air blasts are used to roast the ore.

$$\mathrm{ZnCO_3\,(s) + heat \rightarrow ZnO\,(s) + CO_2\,(g)}$$

2. Then the ZnO is treated with carbon.

$$\begin{aligned}\mathrm{ZnO\,(s) + C\,(s) + heat} &\rightarrow \mathrm{Zn\,(g) + CO\,(g)}\\ \mathrm{ZnO\,(s) + CO\,(g) + heat} &\rightarrow \mathrm{Zn\,(g) + CO_2\,(g)}\end{aligned}$$

The result is the pure metal, which can then be fabricated into a variety of products.

Changes in Oxidation Number in Redox Reactions

Consider the reaction below between elemental iron and copper sulfate:

$$\mathrm{Fe + CuSO_4 \rightarrow FeSO_4 + Cu}$$

In the course of the reaction, the oxidation number of Fe increases from zero to $+2$. The oxidation number of copper decreases from $+2$ to 0. This result is in accordance with the activity series. Iron is above copper in the series, so will be more likely to form Fe^{2+} while converting the Cu^{2+} to metallic copper $\left(\mathrm{Cu}^{0}\right)$.

A loss of negatively-charged electrons corresponds to an increase in oxidation number, while a gain of electrons corresponds to a decrease in oxidation number. Therefore, the element or ion that is oxidized undergoes an increase in oxidation number. The element or ion that is reduced undergoes a decrease in oxidation number. The table below summarizes the processes of oxidation and reduction.

Processes of Oxidation and Reduction

Table 5.10.1 : Processes of Oxidation and Reduction

Oxidation	Reduction
Complete loss of electrons (ionic reaction).	Complete gain of electrons (ionic reaction).
Gain of oxygen.	Loss of oxygen.
Loss of hydrogen in a molecular compound.	Gain of hydrogen in a molecular compound.
Increase in oxidation number.	Decrease in oxidation number.

5.10.1 Example

Use changes in oxidation number to determine which atoms are oxidized and which atoms are reduced in the following reaction. Identify the oxidizing and reducing agent.

$$\mathrm{Fe_2O_3\,(s) + 3CO\,(g) \rightarrow 2Fe\,(s) + 3CO_2\,(g)}$$

Solution:

Step 1: Plan the problem.

Use the oxidation number rules to assign oxidation numbers to each atom in the balanced equation. Coefficients do not affect oxidation numbers. The oxidized atom increases in oxidation number and the reduced atom decreases in oxidation number.

Step 2: Solve.

$$\mathrm{\overset{+3\ \ -2}{Fe_2O_3}\,(s) + 3\overset{+2\ -2}{CO}\,(g) \rightarrow 2\overset{0}{Fe}\,(s) + 3\overset{+4\ -2}{CO_2}\,(g)}$$

The element carbon is oxidized because its oxidation number increases from $+2$ to $+4$. The iron (III) ion within the $\mathrm{Fe_2O_3}$ is reduced because its oxidation number decreases from $+3$ to 0. The carbon monoxide (CO) is the reducing agent since it

contains the element that is oxidized. The Fe^{3+} ion is the oxidizing agent since it is reduced in the reaction.

Summary

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5.11: Identifying Reaction Types

The reaction of copper wire with nitric acid produces a colorful mix of products that include copper (II) nitrate, nitrogen dioxide, and water. Copper salts are blue in solution, reflecting the rather unique arrangements of electrons in the d orbital as the copper ionizes from metallic copper.

Identifying Reaction Types

A redox reaction must involve a change in oxidation number for two of the elements involved in the reaction. The oxidized element increases in oxidation number, while the reduced element decreases in oxidation number.

Single-replacement reactions are redox reactions because two different elements appear as free elements (oxidation number of zero) on one side of the equation and as part of a compound on the other side. Therefore, oxidation numbers must change.

$$\mathrm{Zn} + 2\mathrm{HCl} \rightarrow \mathrm{ZnCl_2} + \mathrm{H_2}$$

Zn is oxidized from $\mathrm{Zn^0}$ to $\mathrm{Zn^{2+}}$ and the H is reduced from $\mathrm{H^+}$ to $\mathrm{H^0}$.

Combustion reactions are redox reactions because elemental oxygen $(\mathrm{O_2})$ acts as the oxidizing agent and is itself reduced.

$$\mathrm{CH_4} + 2\mathrm{O_2} \rightarrow \mathrm{CO_2} + 2\mathrm{H_2O}$$

Most combination and decomposition reactions are redox reactions, since elements are usually transformed into compounds and vice-versa. The thermite reaction involves ferric oxide and metallic aluminum:

$$\mathrm{Fe_2O_3} + 2\mathrm{Al} \rightarrow \mathrm{Al_2O_3} + 2\mathrm{Fe}$$



Figure 5.11.1: *Thermite grenade demonstration.*

We see that the iron is reduced and the aluminum oxidized during the course of the reaction.

So what types of reactions are not redox reactions? Double-replacement reactions, such as the one below, are not redox reactions because ions are simply recombined without any transfer of electrons.

$$\overset{+1}{\mathrm{Na_2}}\,\overset{+6}{\mathrm{S}}\,\overset{-2}{\mathrm{O_4}}\,(aq) + \overset{+2}{\mathrm{Ba}}(\overset{+5}{\mathrm{N}}\,\overset{-2}{\mathrm{O_3}})\,(aq) \rightarrow 2\overset{+1}{\mathrm{Na}}\,\overset{+5}{\mathrm{N}}\,\overset{-2}{\mathrm{O_3}}\,(aq) + \overset{+2}{\mathrm{Ba}}\,\overset{+6}{\mathrm{S}}\,\overset{-2}{\mathrm{O_4}}\,(s)$$

Note that the oxidation numbers for each element remain unchanged in the reaction.

Acid-base reactions involve a transfer of a hydrogen ion instead of an electron. Acid-base reactions, like the one below, are also not redox reactions.

$$\overset{+1}{\mathrm{H}}\,\overset{-1}{\mathrm{F}}\,(aq) + \overset{-3}{\mathrm{N}}\overset{+1}{\mathrm{H_3}}\,(aq) \rightarrow \overset{-3}{\mathrm{N}}\overset{+1}{\mathrm{H_4^+}}\,(aq) + \overset{-1}{\mathrm{F^-}}$$

Again, the transfer of an $\mathrm{H^+}$ ion leaves the oxidation numbers unaffected. In summary, redox reactions can always be recognized by a change in oxidation number of two of the atoms in the reaction. Any reaction in which no oxidation numbers change is not a redox reaction.

Summary

- A redox reaction must involve a change in oxidation number for two of the elements involved in the reaction.
- The oxidized element increases in oxidation number, while the reduced element decreases in oxidation number.
- Single-replacement reactions and combustion reactions **are** redox reactions.
- **Most** combination and decomposition reactions are redox reactions.
- Double-replacement reactions and acid-base reactions **are not** redox reactions.

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5.12: Properties of Acids

A cup of coffee first thing in the morning can help start the day. However, keeping the coffee maker clean can be a problem. Lime deposits build up after a while and slow down the brewing process. The best cure for this is to put vinegar (dilute acetic acid) in the pot and run it through the brewing cycle. The vinegar dissolves the deposits and cleans the maker, which will speed up the brewing process back to its original rate. Just be sure to run water through the brewing process after the vinegar, or you will get some really horrible coffee!

Acids

Acids are very common in some of the foods that we eat. Citrus fruits such as oranges and lemons contain citric acid and ascorbic acid, which is better known as vitamin C. Carbonated sodas contain phosphoric acid. Vinegar contains acetic acid. Your own stomach utilizes hydrochloric acid to digest food.

Acids are a distinct class of compounds because of the properties of their aqueous solutions. These properties are:

1. Aqueous solutions of acids are electrolytes, meaning that they conduct electrical current. Some acids are strong electrolytes because they ionize completely in water, yielding a great many ions. Other acids are weak electrolytes that exist primarily in a non-ionized form when dissolved in water.
2. Acids have a sour taste. Lemons, vinegar, and sour candies all contain acids.
3. Acids change the color of certain acid-base indicates. Two common indicators are litmus and phenolphthalein. Blue litmus turns red in the presence of an acid, while phenolphthalein turns colorless.
4. Acids react with active metals to yield hydrogen gas. Recall that an activity series is a list of metals in descending order of reactivity. Metals that are above hydrogen in the activity series will replace the hydrogen from an acid in a single-replacement reaction, as shown below:

$$\mathrm{Zn}\,(s) + \mathrm{H_2SO_4}\,(aq) \rightarrow \mathrm{ZnSO_4}\,(aq) + \mathrm{H_2}\,(g)$$

5. Acids react with bases to produce a salt compound and water. When equal moles of an acid and a base are combined, the acid is neutralized by the base. The products of this reaction are an ionic compound, which is labeled as a salt, and water.

Summary

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5.13: Properties of Bases

Perhaps you have eaten too much pizza and felt very uncomfortable hours later. This feeling is due to excess stomach acid being produced. The discomfort can be dealt with by taking an antacid. The base in the antacid will react with the HCl in the stomach and neutralize it, taking care of that unpleasant feeling.

Bases

Bases have properties that mostly contrast with those of acids.

1. Aqueous solutions of bases are also electrolytes. Bases can be either strong or weak, just as acids can.
2. Bases often have a bitter taste and are found in foods less frequently than acids. Many bases, like soaps, are slippery to the touch.
3. Bases also change the color of indicators. Litmus turns blue in the presence of a base while phenolphthalein turns pink.
4. Bases do not react with metals in the way that acids do.
5. Bases react with acids to produce a salt and water.



Figure* 5.13.1*: *Phenolphthalein indicator in presence of base.*

Please note that tasting chemicals and touching them are NOT good lab practices and should be avoided—in other words, don't do this at home.

Bases are less common as foods, but they are nonetheless present in many household products. Many cleaners contain ammonia, a base. Sodium hydroxide is found in drain cleaner. **Antacids**, which combat excess stomach acid, are comprised of bases such as magnesium hydroxide or sodium hydrogen carbonate.

Summary

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5.14: Arrhenius Acids

Venus is the planet nearest to Earth, but has a very different and hostile environment. It has a surface temperature that averages around 450°C. The atmosphere is composed of carbon dioxide, but clouds of sulfuric acid move through the upper atmosphere, helping to create the extremely unfriendly conditions. Because of these conditions, Venus is not a place you want to visit on vacation.

Arrhenius Acids

Swedish chemist Svante Arrhenius (1859-1927) was the first to propose a theory to explain the observed behavior of acids and bases. Because of their ability to conduct a current, he knew that both acids and bases contained ions in solution. An **Arrhenius acid** is a compound that ionizes to yield hydrogen ions $\left(\text{H}^{+}\right)$ in aqueous solution.

Acids are molecular compounds with ionizable hydrogen atoms. Only hydrogen atoms that are part of a highly polar covalent bond are ionizable. Hydrogen chloride $\left(\text{HCl}\right)$ is a gas at room temperature and under normal pressure. The $\text{H}-\text{Cl}$ bond in hydrogen chloride is a polar bond. The hydrogen atom is electron deficient because of the higher electronegativity of the chlorine atom. Consequently, the hydrogen atom is attracted to the lone pair of electrons in a water molecule when HCl is dissolved in water. The result is that the $\text{H}-\text{Cl}$ bond breaks, with both bonding electrons remaining with the Cl, forming a chloride ion. The H^{+} ion attaches to the water molecule, forming a polyatomic ion called the hydronium ion. The **hydronium ion** $\left(\text{H}_3\text{O}^{+}\right)$ can be thought of as a water molecule with an extra attached hydrogen ion.

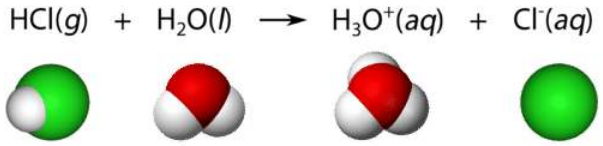


Figure 5.14.1: Formation of a hydronium ion. (CC BY-NC; CK-12)

Equations showing the ionization of an acid in water are frequently simplified by omitting the water molecule:

$$\text{HCl}\left(g\right) \rightarrow \text{H}^{+}\left(aq\right) + \text{Cl}^{-}\left(aq\right)$$

This is merely a simplification of the previous equation, but it is commonly used. Any hydrogen ions in an aqueous solution will be attached to water molecules as hydronium ions.

Not all hydrogen atoms in molecular compounds are ionizable. In methane $\left(\text{CH}_4\right)$, the hydrogen atoms are covalently bonded to carbon in bonds that are only slightly polar. The hydrogen atoms are not capable of ionizing, and methane has no acidic properties. Acetic acid $\left(\text{CH}_3\text{COOH}\right)$ belongs to a class of acids called organic acids. There are four hydrogen atoms in the molecule, but only the one hydrogen that is bonded to an oxygen atom is ionizable.

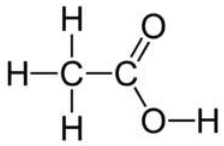


Figure 5.14.2: The $\text{O}-\text{H}$ bond can be ionized to yield the H^{+} ion and the acetate ion. The other hydrogen atoms in this molecule are not acidic. (CC BY-NC; CK-12)

The table below lists some of the more common acids:

Common Acids

Table 5.14.1 : Common Acids

Acid Name	Formula
Hydrochloric acid	HCl
Nitric acid	HNO_3
Sulfuric acid	H_2SO_4
Phosphoric acid	H_3PO_4

Table 5.14.1 : Common Acids

Acetic acid	CH_3COOH
Hypochlorous acid	$HClO$

A **monoprotic acid** is an acid that contains only one ionizable hydrogen. Hydrochloric acid and acetic acid are monoprotic acids. A **polyprotic acid** is an acid that contains multiple ionizable hydrogens. Most common polyprotic acids are either diprotic (such as H_2SO_4) or triprotic (such as H_3PO_4).

Summary

- An Arrhenius acid is a compound that ionizes to yield hydrogen ions $\left(H^+\right)$ in aqueous solution.
- Examples of Arrhenius acids are given.

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5.15: Arrhenius Bases

Sodium hydroxide is a versatile chemical. It can be used for such mundane purposes as cleaning clogged drains. Several commercial preparations contain sodium hydroxide for this purpose. It also has a number of applications in the food processing field. Ice cream is thickened using NaOH. If olives are soaked in a solution containing sodium hydroxide and other chemicals, the olives will turn black. Soft pretzels are made chewy by the application of sodium hydroxide to the food. This compound has been widely used in the synthesis of plastics, for etching aluminum, for paint removal, and is employed in the dehorning of cattle.

Arrhenius Bases

An **Arrhenius base** is a compound that ionizes to yield hydroxide ions $\left(\mathrm{OH}^-\right)$ in aqueous solution. The table below lists several of the more common bases.

Table 5.15.1: Common Bases

Base Name	Formula
Sodium hydroxide	NaOH
Potassium hydroxide	KOH
Magnesium hydroxide	$\mathrm{Mg(OH)_2}$
Calcium hydroxide	$\mathrm{Ca(OH)_2}$

All of the bases listed in the table are solids at room temperature. Upon dissolving in water, each dissociates into a metal cation and the hydroxide ion.

$$\mathrm{NaOH}\,(s) \rightarrow \mathrm{Na}^+\,(aq) + \mathrm{OH}^-\,(aq)$$

Sodium hydroxide is a very caustic substance also known as lye. Lye is used as a rigorous cleaner and is an ingredient in the manufacture of soaps. Care must be taken with strong bases like sodium hydroxide, as exposure can lead to severe burns (see figure below).



Figure 5.15.1: This foot has severe burns due to prolonged contact with a solution of sodium hydroxide, also known as lye. (CC BY-NC; CK-12)

Sodium belongs to the group of elements called the alkali metals. An **alkaline solution** is another name for a solution that is basic. All alkali metals react readily with water to produce the metal hydroxide and hydrogen gas. The resulting solutions are basic.

$$2\mathrm{K}\,(s) + 2\mathrm{H_2O}\,(l) \rightarrow 2\mathrm{KOH}\,(aq) + \mathrm{H_2}\,(g)$$

Bases that consist of an alkali metal cation and the hydroxide anion are all very soluble in water. Compounds of the Group 2 metals (the alkaline earth metals) are also basic. However, these compounds are generally not as soluble in water. Therefore, the dissociation reactions for these compounds are shown as equilibrium reactions:

$$\mathrm{Mg(OH)_2}\,(s) \overset{\mathrm{H_2O}}{\rightleftharpoons} \mathrm{Mg}^{2+}\,(aq) + 2\mathrm{OH}^-\,(aq)$$

These relatively insoluble hydroxides were some of the compounds discussed in the context of the solubility product constant (K_{sp}). The solubility of magnesium hydroxide is $0.0084\ \mathrm{g}$ per liter of water at $25^{\circ}\mathrm{C}$. Because of its low solubility, magnesium hydroxide is not as dangerous as sodium hydroxide. In fact, magnesium hydroxide is the active ingredient in a product called milk of magnesia, which is used as an antacid or a mild laxative.

Summary

- Arrhenius base is a compound that ionizes to yield hydroxide ions $\left(OH^{-}\right)$ in aqueous solution.
- Examples of Arrhenius bases are given.

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5.16: Brønsted-Lowry Acids and Bases

The Arrhenius concept of acids and bases was a significant contribution to the scientific understanding of acids and bases. It replaced and expanded Lavoisier's original idea that all acids contained oxygen. However, the Arrhenius theory also had its shortcomings. It did not take into account the role of the solvent. In addition, this concept did not deal with acid-base behavior in solvents such as benzene, where there could be no ionization. So, formation of a new theory was imperative, which built on the findings of Arrhenius, but also went beyond them.

Brønsted-Lowry Acids and Bases

The Arrhenius definition of acids and bases is somewhat limited. There are some compounds whose properties suggest that they are either acidic or basic, but which do not qualify according to the Arrhenius definition. An example is ammonia $\left(NH_3\right)$. Its aqueous solution turns litmus blue, it reacts with acids, and displays all the other properties of a base. However, it does not contain the hydroxide ion. In 1923, a broader definition of acids and bases was independently proposed by Danish chemist Johannes Brønsted (1879-1947) and English chemist Thomas Lowry (1874-1936). A **Brønsted-Lowry acid** is a molecule or ion that donates a hydrogen ion in a reaction. A **Brønsted-Lowry base** is a molecule or ion that accepts a hydrogen ion in a reaction. A hydrogen ion is commonly referred to as a proton, and so acids and bases are proton donors and proton acceptors, respectively, according to the Brønsted-Lowry definition. All substances that are categorized as acids and bases under the Arrhenius definition are also defined as such under the Brønsted-Lowry definition. The new definition, however, includes some substances that are left out according to the Arrhenius definition.

What kind of molecule would qualify as a Brønsted-Lowry base? These molecules need to be able to accept a hydrogen ion (or proton). Two possibilities come to mind: an anion that can form a neutral compound with a proton, or a molecule in which one or more atoms has lone-pair electrons. The most obvious anion is the Arrhenius base OH^-. This ion can form a water molecule with a proton by accepting the proton. The acetate anion CH_3COO^- is another anion that can combine with a proton to form acetic acid. Lone-pair electron groups would include the nitrogen atom (see figure below). The two electrons at the top of the nitrogen atom are not connected in any type of bond, but they do interact readily with a bare proton.

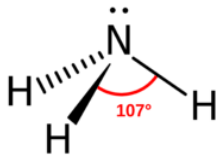


Figure 5.16.1: *Lone pair electrons on nitrogen.* (CC BY-NC; CK-12)

Oxygen is another atom with lone pair electrons that can function as a Brønsted-Lowry base.



Figure 5.16.2: Electrons in an oxygen atom. (CC BY-NC; CK-12)

The two single electrons (to the left and bottom of the atom) can form single covalent bonds with other atoms, while the two pairs of double electrons (top and right) are available to interact with a hydrogen ion.

Summary

- A Brønsted-Lowry acid is a molecule or ion that donates a hydrogen ion in a reaction.
- A Brønsted-Lowry base is a molecule or ion that accepts a hydrogen ion in a reaction.

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5.17: Brønsted-Lowry Acid-Base Reactions

The Roman god Janus was considered the god of gates, doors, beginnings, and endings. He is portrayed with two faces, looking in two directions at once. Janus would have been in a good position to look at the acid-base reactions we see in this concept, since they are equilibrium reactions involving two different forms of both acids and bases.

Brønsted-Lowry Acid-Base Reactions

An acid-base reaction, according to the Brønsted-Lowry definition, is a transfer of a proton from one molecule or ion to another. When ammonia is dissolved in water, it undergoes the following reversible reaction.

$$\underset{\text{base}}{\mathrm{NH_3}\,(aq)} + \underset{\text{acid}}{\mathrm{H_2O}\,(l)} \rightleftharpoons \underset{\text{acid}}{\mathrm{NH_4^+}\,(aq)} + \underset{\text{base}}{\mathrm{OH^-}\,(aq)}$$

In this reaction, the water molecule is donating a proton to the ammonia molecule. The resulting products are the ammonium ion and the hydroxide ion. The water is acting as a Brønsted-Lowry acid, while the ammonia is acting as a Brønsted-Lowry base. The hydroxide ion that is produced causes the solution to be basic.

We can also consider the reverse reaction in the above equation. In that reaction, the ammonia ion donates a proton to the hydroxide ion. The ammonium ion is a Brønsted-Lowry acid, while the hydroxide ion is a Brønsted-Lowry base. Most Brønsted-Lowry acid-base reactions can be analyzed in this way. One acid and one base are reactants, and one acid and one base are products.

In the above reaction, water acted as an acid, which may seem a bit unexpected. Water can also act as a base in a Brønsted-Lowry acid-base reaction, as long as it reacts with a substance that is a better proton donor. Shown below is the reaction of water with the hydrogen sulfate ion.

$$\underset{\text{acid}}{\mathrm{HSO_4^-}\,(aq)} + \underset{\text{base}}{\mathrm{H_2O}\,(l)} \rightleftharpoons \underset{\text{acid}}{\mathrm{H_3O^+}\,(aq)} + \underset{\text{base}}{\mathrm{SO_4^{2-}}\,(aq)}$$

So, water is capable of being either an acid or a base, a characteristic called amphoterism. An **amphoteric substance** is one that is capable of acting as either an acid or a base by donating or accepting hydrogen ions.

Conjugate Acids and Bases

When a substance that is acting as a Brønsted-Lowry acid donates its proton, it becomes a base in the reverse reaction. In the reaction above, the hydrogen sulfate ion $\left(\mathrm{HSO_4^-}\right)$ donates a proton to water and becomes a sulfate ion $\left(\mathrm{SO_4^{2-}}\right)$. The $\mathrm{HSO_4^-}$ and the $\mathrm{SO_4^{2-}}$ are linked to one another by the presence or absence of the $\mathrm{H^+}$ ion. A **conjugate acid-base pair** is a pair of substances related by the loss or gain of a single hydrogen ion. A **conjugate acid** is the particle produced when a base accepts a proton. The hydrogen sulfate ion is the conjugate acid of the sulfate ion. A **conjugate base** is the particle produced when an acid donates a proton. The sulfate ion is the conjugate base of the hydrogen sulfate ion.

In the reaction illustrated below, water serves both as acid and base simultaneously. One water molecule serves as an acid and donates a proton. The other water molecule functions as a base by accepting the proton.

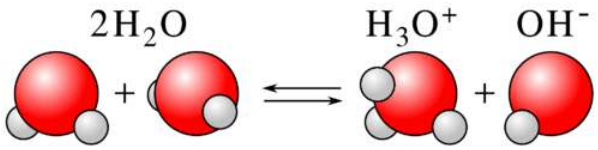


Figure 5.17.1: Water molecules as a conjugate acid-base pair. (CC BY-NC; CK-12)

A typical Brønsted-Lowry acid-base reaction contains two conjugate acid-base pairs, as shown below.

$$\mathrm{HNO_2}\,(aq) + \mathrm{PO_4^{3-}}\,(aq) \rightleftharpoons \mathrm{NO_2^-}\,(aq) + \mathrm{HPO_4^{2-}}\,(aq)$$

One conjugate acid-base pair is $\mathrm{NHO_2/NO_2^-}$, while the other pair is $\mathrm{HPO_4^{2-}/PO_4^{3-}}$.

Summary

- An acid-base reaction, according to the Brønsted-Lowry definition, is a transfer of a proton from one molecule or ion to another.
- A conjugate acid-base pair is a pair of substances related by the loss or gain of a single hydrogen ion.
- A conjugate acid is the particle produced when a base accepts a proton.
- A conjugate base is the particle produced when an acid donates a proton.
- Examples of conjugate acid-base pairs are given.

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5.18: Ion-Product of Water

At one time, you could take the little caps off the top of a car battery and check the condition of the sulfuric acid inside. If it got low, you could add more acid. But, sulfuric acid is hazardous stuff, so the batteries are now sealed to protect people. Because of the acid's dangerous nature, it is not a good idea to cut into a battery to see what it looks like—you could get acid burns.

The Ion-Product of Water

The **self-ionization of water** (the process in which water ionizes to hydronium ions and hydroxide ions) occurs to a very limited extent. When two molecules of water collide, there can be a transfer of a hydrogen ion from one molecule to the other. The products are a positively charged hydronium ion and a negatively charged hydroxide ion.

$$\mathrm{H_2O}\,(l) + \mathrm{H_2O}\,(l) \rightleftharpoons \mathrm{H_3O^+}\,(aq) + \mathrm{OH^-}\,(aq)$$

We often use the simplified form of the reaction:

$$\mathrm{H_2O}\,(l) \rightleftharpoons \mathrm{H^+}\,(aq) + \mathrm{OH^-}\,(aq)$$

The equilibrium constant for the self-ionization of water is referred to as the ion-product for water and is given the symbol K_w.

$$K_\mathrm{w} = \left[\mathrm{H^+}\right]\left[\mathrm{OH^-}\right]$$

The **ion-product of water** (K_w) is the mathematical product of the concentration of hydrogen ions and hydroxide ions. Note that $\mathrm{H_2O}$ is not included in the ion-product expression because it is a pure liquid. The value of K_w is very small, in accordance with a reaction that favors the reactants. At $25^\circ\mathrm{C}$, the experimentally determined value of K_w in pure water is 1.0×10^{-14}.

$$K_\mathrm{w} = \left[\mathrm{H^+}\right]\left[\mathrm{OH^-}\right] = 1.0 \times 10^{-14}$$

In pure water, the concentrations of hydrogen and hydroxide ions are equal to one another. Pure water or any other aqueous solution in which this ratio holds is said to be neutral. To find the molarity of each ion, the square root of K_w is taken.

$$\left[\mathrm{H^+}\right] = \left[\mathrm{OH^-}\right] = 1.0 \times 10^{-7}$$

An **acidic solution** is a solution in which the concentration of hydrogen ions is greater than the concentration of hydroxide ions. For example, hydrogen chloride ionizes to produce $\mathrm{H^+}$ and $\mathrm{Cl^-}$ ions upon dissolving in water.

$$\mathrm{HCl}\,(g) \rightarrow \mathrm{H^+}\,(aq) + \mathrm{Cl^-}\,(aq)$$

This increases the concentration of $\mathrm{H^+}$ ions in the solution. According to Le Chatelier's principle, the equilibrium represented by $\mathrm{H_2O}\,(l) \rightleftharpoons \mathrm{H^+}\,(aq) + \mathrm{OH^-}\,(aq)$ is forced to the left, towards the reactant. As a result, the concentration of the hydroxide ion decreases.

A **basic solution** is a solution in which the concentration of hydroxide ions is greater than the concentration of hydrogen ions. Solid potassium hydroxide dissociates in water to yield potassium ions and hydroxide ions.

$$\mathrm{KOH}\,(s) \rightarrow \mathrm{K^+}\,(aq) + \mathrm{OH^-}\,(aq)$$

The increase in concentration of the $\mathrm{OH^-}$ ions causes a decrease in the concentration of the $\mathrm{H^+}$ ions and the ion-product of $\left[\mathrm{H^+}\right]\left[\mathrm{OH^-}\right]$ remains constant.

5.18.1 Example

Hydrochloric acid (HCl) is a strong acid, meaning it is 100% ionized in solution. What is the $\left[\mathrm{H^+}\right]$ and the $\left[\mathrm{OH^-}\right]$ in a solution of 2.0×10^{-3} M HCl?

Solution

Step 1: List the known values and plan the problem.

Known

- $[\mathrm{HCl}] = 2.0 \times 10^{-3}$ M
- $K_\mathrm{w} = 1.0 \times 10^{-14}$

Unknown

- $\left[\mathrm{H^+}\right] = ?\ \mathrm{M}$
- $\left[\mathrm{OH^-}\right] = ?\ \mathrm{M}$

Because HCl is 100% ionized, the concentration of $\mathrm{H^+}$ ions in solution will be equal to the original concentration of HCl. Each HCl molecule that was originally present ionizes into one $\mathrm{H^+}$ ion and one $\mathrm{Cl^-}$ ion. The concentration of $\mathrm{OH^-}$ can then be determined from the $\left[\mathrm{H^+}\right]$ and K_w.

Step 2: Solve.

$$\begin{aligned} \left[\mathrm{H^+}\right] &= 2.0 \times 10^{-3}\ \mathrm{M} \\ K_\mathrm{w} &= \left[\mathrm{H^+}\right]\left[\mathrm{OH^-}\right] = 1.0 \times 10^{-14} \\ \left[\mathrm{OH^-}\right] &= \frac{K_\mathrm{w}}{\left[\mathrm{H^+}\right]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-3}} = 5.0 \times 10^{-12}\ \mathrm{M} \end{aligned}$$

Step 3: Think about your result.

The $\left[\mathrm{H^+}\right]$ is much higher than the $\left[\mathrm{OH^-}\right]$ because the solution is acidic. As with other equilibrium constants, the unit for K_w is customarily omitted.

Summary

- The self-ionization of water is described and an ionization constant for the process is stated.
- Acidic and basic solutions are defined.
- Calculations using K_w are illustrated.

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5.19: The pH Scale

Grapefruit juice has a pH of somewhere between 2.9 and 3.3, depending on the specific product. Excessive exposure to this juice can cause erosion of tooth enamel and can lead to tooth damage. The acids in grapefruit juice are carbon-based, with citric acid being one of the major constituents. This compound has three ionizable hydrogens on each molecule which contribute to the relatively low pH of the juice. Another component of grapefruit juice is malic acid, containing two ionizable hydrogens per molecule.

The pH Scale

Expressing the acidity of a solution by using the molarity of the hydrogen ion is cumbersome because the quantities are generally very small. Danish scientist Søren Sørensen (1868-1939) proposed an easier system for indicating the concentration of H^+ called the pH scale. The letters pH stand for the power of the hydrogen ion. The **pH** of a solution is the negative logarithm of the hydrogen-ion concentration:

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

In pure water or a neutral solution, the $\left[\text{H}^+\right] = 1.0 \times 10^{-7}\ \text{M}$. Substituting into the pH expression:

$$\text{pH} = -\log\left[1.0 \times 10^{-7}\right] = -\left(-7.00\right) = 7.00$$

The pH of pure water or any neutral solution is thus 7.00. For recording purposes, the numbers to the right of the decimal point in the pH value are the significant figures. Since 1.0×10^{-7} has two significant figures, the pH can be reported as 7.00.

A logarithmic scale condenses the range of acidity to numbers that are easy to use. Consider a solution with $\left[\text{H}^+\right] = 1.0 \times 10^{-4}\ \text{M}$. That is a hydrogen-ion concentration that is 1000 times higher than the concentration in pure water. The pH of such a solution is 4.00, a difference of just 3 pH units. Notice that when the $\left[\text{H}^+\right]$ is written in scientific notation and the coefficient is 1, the pH is simply the exponent with the sign changed. The pH of a solution with $\left[\text{H}^+\right] = 1 \times 10^{-2}\ \text{M}$ is 2 and the pH of a solution with $\left[\text{H}^+\right] = 1 \times 10^{-10}\ \text{M}$ is 10.

As we saw earlier, a solution with $\left[\text{H}^+\right]$ higher than 1.0×10^{-7} is acidic, while a solution with $\left[\text{H}^+\right]$ lower than 1.0×10^{-7} is basic. Consequently, solutions with a pH of less than 7 are acidic, while those with a pH higher than 7 are basic. Figure 5.19.1 illustrates this relationship, along with some examples of various solutions.

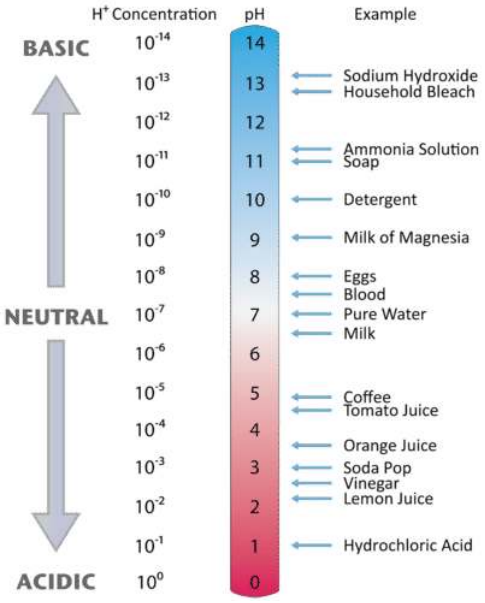


Figure 5.19.1: The pH values for several common materials. (CC BY-NC; CK-12)

Summary

- The pH of a solution is the negative logarithm of the hydrogen-ion concentration.
- Solutions with a pH of less than 7 are acidic, while those with a pH higher than 7 are basic.

- pH values for several common materials are listed.

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5.20: Avogadro's Number



Figure 5.20.1 (Public Domain; User:OSX/Wikimedia Commons via Wikipedia)

Is there an easier way to load this truck?

When the weather is nice, many people begin to work on their yards and homes. For many projects, sand is needed as a foundation for a walk or to add to other materials. You could order up twenty million grains of sand and have people really stare at you. You could order by the pound, but that takes a lot of time weighing out. The best bet is to order by the yard, meaning a cubic yard. The loader can easily scoop up what you need and put it directly in your truck.

Avogadro's Number

It certainly is easy to count objects such as bananas, or something as large as elephants (as long as you stay out of their way). However, counting grains of sugar from a sugar canister would take a long, long time. Atoms and molecules are extremely small—far, far smaller than grains of sugar. Counting atoms or molecules is not only unwise, it is absolutely impossible. One drop of water contains about 10^{22} molecules of water. If you counted 10 molecules every second for 50 years, without stopping, you would have counted only 1.6×10^{10} molecules. Put another way, at that counting rate, it would take you over 30 trillion years to count the water molecules in one tiny drop.

Chemists of the past needed a name that could stand for a very large number of items. Amadeo Avogadro (1776-1856), an Italian scientist, provided such a number. He is responsible for the counting unit of measure called the mole. A **mole** (mol) is the amount of a substance that contains 6.02×10^{23} representative particles of that substance. The mole is the SI unit for amount of a substance. Just like the dozen and the gross, it is a name that stands for a number. There are therefore 6.02×10^{23} water molecules in a mole of water molecules. There also would be 6.02×10^{23} bananas in a mole of bananas, if such a huge number of bananas ever existed.



Figure 5.20.2: Italian scientist Amadeo Avogadro, whose work led to the concept of the mole as a counting unit in chemistry. (Public Domain; C. Sentier via Wikipedia)

The number 6.02×10^{23} is called **Avogadro's number**, the number of representative particles in a mole. It is an experimentally determined number. A **representative particle** is the smallest unit in which a substance naturally exists. For the majority of elements, the representative particle is the atom. Iron, carbon, and helium consist of iron atoms, carbon atoms, and helium atoms, respectively. Seven elements exist in nature as diatomic molecules and they are H_2, N_2, O_2, F_2, Cl_2, Br_2, and I_2. The representative particle for these elements is the molecule. Likewise, all molecular compounds such as H_2O and CO_2 exist as molecules and so the molecule is their representative particle. For ionic compounds such as NaCl and $\text{Ca}(\text{NO}_3)_2$, the representative particle is the formula unit. A mole of any substance contains Avogadro's number $\left(6.02 \times 10^{23}\right)$ of representative particles.



Figure 5.20.3: The animal mole is very different than the counting unit of the mole. Chemists nonetheless have adopted the mole as their unofficial mascot. National Mole Day is a celebration of chemistry that occurs on October 23rd (10/23) of each year. ((left; Left: Michael David Hill, 2005 (Mikiwikipikidikipedia); Right: chrisbb@prodigy.net;(left) Michael David Hill, 2005 (Mikiwikipikidikipedia); (right) chrisbb@prodigy.net via Left: http://commons.wikimedia.org/wiki/File:Close-up_of_mole.jpg; Right: http://www.flickr.com/photos/chrisbrenschmidt/436990097;(left) http://commons.wikimedia.org/wiki/File:Close-up_of_mole.jpg; (right) http://www.flickr.com/photos/chrisbrenschmidt/436990097) CC-BY 2.5; (right) CC-BY 2.0)



Summary

- A mole of any substance contains Avogadro's number $\left(6.02 \times 10^{23}\right)$ of representative particles.

Review

1. What is the SI unit for amount of a substance?
2. What is the representative particle for an element?
3. The formula unit is the representative particle for what?

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5.21: Conversions Between Moles and Atoms



Figure 5.21.1 (Public Domain; Diane A. Reid/National Cancer Institute via Wikipedia)

Big numbers or little numbers?

Do you hate to type subscripts and superscripts? Even with a good word-processing program, having to click on an icon to get a superscript and then remembering to click off after you type the number can be a real hassle. If we did not know about moles and just knew about numbers of atoms or molecules (those big numbers that require lots of superscripts), life would be much more complicated and we would make many more typing errors.

Conversions Between Moles and Atoms

Conversions Between Moles and Number of Particles

Using our unit conversion techniques, we can use the mole label to convert back and forth between the number of particles and moles.

5.21.1 Example : Converting Number of Particles to Moles

The element carbon exists in two primary forms: graphite and diamond. How many moles of carbon atoms is 4.72×10^{24} atoms of carbon?

Solution

Step 1: List the known quantities and plan the problem.

Known

- number of C atoms $= 4.72 \times 10^{24}$
- 1 mole $= 6.02 \times 10^{23}$ atoms

Unknown

- 4.72 x 10^{24} = ? mol C

One conversion factor will allow us to convert from the number of C atoms to moles of C atoms.

Step 2: Calculate.

$$4.72 \times 10^{24} \text{ atoms C} \times \frac{1 \text{ mol C}}{6.02 \times 10^{23} \text{ atoms C}} = 7.84 \text{ mol C}$$

Step 3: Think about your result.

The given number of carbon atoms was greater than Avogadro's number, so the number of moles of C atoms is greater than 1 mole. Since Avogadro's number is a measured quantity with three significant figures, the result of the calculation is rounded to three significant figures.

Suppose that you want to know how many hydrogen atoms are in a mole of water molecules. First, you need to know the chemical formula for water, which is H_2O. There are two atoms of hydrogen in each molecule of water. How many atoms of hydrogen are in two water molecules? There are $2 \times 2 = 4$ hydrogen atoms. How about in a dozen? In that case, a dozen is 12; so $12 \times 2 = 24$ hydrogen atoms in a dozen water molecules. To get the answers (4 and 24), you multiply the given number of molecules by two

atoms of hydrogen per molecule. So, to find the number of hydrogen atoms in a mole of water molecules, the problem can be solved using conversion factors:

$$1\text{ mol }H_2O \times \frac{6.02 \times 10^{23}\text{ molecules }H_2O}{1\text{ mol }H_2O} \times \frac{2\text{ atoms H}}{1\text{ molecule }H_2O} = 1.20 \times 10^{24}\text{ atoms H}$$

The first conversion factor converts from moles of particles to the number of particles. The second conversion factor reflects the number of atoms contained within each molecule.



Figure 5.21.2: Two water molecules contain 4 hydrogen atoms and 2 oxygen atoms. A mole of water molecules contains 2 moles of hydrogen atoms and 1 mole of oxygen atoms. (Public Domain; Ben Mills (Wikimedia: Benjah-bmm27) via Wikipedia)

5.21.2 Example : Atoms, Molecules, and Moles

Sulfuric acid has the chemical formula H_2SO_4. A certain quantity of sulfuric acid contains 4.89×10^{25} atoms of oxygen. How many moles of sulfuric acid is the sample?

Solution:

Step 1: List the known quantities and plan the problem.

Known

- $4.89 \times 10^{25} = \text{O}$ atoms
- $1\text{ mole} = 6.02 \times 10^{23}$ molecules H_2SO_4

Unknown

- mol of H_2SO_4 molecules

Two conversion factors will be used. First, convert atoms of oxygen to molecules of sulfuric acid. Then, convert molecules of sulfuric acid to moles of sulfuric acid.

Step 2: Calculate.

$$4.89 \times 10^{25}\text{ atoms O} \times \frac{1\text{ molecule }H_2SO_4}{4\text{ atoms O}} \times \frac{1\text{ mol }H_2SO_4}{6.02 \times 10^{23}\text{ molecules }H_2SO_4} = 20.3\text{ mol }H_2SO_4$$

Step 3: Think about your result.

The original number of oxygen atoms was about 80 times larger than Avogadro's number. Since each sulfuric acid molecule contains 4 oxygen atoms, there are about 20 moles of sulfuric acid molecules.



Summary

- Methods are described for conversions between moles, atoms, and molecules.

Review

1. What conversion factor would we need to convert moles of helium to atoms of helium?
2. I want to convert atoms to moles. My friend tells me to multiply the number of atoms by 6.02×10^{23} atoms/mole. Is my friend correct?
3. Why do you need to know the formula for a molecule in order to calculate the number of moles of one of the atoms?
4. How many atoms of fluorine are in 5.6×10^{22} molecules of MgF_2?

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5.22: Molar Mass



Figure 5.22.1 (Public Domain; Ben Mills (Wikimedia: Benjah-bmm27) via Wikipedia)

When creating a solution, how do I know how much of each substance to put in?

I want to make a solution that contains 1.8 moles of potassium dichromate. You do not have a balance calibrated in moles, but you do have one calibrated in grams. If you know the relationship between moles and the number of grams in a mole, you can use your balance to measure out the needed amount of material.

Molar Mass

Molar mass is defined as the mass of one mole of representative particles of a substance. By looking at a periodic table, we can conclude that the molar mass of lithium is $6.94\ \text{g}$ the molar mass of zinc is $65.38\ \text{g}$ and the molar mass of gold is $196.97\ \text{g}$ Each of these quantities contains 6.02×10^{23} atoms of that particular element. The units for molar mass are grams per mole, or g/mol.

Molar Masses of Compounds

The molecular formula of the compound carbon dioxide is CO_2. One molecule of carbon dioxide consists of 1 atom of carbon and 2 atoms of oxygen. We can calculate the mass of one molecule of carbon dioxide by adding together the masses of 1 atom of carbon and 2 atoms of oxygen:

$$12.01\ \text{amu} + 2\,(16.00\ \text{amu}) = 44.01\ \text{amu}$$

The **molecular mass** of a compound is the mass of one molecule of that compound. The molecular mass of carbon dioxide is $44.01\ \text{amu}$

The molar mass of any compound is the mass in grams of one mole of that compound. One mole of carbon dioxide molecules has a mass of $44.01\ \text{g}$ while one mole of sodium sulfide formula units has a mass of $78.04\ \text{g}$ The molar masses are $44.01\ \text{g/mol}$and $78.04\ \text{g/mol}$respectively. In both cases, that is the mass of 6.02×10^{23} representative particles. The representative particle of CO_2 is the molecule, while for Na_2S it is the formula unit.

5.22.1 Example : Molar Mass of a Compound

Calcium nitrate, $\text{Ca(NO}_3)_2$, is used as a component in fertilizer. Determine the molar mass of calcium nitrate.

Solution

Step 1: List the known and unknown quantities and plan the problem.

Known

- Formula $= \text{Ca(NO}_3)_2$
- Molar mass $\text{Ca} = 40.08\ \text{g/mol}$
- Molar mass $\text{N} = 14.01\ \text{g/mol}$
- Molar mass $\text{O} = 16.00\ \text{g/mol}$

Unknown

- molar mass $\text{Ca(NO}_3)_2$

First we need to analyze the formula. Since the Ca lacks a subscript, there is one Ca atom per formula unit. The 2 outside the parentheses means that there are two nitrate ions per formula unit and each nitrate ion consists of one nitrogen atom and three

oxygen atoms per formula unit. Thus, 1 mol of calcium nitrate contains 1 mol of Ca atoms, 2 mol of N atoms, and 6 mol of O atoms.

Step 2: Calculate

Use the molar masses of each atom together with the number of atoms in the formula and add together.

$$1 \text{ mol Ca} \times \frac{40.08 \text{ g Ca}}{1 \text{ mol Ca}} = 40.08 \text{ g Ca}$$

$$2 \text{ mol N} \times \frac{14.01 \text{ g N}}{1 \text{ mol N}} = 28.02 \text{ g N}$$

$$6 \text{ mol O} \times \frac{16.00 \text{ g O}}{1 \text{ mol O}} = 96.00 \text{ g O}$$

$$\text{Molar mass of } \text{Ca}(\text{NO}_3)_2 = 40.08 \text{ g} + 28.02 \text{ g} + 96.00 \text{ g} = 164.10 \text{ g/mol}$$



Summary

- Calculations are described for the determination of molar mass of an atom or a compound.

Review

1. What is the molar mass of Pb?
2. Where do you find the molar mass of an element?
3. How many moles of Cl are in one mole of the $CaCl_2$?
4. How many moles of H are in one mole of the compound $(NH_4)_3PO_4$?
5. Calculate the molar mass of $CaCl_2$.

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5.23: Conversions Between Moles and Mass



Figure 5.23.1 (Public Domain; User:Estormiz/Wikimedia Commons via Wikipedia)

How can we get more product?

Chemical manufacturing plants are always seeking to improve their processes. One way that improvement comes about is through measuring the amount of material produced in a reaction. By knowing how much is made, the scientists and engineers can try different ways of getting more product at less cost.

Conversions Between Moles and Mass

The molar mass of any substance is the mass in grams of one mole of representative particles of that substance. The representative particles can be atoms, molecules, or formula units of ionic compounds. This relationship is frequently used in the laboratory. Suppose that for a certain experiment, you need 3.00 moles of calcium chloride $(\mathrm{CaCl_2})$. Since calcium chloride is a solid, it would be convenient to use a balance to measure the mass that is needed. The molar mass of $\mathrm{CaCl_2}$ is $110.98\ \mathrm{g/mol}$ The conversion factor that can be used is then based on the equality that $1\ \mathrm{mol} = 110.98\ \mathrm{g\ CaCl_2}$. Dimensional analysis will allow you to calculate the mass of $\mathrm{CaCl_2}$ that you should measure.

$$3.00\ \mathrm{mol\ CaCl_2} \times \frac{110.98\ \mathrm{g\ CaCl_2}}{1\ \mathrm{mol\ CaCl_2}} = 333\ \mathrm{g\ CaCl_2}$$

When you measure the mass of $333\ \mathrm{g}$ of $\mathrm{CaCl_2}$, you are measuring 3.00 moles of $\mathrm{CaCl_2}$.



Figure 5.23.2: Calcium chloride is used as a drying agent and as a road deicer. (Public Domain; Martin Walker (User:Walkerma/Wikimedia Commons) via Wikipedia)

5.23.1 Example : Converting Moles to Mass

Chromium metal is used for decorative electroplating of car bumpers and other surfaces. Find the mass of 0.560 moles of chromium.

Solution

Step 1: List the known quantities and plan the problem.

Known

- Molar mass of $\mathrm{Cr} = 52.00\ \mathrm{g/mol}$
- $0.560\ \mathrm{mol\ Cr}$

Unknown

- $0.560\ \mathrm{mol\ Cr}$= ? g

One conversion factor will allow us to convert from the moles of Cr to mass.

Step 2: Calculate.

$$0.560 \text{ mol Cr} \times \frac{52.00 \text{ g Cr}}{1 \text{ mol Cr}} = 29.1 \text{ g Cr}$$

Step 3: Think about your result.

Since the desired amount was slightly more than one half of a mole, the mass should be slightly more than one half of the molar mass. The answer has three significant figures because of the 0.560 mol

A similar conversion factor utilizing molar mass can be used to convert from the mass of a substance to moles. In a laboratory situation, you may perform a reaction and produce a certain amount of a product which can be massed. It will often then be necessary to determine the number of moles of the product that was formed. The next problem illustrates this situation.

5.23.2 Example : Converting Mass to Moles

A certain reaction produces 2.81 g of copper (II) hydroxide, Cu(OH)_2. Determine the number of moles produced in the reaction.

Step 1: List the known quantities and plan the problem.

Known

- mass = 2.81g

Unknown

- mol Cu(OH)_2

One conversion factor will allow us to convert from mass to moles.

Step 2: Calculate.

First, it is necessary to calculate the molar mass of Cu(OH)_2 from the molar masses of Cu, O, and H. The molar mass is 97.57 g/mol

$$2.81 \text{ g Cu(OH)}_2 \times \frac{1 \text{ mol Cu(OH)}_2}{97.57 \text{ g Cu(OH)}_2} = 0.0288 \text{ mol Cu(OH)}_2$$

Step 3: Think about your result.

The relatively small mass of product formed results in a small number of moles.



Summary

- Calculations involving conversions between moles of a material and the mass of that material are described.

Review

1. You have 19.7 grams of a material and wonder how many moles were formed. Your friend tells you to multiply the mass by grams/mole. Is your friend correct?
2. How many grams of MgO are in 3.500 moles?
3. How many moles of H_2O are in 15.2 grams of pure ice?

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5.24: Everyday Stoichiometry



Figure 5.24.1 (Public Domain; User:Skatebiker/Wikipedia via Wikipedia)

How much equipment do you need for an experiment?

You are in charge of setting out the lab equipment for a chemistry experiment. If you have twenty students in the lab (and they will be working in teams of two) and the experiment calls for three beakers and two test tubes, how much glassware do you need to set out? Figuring this out involves a type of balanced equation and the sort of calculations that you would do for a chemical reaction.

Everyday Stoichiometry

You have learned about chemical equations and the techniques used in order to balance them. Chemists use balanced equations to allow them to manipulate chemical reactions in a quantitative manner. Before we look at a chemical reaction, let's consider an equation for the ideal ham sandwich.



Figure 5.24.2: The ideal ham sandwich. (CK-12 Curriculum Materials license; CK-12 Foundation via CK-12 Foundation)

Our ham sandwich is composed of 2 slices of ham (H), a slice of cheese (C), a slice of tomato (T), 5 pickles (P), and 2 slices of bread (B). The equation for our sandwich is:

$$2\mathrm{H} + \mathrm{C} + \mathrm{T} + 5\mathrm{P} + 2\mathrm{B} \rightarrow \mathrm{H_2CTP_5B_2}$$

Now let us suppose that you are having some friends over and need to make five ham sandwiches. How much of each sandwich ingredient do you need? You take the number of each ingredient required for one sandwich (its coefficient in the above equation) and multiply by five. Using ham and cheese as examples, and using a conversion factor, you can calculate:

$$5\mathrm{H_2CTP_5B_2} \times \frac{2\ \mathrm{H}}{1\mathrm{H_2CTP_5B_2}} = 10\ \mathrm{H}$$

$$5\mathrm{H_2CTP_5B_2} \times \frac{1\mathrm{C}}{1\mathrm{H_2CTP_5B_2}} = 5\ \mathrm{C}$$

The conversion factors contain the coefficient of each specific ingredient as the numerator and the formula of one sandwich as the denominator. The result is what you would expect. In order to make five ham sandwiches, you need 10 slices of ham and 5 slices of cheese.

This type of calculation demonstrates the use of stoichiometry. **Stoichiometry** is the calculation of the amount of substances in a chemical reaction from the balanced equation. The sample problem below is another stoichiometry problem involving ingredients of the ideal ham sandwich.

5.24.1 Example : Ham Sandwich Stoichiometry

Kim looks in the refrigerator and finds that she has 8 slices of ham. In order to make as many sandwiches as possible, how many pickles does she need? Use the equation above.

Solution

Step 1: List the known quantities and plan the problem.

- Have 8 ham slices (H)
- $2\ \mathrm{H} = 5\ \mathrm{P}$ (conversion factor)

Unknown

- How many pickles (P) needed?

The coefficients for the two reactants (ingredients) are used to make a conversion factor between ham slices and pickles.

Step 2: Solve.

$$8\ \mathrm{H} \times \frac{5\ \mathrm{P}}{2\ \mathrm{H}} = 20\ \mathrm{P}$$

Since 5 pickles combine with 2 ham slices in each sandwich, 20 pickles are needed to fully combine with 8 ham slices.

Step 3: Think about your result.

The 8 ham slices will make 4 ham sandwiches. With 5 pickles per sandwich, the 20 pickles are used in the 4 sandwiches.

Summary

- An example of everyday stoichiometry is given.

Review

1. A smoothie contains 1 banana (B), 4 strawberries (St), 1 container of yogurt (Y), and 3 ice cubes (Ic). Write a balanced equation to describe the relationship.
2. Write a conversion factor to show the relationship between the number of ice cubes and the number of smoothies produced.
3. How many strawberries would you need to make 12 smoothies?

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5.25: Mole Ratios



Figure 5.25.1 (Public Domain; User:Ilemme/Wikipedia via Commons Wikimedia, File:Col 03 scup porch chairs.JPG [commons.wikimedia.org])

What does this porch need?

You want to add some sections to the porch seen above. Before you go to the hardware store to buy lumber, you need to determine the unit composition (the material between two large uprights). You count how many posts, how many boards, how many rails – then you decide how many sections you want to add before you calculate the amount of building material needed for your porch expansion.

Mole Ratios

Stoichiometry problems can be characterized by two things: (1) the information *given* in the problem, and (2) the information that is to be solved for, referred to as the *unknown*. The given and the unknown may both be reactants, both be products, or one may be a reactant while the other is a product. The amounts of the substances can be expressed in moles. However, in a laboratory situation, it is common to determine the amount of a substance by finding its mass in grams. The amount of a gaseous substance may be expressed by its volume. In this concept, we will focus on the type of problem where both the given and the unknown quantities are expressed in moles.

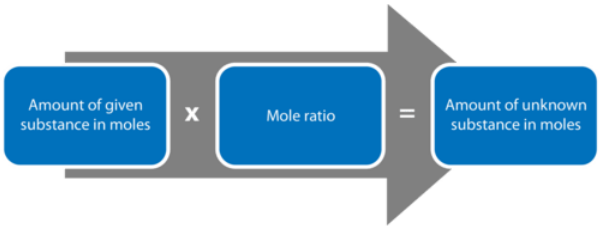


Figure 5.25.2: Mole ratio relationship. (CC BY-NC 3.0; Christopher Auyeung via CK-12 Foundation)

Chemical equations express the amounts of reactants and products in a reaction. The coefficients of a balanced equation can represent either the number of molecules or the number of moles of each substance. The production of ammonia $\left(\mathrm{NH}_3\right)$ from nitrogen and hydrogen gases is an important industrial reaction called the Haber process, after German chemist Fritz Haber.

$$\mathrm{N}_2\,(g) + 3\mathrm{H}_2\,(g) \rightarrow 2\mathrm{NH}_3\,(g)$$

The balanced equation can be analyzed in several ways, as shown in the figure below.

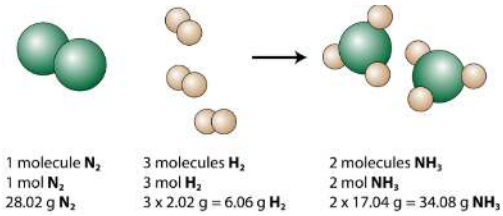


Figure 5.25.3: This representation of the production of ammonia from nitrogen and hydrogen shows several ways to interpret the quantitative information of a chemical reaction. (CC BY-NC 3.0; Christopher Auyeung via CK-12 Foundation)

We see that 1 molecule of nitrogen reacts with 3 molecules of hydrogen to form 2 molecules of ammonia. This is the smallest possible relative amount of the reactants and products. To consider larger relative amounts, each coefficient can be multiplied by

the same number. For example, 10 molecules of nitrogen would react with 30 molecules of hydrogen to produce 20 molecules of ammonia.

The most useful quantity for counting particles is the mole. So if each coefficient is multiplied by a mole, the balanced chemical equation tells us that 1 mole of nitrogen reacts with 3 moles of hydrogen to produce 2 moles of ammonia. This is the conventional way to interpret any balanced chemical equation.

Finally, if each mole quantity is converted to grams by using the molar mass, we can see that the law of conservation of mass is followed. 1 mol of nitrogen has a mass of 28.02 g while 3 mol of hydrogen has a mass of 6.06 g, and 2 mol of ammonia has a mass of 34.08 g

$$28.02 \text{ g } N_2 + 6.06 \text{ g } H_2 \rightarrow 34.08 \text{ g } NH_3$$

Mass and the number of atoms must be conserved in any chemical reaction. The number of molecules is not necessarily conserved.



Figure 5.25.4: An apparatus for running the Haber process. (Public Domain; User: JGvBerkel/Wikimedia Commons via Commons Wikimedia, Haber Ammonia [commons.wikimedia.org])

A **mole ratio** is a conversion factor that relates the amounts in moles of any two substances in a chemical reaction. The numbers in a conversion factor come from the coefficients of the balanced chemical equation. The following six mole ratios can be written for the ammonia forming reaction above.

$$\frac{1 \text{ mol } N_2}{3 \text{ mol } H_2} \quad or \quad \frac{3 \text{ mol } H_2}{1 \text{ mol } N_2}$$

$$\frac{1 \text{ mol } N_2}{2 \text{ mol } NH_3} \quad or \quad \frac{2 \text{ mol } NH_3}{1 \text{ mol } N_2}$$

$$\frac{3 \text{ mol } H_2}{2 \text{ mol } NH_3} \quad or \quad \frac{2 \text{ mol } NH_3}{3 \text{ mol } H_2}$$

In a mole ratio problem, the given substance, expressed in moles, is written first. The appropriate conversion factor is chosen in order to convert from moles of the given substance to moles of the unknown.

5.25.1 Example : Mole Ratio

How many moles of ammonia are produced if 4.20 moles of hydrogen are reacted with an excess of nitrogen?

Solution

Step 1: List the known quantities and plan the problem.

Known

- given: H_2 = 4.20 mol

Unknown

- mol of NH_3

The conversion is from mol H_2 to mol NH_3. The problem states that there is an excess of nitrogen, so we do not need to be concerned with any mole ratio involving N_2. Choose the conversion factor that has the NH_3 in the numerator and the H_2 in the denominator.

Step 2: Solve.

$$4.20 \text{ mol } H_2 \times \frac{2 \text{ mol } NH_3}{3 \text{ mol } H_2} = 2.80 \text{ mol } NH_3$$

The reaction of 4.20 molof hydrogen with excess nitrogen produces 2.80 molof ammonia.

Step 3: Think about your result.

The result corresponds to the 3:2 ratio of hydrogen to ammonia from the balanced equation.



Summary

- Mole ratios allow comparison of the amounts of any two materials in a balanced equation.
- Calculations can be made to predict how much product can be obtained from a given number of moles of reactant.

Review

- If a reactant is in excess, why do we not worry about the mole ratios involving that reactant?
- What is the mole ratio of H to N in the ammonia molecule?
- The formula for ethanol is CH_3CH_2OH. What is the mole ratio of H to C in this molecule?

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5.26: Mass-Mole and Mole-Mass Stoichiometry



Figure 5.26.1 (CK-12 Curriculum Materials license; CK-12 Foundation via CK-12 Foundation)

Need nails?

When you are doing a large construction project, you have a good idea of how many nails you will need (lots!). When you go to the hardware store, you don't want to sit there and count out several hundred nails. You can buy nails by weight, so you determine how many nails are in a pound, calculate how many pounds you need, and you're on your way to begin building.

While the mole ratio is ever-present in all stoichiometry calculations, amounts of substances in the laboratory are most often measured by mass. Therefore, we need to use mole-mass calculations in combination with mole ratios to solve several different types of mass-based stoichiometry problems.

Mass to Moles Problems

In this type of problem, the mass of one substance is given, usually in grams. From this, you are to determine the amount in moles of another substance that will either react with or be produced from the given substance.

$$\text{mass of given} \rightarrow \text{moles of given} \rightarrow \text{moles of unknown}$$

The mass of the given substance is converted into moles by use of the molar mass of that substance from the periodic table. Then, the moles of the given substance are converted into moles of the unknown by using the mole ratio from the balanced chemical equation.

5.26.1 Example : Mass-Mole Stoichiometry

Tin metal reacts with hydrogen fluoride to produce tin (II) fluoride and hydrogen gas, according to the following balanced equation.

$$\mathrm{Sn}\,(s) + 2\mathrm{HF}\,(g) \rightarrow \mathrm{SnF_2}\,(s) + \mathrm{H_2}\,(g)$$

How many moles of hydrogen fluoride are required to react completely with $75.0\ \mathrm{g}$ of tin?

Solution:

Step 1: List the known quantities and plan the problem.

Known

- Given: $75.0\ \mathrm{g\ Sn}$
- Molar mass of $\mathrm{Sn} = 118.69\ \mathrm{g/mol}$
- $1\ \mathrm{mol\ Sn} = 2\ \mathrm{mol\ HF}$ (mole ratio)

Unknown

- mol HF

Use the molar mass of Sn to convert the grams of Sn to moles. Then use the mole ratio to convert from mol Sn to mol HF. This will be done in a single two-step calculation.

$\mathrm{g\ Sn} \rightarrow \mathrm{mol\ Sm} \rightarrow \mathrm{mol\ HF}$

Step 2: Solve.

$$75.0\ \mathrm{g\ Sn} \times \frac{1\ \mathrm{mol\ Sn}}{118.69\ \mathrm{g\ Sn}} \times \frac{2\ \mathrm{mol\ HF}}{1\ \mathrm{mol\ Sn}} = 1.26\ \mathrm{mol\ HF}$$

Step 3: Think about your result.

The mass of tin is less than one mole, but the 1:2 ratio means that more than one mole of HF is required for the reaction. The answer has three significant figures because the given mass has three significant figures.

Moles to Mass Problems

In this type of problem, the amount of one substance is given in moles. From this, you are to determine the mass of another substance that will either react with or be produced from the given substance.

$$\text{moles of given} \rightarrow \text{moles of unknown} \rightarrow \text{mass of unknown}$$

The moles of the given substance are first converted into moles of the unknown by using the mole ratio from the balanced chemical equation. Then, the moles of the unknown are converted into mass in grams by use of the molar mass of that substance from the periodic table.

5.26.2 Example : Mole-Mass Stoichiometry

Hydrogen sulfide gas burns in oxygen to produce sulfur dioxide and water vapor:

$$2\text{H}_2\text{S}\,(g) + 3\text{O}_2\,(g) \rightarrow 2\text{SO}_2\,(g) + 2\text{H}_2\text{O}\,(g)$$

What mass of oxygen gas is consumed in a reaction that produces $4.60\ \text{mol SO}_2$?

Solution:

Step 1: List the known quantities and plan the problem.

Known

- Given: $4.60\ \text{mol SO}_2$
- $2\ \text{mol SO}_2 = 3\ \text{mol O}_2$ (mole ratio)
- Molar mass of $\text{O}_2 = 32.00\ \text{g/mol}$

Unknown

- mass O_2 = ? g

Use the mole ratio to convert from mol SO_2 to mol O_2. Then convert mol O_2 to grams. This will be done in a single two-step calculation.

$\text{mol SO}_2 \rightarrow \text{mol O}_2 \rightarrow \text{g O}_2$

Step 2: Solve.

$$4.60\ \text{mol SO}_2 \times \frac{3\ \text{mol O}_2}{2\ \text{mol SO}_2} \times \frac{32.00\ \text{g O}_2}{1\ \text{mol O}_2} = 221\ \text{g O}_2$$

Step 3: Think about your result.

According to the mole ratio, $6.90\ \text{mol O}_2$ is produced with a mass of 221 g. The answer has three significant figures because the given number of moles has three significant figures.



Summary

- Calculations involving conversions of mass to moles and moles to mass are described.

Review

1. In the first problem, what would happen if you multiply grams Sn by 118.69 grams/mole Sn?
2. Why is a balanced equation needed?
3. Does the physical form of the material matter for these calculations?

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5.27: Mass-Mass Stoichiometry



Figure 5.27.1 (CC by 2.0; Pauline Mak via Flickr)

How many walnuts are needed to equal 250 grams?

I want to send 250 grams of shelled walnuts to a friend (don't ask why- just go with the question). How many walnuts in shells do I need to buy? To figure this out, I need to know how much the shell of a walnut weighs (about 40% of the total weight of the unshelled walnut). I can then calculate the mass of walnuts that will yield 250 grams of shelled walnuts, and then determine how many walnuts I need to buy.

Mass to Mass Problems

Mass-mass calculations are the most practical of all mass-based stoichiometry problems. Moles cannot be measured directly, while the mass of any substance can generally be easily measured in the lab. This type of problem is three steps, and is a combination of the two previous types.

$$\text{mass of given} \rightarrow \text{moles of given} \rightarrow \text{moles of unknown} \rightarrow \text{mass of unknown}$$

The mass of the given substance is converted into moles by use of the molar mass of that substance from the periodic table. Then, the moles of the given substance are converted into moles of the unknown by using the mole ratio from the balanced chemical equation. Finally, the moles of the unknown are converted to mass by use of its molar mass.

5.27.1 Example : Mass-Mass Stoichiometry

Ammonium nitrate decomposes to dinitrogen monoxide and water, according to the following equation.

$$\mathrm{NH_4NO_3}\,(s) \rightarrow \mathrm{N_2O}\,(g) + 2\mathrm{H_2O}\,(l)$$

In a certain experiment, $45.7\ \mathrm{g}$ of ammonium nitrate is decomposed. Find the mass of each of the products formed.

Solution

Step 1: List the known quantities and plan the problem.

Known

- Given: $45.7\ \mathrm{g\ NH_4NO_3}$
- $1\ \mathrm{mol\ NH_4NO_3} = 1\ \mathrm{mol\ N_2O} = 2\ \mathrm{mol\ H_2O}$
- Molar mass of $\mathrm{NH_4NO_3} = 80.06\ \mathrm{g/mol}$
- Molar mass of $\mathrm{N_2O} = 44.02\ \mathrm{g/mol}$
- Molar mass of $\mathrm{H_2O} = 18.02\ \mathrm{g/mol}$

Unknown

- Mass $\mathrm{N_2O} = ?\ \mathrm{g}$
- Mass $\mathrm{H_2O} = ?\ \mathrm{g}$

Perform two separate three-step mass-mass calculations, as shown below.

$$\mathrm{g\ NH_4NO_3} \rightarrow \mathrm{mol\ NH_4NO_3} \rightarrow \mathrm{mol\ N_2O} \rightarrow \mathrm{g\ N_2O}$$

$$\mathrm{g\ NH_4NO_3} \rightarrow \mathrm{mol\ NH_4NO_3} \rightarrow \mathrm{mol\ H_2O} \rightarrow \mathrm{g\ H_2O}$$

Step 2: Solve.

$$45.7\ \text{g}\ \text{NH}_4\text{NO}_3 \times \frac{1\ \text{mol}\ \text{NH}_4\text{NO}_3}{80.06\ \text{g}\ \text{NH}_4\text{NO}_3} \times \frac{1\ \text{mol}\ \text{N}_2\text{O}}{1\ \text{mol}\ \text{NH}_4\text{NO}_3} \times \frac{44.02\ \text{g}\ \text{N}_2\text{O}}{1\ \text{mol}\ \text{N}_2\text{O}} = 25.1\ \text{g}\ \text{N}_2\text{O}$$

$$45.7\ \text{g}\ \text{NH}_4\text{NO}_3 \times \frac{1\ \text{mol}\ \text{NH}_4\text{NO}_3}{80.06\ \text{g}\ \text{NH}_4\text{NO}_3} \times \frac{2\ \text{H}_2\text{O}}{1\ \text{mol}\ \text{NH}_4\text{NO}_3} \times \frac{18.02\ \text{g}\ \text{H}_2\text{O}}{1\ \text{mol}\ \text{H}_2\text{O}} = 20.6\ \text{g}\ \text{H}_2\text{O}$$

Step 3: Think about your result.

The total mass of the two products is equal to the mass of ammonium nitrate which decomposed, demonstrating the law of conservation of mass. Each answer has three significant figures.



Summary

- Mass-mass calculations involve converting the mass of a reactant to moles of reactant, then using mole ratios to determine moles of product which can then be converted to mass of product.

Review

1. If matter is neither created nor destroyed, why can’t we just go directly from grams of reactant to grams of product?
2. Why is it important to get the subscripts correct in the formulas?
3. Why do the coefficients need to be correct?

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CHAPTER OVERVIEW

6: Energy

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6.1: Properties of Light



Figure 6.1.1 (Public Domain; Jon Sullivan / pdphoto.org via Wikipedia)

What are waves?

Waves can come in many sizes. Here we see a large wave crashing on the beach. Other waves can be very small and regular. We normally think of waves as being made of water, but there are forms of energy that take on the characteristics of waves. The idea of a wave has played a major role in our understanding of how the atom is put together and why it behaves the way it does.

Properties of Light

The nuclear atomic model proposed by Rutherford was a great improvement over previous models, but was still not complete. It did not fully explain the location and behavior of the electrons in the vast space outside of the nucleus. In fact, it was well known that oppositely charged particles attract one another. Rutherford's model did not explain why the electrons don't simply move toward, and eventually collide with, the nucleus. Experiments in the early twentieth century began to focus on the absorption and emission of light by matter. These studies showed how certain phenomena associated with light reveal insight into the nature of matter, energy, and atomic structure.

Wave Nature of Light

In order to begin to understand the nature of the electron, we first need to look at the properties of light. Prior to 1900, scientists thought light behaved solely as a wave. As we will see later, this began to change as new experiments demonstrated that light also has some of the characteristics of a particle. First, we will examine the wavelike properties of light.

Visible light is one type of **electromagnetic radiation**, which is a form of energy that exhibits wavelike behavior as it moves through space. Other types of electromagnetic radiation include gamma rays, x-rays, ultraviolet light, infrared light, microwaves, and radio waves. The figure below shows the **electromagnetic spectrum**, which is all forms of electromagnetic radiation. Notice that visible light makes up only a very, very small portion of the entire electromagnetic spectrum. All electromagnetic radiation moves through a vacuum at a constant speed of $2.998 \times 10^8\ \mathrm{m/s}$. While the presence of air molecules slows the speed of light by a very small amount, we will use the value of $3.00 \times 10^8\ \mathrm{m/s}$ as the speed of light in air.

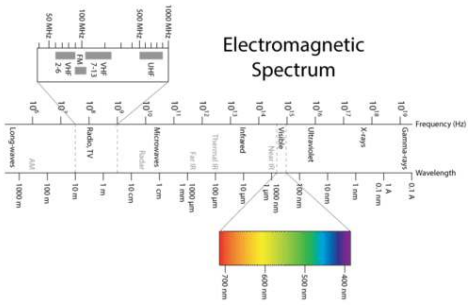


Figure 6.1.2: The electromagnetic spectrum encompasses a very wide range of wavelengths and frequencies. Visible light is only a very small portion of the spectrum with wavelengths from 400-700 nm. (CC BY-NC 3.0; Zachary Wilson via CK-12 Foundation)

The figure above shows how the electromagnetic spectrum displays a wide variation in wavelength and frequency. Radio waves have wavelengths of as long as hundreds of meters, while the wavelength of gamma rays are on the order of $10^{-12}\ \mathrm{m}$. The corresponding frequencies range from 10^6 to $10^{21}\ \mathrm{Hz}$. Visible light can be split into colors with the use of a prism (see below), yielding the visible spectrum of light. Red light has the longest wavelength and lowest frequency, while violet light has the shortest

wavelength and highest frequency. Visible light wavelength ranges from about 400 to 700 nm with frequencies in the range of 10^{14} Hz.

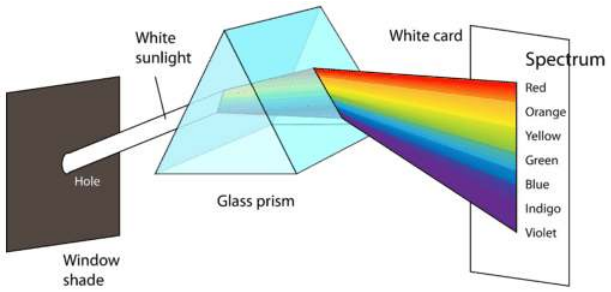


Figure 6.1.3: A small beam of white light is refracted (bent) as it passes through a glass prism. The shorter the wavelength of light, the greater is the refraction, so the light is separated into all of its colors. (CC BY-NC 3.0; Christopher Auyeung via CK-12 Foundation)



Summary

- Electromagnetic radiation is a form of energy.
- Visible light has wavelengths from 400-700 nm.
- The speed of light in air is 3.00×10^8 m/s.

Review

1. What did Rutherford's nuclear atomic model not explain?
2. Prior to 1900, what did scientists believe about the nature of light?
3. What is visible light?
4. What is the range of wavelengths for visible light?

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6.2: Wavelength and Frequency Calculations



Figure 6.2.1 (CC BY 2.0; Piervincenzo Madeo (Flickr:piervix) via Flickr)

Do you enjoy going to the beach?

During the summer, almost everyone enjoys going to the beach. Beach-goers can swim, have picnics, and work on their tans. But if a beach-goer gets too much sun, they can burn. A particular set of solar wavelengths are especially harmful to the skin. This portion of the solar spectrum is known as UV B, with wavelengths of $280\text{-}320\ \text{nm}$. Sunscreens are effective in protecting skin against both the immediate skin damage and the long-term possibility of skin cancer.

Waves

Waves are characterized by their repetitive motion. Imagine a toy boat riding the waves in a wave pool. As the water wave passes under the boat, it moves up and down in a regular and repetitive fashion. While the wave travels horizontally, the boat only travels vertically up and down. The figure below shows two examples of waves.

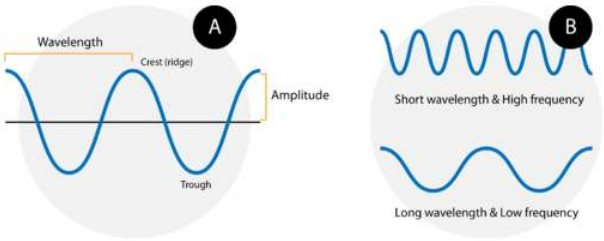


Figure 6.2.2: (A) A wave consists of alternating crests and troughs. The wavelength (λ) is defined as the distance between any two consecutive identical points on the waveform. The amplitude is the height of the wave. (B) A wave with a short wavelength (top) has a high frequency because more waves pass a given point in a certain amount of time. A wave with a longer wavelength (bottom) has a lower frequency. (CC BY-NC 3.0; Christopher Auyeung via CK-12 Foundation)

A wave cycle consists of one complete wave—starting at the zero point, going up to a wave **crest**, going back down to a wave **trough**, and back to the zero point again. The **wavelength** of a wave is the distance between any two corresponding points on adjacent waves. It is easiest to visualize the wavelength of a wave as the distance from one wave crest to the next. In an equation, wavelength is represented by the Greek letter lambda (λ). Depending on the type of wave, wavelength can be measured in meters, centimeters, or nanometers $\left(1\ \text{m} = 10^9\ \text{nm}\right)$. The **frequency**, represented by the Greek letter nu (ν), is the number of waves that pass a certain point in a specified amount of time. Typically, frequency is measured in units of cycles per second or waves per second. One wave per second is also called a Hertz (Hz) and in SI units is a reciprocal second $\left(\text{s}^{-1}\right)$.

Figure B above shows an important relationship between the wavelength and frequency of a wave. The top wave clearly has a shorter wavelength than the second wave. However, if you picture yourself at a stationary point watching these waves pass by, more waves of the first kind would pass by in a given amount of time. Thus the frequency of the first wave is greater than that of the second wave. Wavelength and frequency are therefore inversely related. As the wavelength of a wave increases, its frequency decreases. The equation that relates the two is:

$$c = \lambda\nu$$

The variable c is the speed of light. For the relationship to hold mathematically, if the speed of light is used in m/s, the wavelength must be in meters and the frequency in Hertz.

6.2.1 Example

The color orange within the visible light spectrum has a wavelength of about $620\ \text{nm}$. What is the frequency of orange light?

Solution

Step 1: List the known quantities and plan the problem.

Known

- Wavelength $(\lambda) = 620\ \text{nm}$
- Speed of light $(c) = 3.00 \times 10^8\ \text{m/s}$
- Conversion factor $1\ \text{m} = 10^9\ \text{nm}$

Unknown

- Frequency

Convert the wavelength to m, then apply the equation $c = \lambda\nu$ and solve for frequency. Dividing both sides of the equation by λ yields:

$$\nu = \frac{c}{\lambda}$$

Step 2: Calculate.

$$620\ \text{nm} \times \left(\frac{1\ \text{m}}{10^9\ \text{nm}}\right) = 6.20 \times 10^{-7}\ \text{m}$$

$$\nu = \frac{c}{\lambda} = \frac{3.0 \times 10^8\ \text{m/s}}{6.20 \times 10^{-7}} = 4.8 \times 10^{14}\ \text{Hz}$$

Step 3: Think about your result.

The value for the frequency falls within the range for visible light.



Summary

- All waves can be defined in terms of their frequency and intensity.
- $c = \lambda\nu$ expresses the relationship between wavelength and frequency.

Review

1. Define wavelength.
2. Define frequency.
3. What is the relationship between wavelength and frequency?

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6.3: Quantization of Energy

Every so often, you may hear a commercial or a news story with the words "quantum leap" in it. The quantum leap is supposed to be a major breakthrough—a big change, something extraordinarily large. The reality is far different. Instead of a big extravagant change, the "quantum" that scientists know about is a very small difference in the location of an electron around a nucleus—hardly an enormous shift at all.

Quantization of Energy

German physicist Max Planck (1858-1947) studied the emission of light by hot objects. You have likely seen a heated metal object glow an orange-red color (see below).



Figure 6.3.1: A heated object may glow different colors. The atoms in this piece of metal are releasing energy in discrete units called quanta. (Public Domain; Jack Delano, courtesy of the Library of Congress via Wikipedia)

Classical physics, which explains the behavior of large, everyday objects, predicted that a hot object would emit electromagnetic energy in a continuous fashion. In other words, every wavelength of light could possibly be emitted. Instead, what Planck found by analyzing the spectra was that the energy of the hot body could only be lost in small discrete units. A **quantum** is the minimum quantity of energy that can either be lost or gained by an atom. An analogy is that a brick wall can only undergo a change in height by units of one or more bricks, and not by any possible height. Planck showed that the amount of radiant energy absorbed or emitted by an object is directly proportional to the frequency of the radiation.

$$E = h\nu$$

In the equation, E is the energy, in joules, of a quantum of radiation, ν is the frequency, and h is a fundamental constant called **Planck's constant**. The value of Planck's constant is $h = 6.626 \times 10^{-34}\ \text{J} \cdot \text{s}$. The energy of any system must increase or decrease in units of $h \times \nu$. A small energy change results in the emission or absorption of low-frequency radiation, while a large energy change results in the emission or absorption of high-frequency radiation.

6.3.1 Example

What is the energy of a photon of green light with a frequency of $5.75 \times 10^{14}\ \text{Hz}$?

Solution

Step 1: List the known quantities and plan the problem.

Known

- Frequency $(\nu) = 5.75 \times 10^{14}\ \text{Hz}$
- Planck's constant $(h) = 6.626 \times 10^{-34}\ \text{J} \cdot \text{s}$

Unknown

- energy (E)

Apply the equation $E = h\nu$ to solve for the energy.

Step 2: Calculate.

$$E = \left(6.626 \times 10^{-34}\ \text{J} \cdot \text{s}\right) \times \left(5.75 \times 10^{14}\ \text{Hz}\right) = 3.81 \times 10^{-19}\ \text{J}$$

Step 3: Think about your result.

While the resulting energy may seem very small, this is for only one photon of light. Visible quantities of light consist of huge quantities of photons. Recall that a hertz is equal to a reciprocal second, so the units agree in the equation.

Summary

- A quantum is the minimum quantity of energy that can be lost or gained by an atom.
- The value of Planck's constant is $h = 6.626 \times 10^{-34}\ \mathrm{J \cdot s}$.

Review

1. What did classical physics predict about hot objects?
2. What did Planck find?
3. What is a quantum?

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6.4: Atomic Emission Spectra



Figure 6.4.1 (Public Domain; Department of Defense Warrior Games via Commons Wikimedia, Archery at the 2017 Warrior Games [commons.wikimedia.org])

How much energy does it take to shoot an arrow?

Archery as a sport or a means of defense has existed for centuries. At rest, there is no tension on the bowstring and no force on the arrow. When the string and arrow are pulled back, we now have a situation where kinetic energy (pulling of the string) has been converted to potential energy (the tension on the string). The archer releases the arrow and the potential energy is translated into kinetic energy as the arrow moves. It turns out that electrons behave the same way when energy is put into the system or released from the system.

Atomic Emission Spectra

The electrons in an atom tend to be arranged in such a way that the energy of the atom is as low as possible. The **ground state** of an atom is the lowest energy state of the atom. When those atoms are given energy, the electrons absorb the energy and move to a higher energy level. These energy levels of the electrons in atoms are quantized, meaning again that the electron must move from one energy level to another in discrete steps, rather than continuously. An **excited state** of an atom is a state where its potential energy is higher than the ground state. An atom in the excited state is not stable. When it returns back to the ground state, it releases the energy that it had previously gained in the form of electromagnetic radiation.

So how do atoms gain energy in the first place? One way is to pass an electric current through an enclosed sample of a gas at low pressure. Since the electron energy levels are unique for each element, every gas discharge tube will glow with a distinctive color, depending on the identity of the gas (see below).

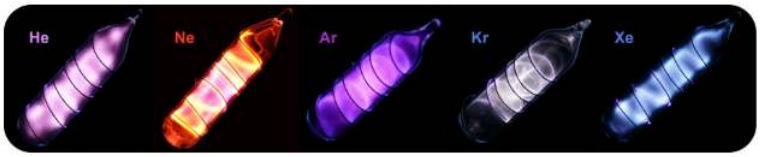


Figure 6.4.2: Gas discharge tubes are enclosed glass tubes filled with a gas at low pressure, through which an electric current is passed. Electrons in the gaseous atoms first become excited, and then fall back to lower energy levels, emitting light of a distinctive color in the process. Shown are gas discharge tubes of helium, neon, argon, krypton, and xenon. (CC by 3.0; User:Jurii/Wikimedia Commons, Heinrich Pniok (Wikimedia: Alchemist-hp) via Commons Wikimedia, Glowing noble gases [commons.wikimedia.org])

"Neon" signs are familiar examples of gas discharge tubes. However, only signs that glow with the red-orange color seen in the figure are actually filled with neon. Signs of other colors contain different gases or mixtures of gases.

Scientists studied the distinctive pink color of the gas discharge created by hydrogen gas. When a narrow beam of this light was viewed through a prism, the light was separated into four lines of very specific wavelengths (and frequencies since λ and ν are inversely related). An **atomic emission spectrum** is the pattern of lines formed when light passes through a prism to separate it into the different frequencies of light it contains. The figure below shows the atomic emission spectrum of hydrogen.

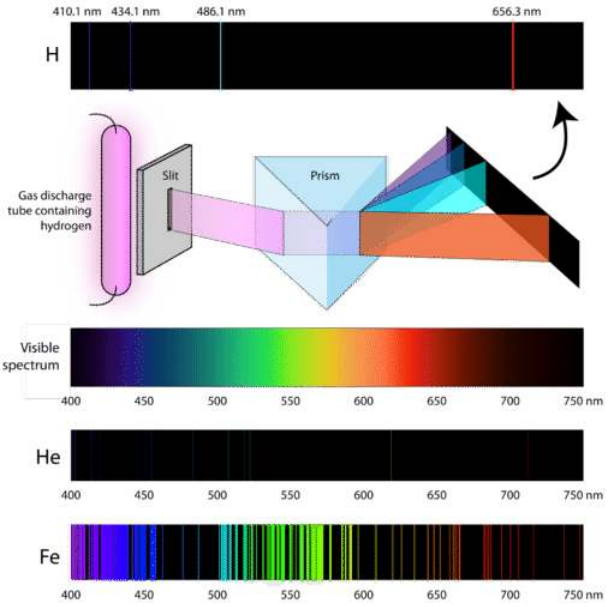


Figure 6.4.3: When light from a hydrogen gas discharge tube is passed through a prism, the light is split into four visible lines. Each of these spectral lines corresponds to a different electron transition from a higher energy state to a lower energy state. Every element has a unique atomic emission spectrum, as shown by the examples of helium (He) and iron (Fe). (CC BY-NC 3.0; Christopher Auyeung, using emission spectra available in the public domain via CK-12 Foundation; H spectrum: Commons Wikimedia, Emission Spectrum- H [commons.wikimedia.org]; visible spectrum: Commons Wikimedia, Linear Visible Spectrum [commons.wikimedia.org]; He spectrum: Commons Wikimedia, Helium Emission Spectrum [commons.wikimedia.org]; Fe spectrum: Commons Wikimedia, Emission Spectrum-Fe [commons.wikimedia.org])

Classical theory was unable to explain the existence of atomic emission spectra, also known as line-emission spectra. According to classical physics, a ground state atom would be able to absorb any amount of energy rather than only discrete amounts. Likewise, when the atoms relaxed back to a lower energy state, any amount of energy could be released. This would result in what is known as a **continuous spectrum**, where all wavelengths and frequencies are represented. White light viewed through a prism and a rainbow are examples of continuous spectra. Atomic emission spectra were more proof of the quantized nature of light and led to a new model of the atom based on quantum theory.



Summary

- Atomic emission spectra are produced when excited electrons return to the ground state.
- The emitted light of electrons corresponds to energies of the specific electrons.

Review

1. What is the ground state of an atom?
2. What is an excited state?
3. Why do we see emission lines when electrons return to the ground state?

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6.5: Bohr's Atomic Model



Figure 6.5.1 (Public Domain; the US Department of Agriculture via Wikipedia)

How does this worker's energy change as he climbs up and down the ladder?

Climbing a ladder takes energy. At every step, you push yourself up against gravity, and accumulate potential energy. Coming back down releases that potential energy as you descend step by step. If you are not careful, you can release that potential energy all at once by falling off the ladder (never a good thing). In addition, you take the climb or descent in steps. There is no "in-between" position on the ladder—your foot either hits a rung, or it hits empty space, and you are in trouble until you find a rung to stand on.

Bohr's Atomic Model

Following the discoveries of hydrogen emission spectra and the photoelectric effect, the Danish physicist Niels Bohr (1885-1962) proposed a new model of the atom in 1915. Bohr proposed that electrons do not radiate energy as they orbit the nucleus, but exist in states of constant energy that he called **stationary states**. This means that the electrons orbit at fixed distances from the nucleus (see below). Bohr's work was primarily based on the emission spectra of hydrogen. This is also referred to as the planetary model of the atom. It explained the inner workings of the hydrogen atom. Bohr was awarded the Nobel Prize in physics in 1922 for his work.

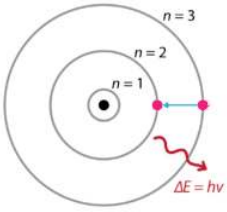


Figure 6.5.2: Bohr's atomic model hydrogen emission spectra. (CC BY-NC 3.0; Zachary Wilson via CK-12 Foundation)

Bohr explained that electrons can be moved into different orbits with the addition of energy. When the energy is removed, the electrons return back to their ground state, emitting a corresponding amount of energy—a quantum of light, or photon. This was the basis for what later became known as **quantum theory**. This is a theory based on the principle that matter and energy have the properties of both particles and waves. It accounts for a wide range of physical phenomena, including the existence of discrete packets of energy and matter, the uncertainty principle, and the exclusion principle.

According to the Bohr model, often referred to as a **planetary model**, the electrons encircle the nucleus of the atom in specific allowable paths called orbits. When the electron is in one of these orbits, its energy is fixed. The ground state of the hydrogen atom, where its energy is lowest, is when the electron is in the orbit that is closest to the nucleus. The orbits that are further from the nucleus are all of successively greater energy. The electron is not allowed to occupy any of the spaces in between the orbits. An everyday analogy to the Bohr model is the rungs of a ladder. As you move up or down a ladder, you can only occupy specific rungs and cannot be in the spaces in between rungs. Moving up the ladder increases your potential energy, while moving down the ladder decreases your energy.

Bohr's work had a strong influence on our modern understanding of the inner workings of the atom. However, his model worked well as an explanation for the emissions of the hydrogen atom, but was seriously limited when applied to other atoms. Shortly after

Bohr published his planetary model of the atom, several new discoveries were made, which resulted in, yet again, a revised view of the atom.



Summary

- The Bohr model postulates that electrons orbit the nucleus at fixed energy levels.
- Orbits further from the nucleus exist at higher energy levels.
- When electrons return to a lower energy level, they emit energy in the form of light.

Review

1. When did Bohr propose his model of the atom?
2. What is a stationary state?
3. What is the ground state?
4. Can the electron occupy any space between the orbits?

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6.6: Chemical Potential Energy

Gunpowder was originally developed by the Chinese in the ninth century AD, primarily for rockets. This material is composed of charcoal, sulfur, and saltpeter (potassium nitrate). The explosive reaction that occurs involves the conversion of the charcoal to carbon dioxide, with the potassium nitrate providing the extra oxygen needed for a rapid reaction. Although sulfur was included to stabilize the product, gunpowder is still highly explosive.

Types of Energy

Two basic types of energy exist: potential energy and kinetic energy. **Potential energy** is stored energy. It has not yet been released, but is ready to go. **Kinetic energy** is the energy of motion. It causes work to be done through movement.

Chemical Potential Energy

Energy is the capacity for doing work or supplying heat. When you fill your car with gasoline, you are providing it with potential energy. **Chemical potential energy** is the energy stored in the chemical bonds of a substance. The various chemicals that make up gasoline contain a large amount of chemical potential energy that is released when the gasoline is burned in a controlled way in the engine of the car. The release of that energy does two things: some of the potential energy is transformed into work, which is used to move the car; at the same time, some of the potential energy is converted to heat and makes the car's engine very hot. The energy changes of a system occur as either heat or work, or some combination of both.



Figure 6.6.1: A dragster is able to accelerate because of the chemical potential energy of its fuel. The burning of the fuel also produces large amounts of heat. (CC BY-NC; CK-12)

Dynamite is another example of chemical potential energy. The major component of dynamite is nitroglycerin, a very unstable material. By mixing it with diatomaceous earth, the stability is increased and it is less likely to explode if it receives a physical shock. When ignited, the nitroglycerin explodes rapidly, releasing large amounts of nitrogen and other gases along with a massive amount of heat.



Figure 6.6.2: Dynamite explosion. (CC BY-NC; CK-12)

Summary

- Potential energy is stored energy.
- Kinetic energy is the energy of motion.
- Chemical potential energy is energy available in the chemical bonds of a compound.

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6.7: Heat

Blacksmiths heat solid iron in order to shape it into a variety of different objects. Iron is a rigid, solid metal. At room temperature, it is extremely difficult to bend iron. However, when heated to a high enough temperature, iron can be easily worked. The heat energy in the forge is transferred to the metal, making the iron atoms vibrate more and move around more readily.

Heat is energy that is transferred from one object or substance to another because of a difference in temperature between the two. Heat always flows from an object at a higher temperature to an object at a lower temperature (see figure below). The flow of heat will continue until the two objects are at the same temperature.

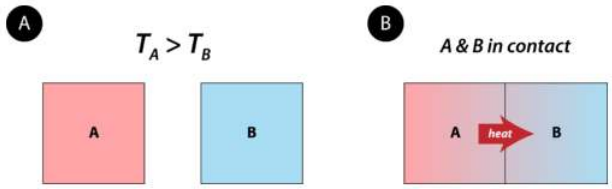


***Figure* 6.7.1:** *Object A starts with a higher temperature than object B. No heat flows when the objects are isolated from each other. When brought into contact, heat flows from A to B until the temperatures of the two objects are the same.*

Thermochemistry is the study of energy changes that occur during chemical reactions and during changes of state. When chemical reactions occur, some chemical bonds are broken, while new chemical bonds form. As a result of the rearrangement of atoms, the total chemical potential energy of the system either increases or decreases.

Summary

- Heat is transferred energy from a site of higher energy to a site of lower energy.
- Thermochemistry is the study of energy changes that occur during chemical reactions and during changes of state.

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6.8: Exothermic and Endothermic Processes

A campfire is an example of basic thermochemistry. The reaction is initiated by the application of heat from a match. The reaction converting wood to carbon dioxide and water (among other things) continues, releasing heat energy in the process. This heat energy can then be used to cook food, roast marshmallows, or simply to keep warm when it's cold outside.

Exothermic and Endothermic Processes

When physical or chemical changes occur, they are generally accompanied by a transfer of energy. The **law of conservation of energy** states that in any physical or chemical process, energy is neither created nor destroyed. In other words, the entire energy in the universe is conserved. In order to better understand the energy changes taking place during a reaction, we need to define two parts of the universe: *the system* and *the surroundings*. The **system** is the specific portion of matter in a given space that is being studied during an experiment or an observation. The **surroundings** is everything in the universe that is not part of the system. In practical terms for a laboratory chemist, the system is the particular chemicals being reacted, while the surroundings is the immediate vicinity within the room. During most processes, energy is exchanged between the system and the surroundings. If the system loses a certain amount of energy, that same amount of energy is gained by the surroundings. If the system gains a certain amount of energy, that energy is supplied by the surroundings.

A chemical reaction or physical change is **endothermic** if heat is absorbed by the system from the surroundings. In the course of an endothermic process, the system gains heat from the surroundings, and so the temperature of the surroundings decreases. The quantity of heat for a process is represented by the letter q. The sign of q for an endothermic process is positive because the system is gaining heat. A chemical reaction or physical change is **exothermic** if heat is released by the system into the surroundings. Because the surroundings are gaining heat from the system, the temperature of the surroundings increases. The sign of q for an exothermic process is negative because the system is losing heat.

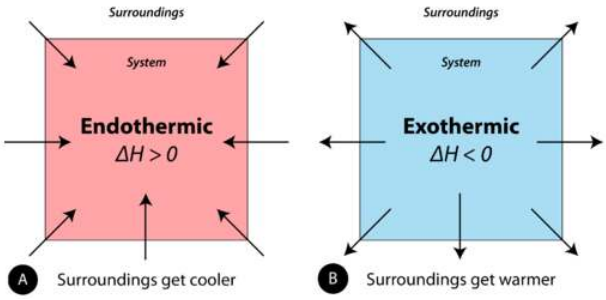


Figure 6.8.1: (A) Endothermic reaction. (B) Exothermic reaction. (CC BY-NC; CK-12)

Units of Heat

Heat flow is measured in one of two common units: the calorie and the joule. The joule (J) is the SI unit of energy. The calorie is familiar because it is commonly used when referring to the amount of energy contained within food. A **calorie** (cal) is the quantity of heat required to raise the temperature of 1 gram of water by $1^{\circ}\mathrm{C}$. For example, raising the temperature of $100\ \mathrm{g}$ of water from $20^{\circ}\mathrm{C}$ to $22^{\circ}\mathrm{C}$ would require $100 \times 2 = 200\ \mathrm{cal}$.

Calories contained within food are actually kilocalories (kcal). In other words, if a certain snack contains 85 food calories, it actually contains $85\ \mathrm{kcal}$ or $85,000\ \mathrm{cal}$ In order to make the distinction, the dietary calorie is written with a capital C.

$$1\ \text{kilocalorie} = 1\ \text{Calorie} = 1000\ \text{calories}$$

To say that the snack "contains" 85 Calories means that $85\ \mathrm{kcal}$ of energy are released when that snack is processed by the human body.

Heat changes in chemical reactions are typically measured in joules rather than calories. The conversion between a joule and a calorie is shown below.

$$1\ \mathrm{J} = 0.2390\ \mathrm{cal} \text{ or } 1\ \mathrm{cal} = 4.184\ \mathrm{J}$$

We can calculate the amount of heat released in kilojoules when a 400 Calorie hamburger is digested:

$$400.\ \text{Cal} = 400.\ \text{kcal} \times \frac{4.184\ \text{kJ}}{1\ \text{kcal}} = 1.67 \times 10^3\ \text{kJ}$$

Summary

- The law of conservation of energy states that in any physical or chemical process, energy is neither created nor destroyed.
- A specific portion of matter in a given space that is being studied during an experiment or an observation is the *system*.
- The *surroundings* is everything in the universe that is not part of the system.
- A chemical reaction or physical change is endothermic if heat is absorbed by the system from the surroundings.
- A reaction or change is exothermic if heat is released by the system into the surroundings.

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6.9: Heat Capacity and Specific Heat

If a swimming pool and wading pool, both full of water at the same temperature, were subjected to the same input of heat energy, the wading pool would certainly rise in temperature more quickly than the swimming pool. The heat capacity of an object depends both on its mass and its chemical composition. Because of its much larger mass, the swimming pool of water has a larger heat capacity than the wading pool.

Heat Capacity and Specific Heat

Different substances respond to heat in different ways. If a metal chair sits in the bright sun on a hot day, it may become quite hot to the touch. An equal mass of water under the same sun exposure will not become nearly as hot. This means that water has a high **heat capacity** (the amount of heat required to raise the temperature of an object by $1^{\circ}\mathrm{C}$). Water is very resistant to changes in temperature, while metals generally are not. The **specific heat** of a substance is the amount of energy required to raise the temperature of 1 gram of the substance by $1^{\circ}\mathrm{C}$. The table below lists the specific heats of some common substances. The symbol for specific heat is c_p, with the p subscript referring to the fact that specific heats are measured at constant pressure. The units for specific heat can either be joules per gram per degree $\left(\mathrm{J/g^{\circ}C}\right)$ or calories per gram per degree $\left(\mathrm{cal/g^{\circ}C}\right)$. This text will use $\mathrm{J/g^{\circ}C}$ for specific heat.

Table 6.9.1: Specific Heats of Some Common Substances

Substance	Specific Heat $\left(\mathrm{J/g^{\circ}C}\right)$
Water (l)	4.18
Water (s)	2.06
Water (g)	1.87
Ammonia (g)	2.09
Ethanol (l)	2.44
Aluminum (s)	0.897
Carbon, graphite (s)	0.709
Copper (s)	0.385
Gold (s)	0.129
Iron (s)	0.449
Lead (s)	0.129
Mercury (l)	0.140
Silver (s)	0.233

Notice that water has a very high specific heat compared to most other substances. Water is commonly used as a coolant for machinery because it is able to absorb large quantities of heat (see table above). Coastal climates are much more moderate than inland climates because of the presence of the ocean. Water in lakes or oceans absorbs heat from the air on hot days and releases it back into the air on cool days.



Figure 6.9.1: This power plant in West Virginia, like many others, is located next to a large lake so that the water from the lake can be used as a coolant. Cool water from the lake is pumped into the plant, while warmer water is pumped out of the plant and back into the lake. (CC BY-NC; CK-12)

Summary

- Heat capacity is the amount of heat required to raise the temperature of an object by $1^{\circ}\mathrm{C}$.
- The specific heat of a substance is the amount of energy required to raise the temperature of 1 gram of the substance by $1^{\circ}\mathrm{C}$.

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6.10: Specific Heat Calculations

Water has a high capacity for absorbing heat. In a car radiator, it serves to keep the engine cooler than it would otherwise run. As the water circulates through the engine, it absorbs heat from the engine block. When it passes through the radiator, the cooling fan and the exposure to the outside environment allow the water to cool somewhat before it makes another passage through the engine.

Specific Heat Calculations

The specific heat of a substance can be used to calculate the temperature change that a given substance will undergo when it is either heated or cooled. The equation that relates heat (q) to specific heat (c_p), mass (m), and temperature change (ΔT) is shown below.

$$q = c_p \times m \times \Delta T$$

The heat that is either absorbed or released is measured in joules. The mass is measured in grams. The change in temperature is given by $\Delta T = T_f - T_i$, where T_f is the final temperature and T_i is the initial temperature.

6.10.1 Example

A $15.0\ \text{g}$ piece of cadmium metal absorbs $134\ \text{J}$ of heat while rising from 24.0°C to 62.7°C. Calculate the specific heat of cadmium.

Solution

Step 1: List the known quantities and plan the problem.

Known

- Heat $= q = 134\ \text{J}$
- Mass $= m = 15.0\ \text{g}$
- $\Delta T = 62.7^\circ\text{C} - 24.0^\circ\text{C} = 38.7^\circ\text{C}$

Unknown

The specific heat equation can be rearranged to solve for the specific heat.

Step 2: Solve.

$$c_p = \frac{q}{m \times \Delta T} = \frac{134\ \text{J}}{15.0\ \text{g} \times 38.7^\circ\text{C}} = 0.231\ \text{J/g}^\circ\text{C}$$

Step 3: Think about your result.

The specific heat of cadmium, a metal, is fairly close to the specific heats of other metals. The result has three significant figures.

Since most specific heats are known, they can be used to determine the final temperature attained by a substance when it is either heated or cooled. Suppose that $60.0\ \text{g}$ of water at 23.52°C was cooled by the removal of $813\ \text{J}$ of heat. The change in temperature can be calculated using the specific heat equation:

$$\Delta T = \frac{q}{c_p \times m} = \frac{813\ \text{J}}{4.18\ \text{J/g}^\circ\text{C} \times 60.0\ \text{g}} = 3.24^\circ\text{C}$$

Since the water was being cooled, the temperature decreases. The final temperature is:

$$T_f = 23.52^\circ\text{C} - 3.24^\circ\text{C} = 20.28^\circ\text{C}$$

Summary

- The specific heat of a substance can be used to calculate the temperature change of the substance when it is heated or cooled.
- Specific heat calculations are illustrated.

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6.11: Enthalpy

The factors influencing a reaction are complicated and varied. Since a catalyst affects activation energy, we might assume it would have some sort of impact on the amount of heat that is absorbed or released by the reaction—but it does not. The change in heat content of a reaction depends solely on the chemical compositions of the reactants and products, not on the path taken to get from one to the other.

Enthalpy

Heat changes in chemical reactions are often measured in the laboratory under conditions in which the reacting system is open to the atmosphere. In these cases, the system is at a constant pressure. **Enthalpy** $(\boldsymbol{H})$ is the heat content of a system at constant pressure. Chemists routinely measure changes in enthalpy of chemical systems as reactants are converted into products. The heat that is absorbed or released by a reaction at constant pressure is the same as the enthalpy change, and is given the symbol ΔH. Unless otherwise specified, all reactions in this material are assumed to take place at constant pressure.

The change in enthalpy of a reaction is a measure of the differences in enthalpy of the reactants and products. The enthalpy of a system is determined by the energies needed to break chemical bonds and the energies needed to form chemical bonds. Energy needs to be put into the system in order to break chemical bonds—they do not come apart spontaneously in most cases. Bond formation to produce products will involve release of energy. The change in enthalpy shows the trade-offs made in these two processes. Does it take more energy to break bonds than that needed to form bonds? If so, the reaction is endothermic and the enthalpy change is positive. If more energy is produced in bond formation than that needed for bond breaking, the reaction is exothermic and the enthalpy is negative.

Several factors influence the enthalpy of a system. Enthalpy is an extensive property, determined in part by the amount of material being dealt with. The state of reactants and products (solid, liquid, or gas) influences the enthalpy value for a system. The direction of the reaction affects the enthalpy value. A reaction that takes place in the opposite direction has the same numerical enthalpy value, but the opposite sign.

Summary

- Enthalpy, the heat content of a system at constant pressure, is related to the heat of reaction.
- The enthalpy of a system is determined by the energies needed to break chemical bonds and the energies needed to form chemical bonds.
- Factors that influencing enthalpy include: amount of materials, the state of reactants and products, and direction of the reaction.

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6.12: Calorimetry

At one time, calories in foods were measured with a bomb calorimeter. A weighed amount of the food would be placed in the calorimeter and the system was then sealed and filled with oxygen. An electric spark ignited the food-oxygen mixture. The amount of heat released when the food burned gave an idea of the calories present within the food. Today, calories are calculated from the protein, carbohydrate, and fat content of food (all determined by chemical analysis).

Calorimetry

Calorimetry is the measurement of the transfer of heat into or out of a system during a chemical reaction or physical process. A **calorimeter** is an insulated container that is used to measure heat changes. The majority of reactions that can be analyzed in a calorimetry experiment are either liquids or aqueous solutions. A frequently used and inexpensive calorimeter is a set of nested foam cups fitted with a lid to limit the heat exchange between the liquid in the cup and the air in the surroundings (see figure below). In a typical calorimetry experiment, specific volumes of the reactants are dispensed into separate containers and the temperature of each is measured. They are then mixed into the calorimeter, which starts the reaction. The reactant mixture is stirred until the reaction is complete, while the temperature of the reaction is continuously monitored.

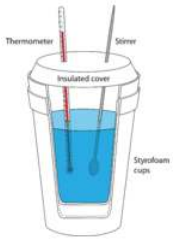


Figure 6.12.1: A simple constant-pressure calorimeter. (CC BY-NC; CK-12)

The key to all calorimetry experiments is the assumption that there is no heat exchange between the insulated calorimeter and the room. Consider the case of a reaction taking place between aqueous reactants: the water in which the solids have been dissolved is the surroundings, while the dissolved substances are the system. The temperature change that is measured is the temperature change that is occurring in the surroundings. If the temperature of the water increases as the reaction occurs, the reaction is exothermic. Heat was released by the system into the surrounding water. An endothermic reaction absorbs heat from the surroundings, so the temperature of the water decreases as heat leaves the surroundings to enter the system.

The temperature change of the water is measured in the experiment and the specific heat of water can be used to calculate the heat absorbed by the surroundings (q_{surr}).

$$q_{\text{surr}} = m \times c_p \times \Delta T$$

In the equation, m is the mass of the water, c_p is the specific heat of the water, and ΔT is $T_f - T_i$. The heat absorbed by the surroundings is equal, but opposite in sign, to the heat released by the system. Because the heat change is determined at constant pressure, the heat released by the system (q_{sys}) is equal to the enthalpy change (ΔH).

$$q_{\text{sys}} = \Delta H = -q_{\text{surr}} = -\left(m \times c_p \times \Delta T\right)$$

The sign of ΔH is positive for an endothermic reaction and negative for an exothermic reaction.

6.12.1 Example

In an experiment, $25.0\ \text{mL}$ of $1.00\ \text{M HCl}$ at 25.0°C is added to $25.0\ \text{mL}$ of $1.00\ \text{M NaOH}$ at 25.0°C in a foam cup calorimeter. A reaction occurs and the temperature rises to 32.0°C. Calculate the enthalpy change (ΔH) in kJ for this reaction. Assume the densities of the solutions are $1.00\ \text{g/mL}$and that their specific heat is the same as that of water.

Solution

Step 1: List the known quantities and plan the problem.

Known

- $c_p = 4.18\ \text{J/g}^{\circ}\text{C}$
- $V_{\text{final}} = 25.0\ \text{mL} + 25.0\ \text{mL} = 50.0\ \text{mL}$

- $\Delta T = 32.0^{\circ}\text{C} - 25.0^{\circ}\text{C} = 7.0^{\circ}\text{C}$
- Density $= 1.00\ \text{g/mL}$

Unknown

The volume and density can be used to find the mass of the solution after mixing. Then calculate the change in enthalpy by using $\Delta H = q_{\text{sys}} = -q_{\text{surr}} = -\left(m \times c_p \times \Delta T\right)$.

Step 2: Solve.

$$m = 50.0\ \text{mL} \times \frac{1.00\ \text{g}}{\text{mL}} = 50.0\ \text{g}$$

$$\Delta H = -\left(m \times c_p \times \Delta T\right) = -\left(50.0\ \text{g} \times 4.18\ \text{J/g}^{\circ}\text{C} \times 7.0^{\circ}\text{C}\right) = -1463\ \text{J} = -1.5\ \text{kJ}$$

Step 3: Think about the result.

The enthalpy change is negative because the reaction releases heat to the surroundings, resulting in an increase in the temperature of the water.

Summary

- Calorimetry is the measurement of the transfer of heat into or out of a system during a chemical reaction or physical process.
- A calorimeter is an insulated container that is used to measure heat changes.
- Calculations involving enthalpy changes are illustrated.

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6.13: Thermochemical Equations

Heating a home is becoming more and more expensive. The decision to use gas, oil, electricity, or wood can be multi-faceted. Part of the decision is based on which fuel will provide the highest amount of energy release when burned. Studies of thermochemistry can be very useful in getting reliable information for making these important choices.

Thermochemical Equation

When methane gas is combusted, heat is released, making the reaction exothermic. Specifically, the combustion of 1 mol of methane releases 890.4 kilojoules of heat energy. This information can be shown as part of a balanced equation:

$$\mathrm{CH_4}\,(g) + 2\mathrm{O_2}\,(g) \rightarrow \mathrm{CO_2}\,(g) + 2\mathrm{H_2O}\,(l) + 890.4\ \mathrm{kJ}$$

The equation tells us that 1 mol of methane combines with 2 mol of oxygen to produce 1 mol of carbon dioxide and 2 mol of water. In the process, 890.4 kJ is released and so it is written as a product of the reaction. A **thermochemical equation** is a chemical equation that includes the enthalpy change of the reaction. The process in the above thermochemical equation can be shown visually in the figure below.

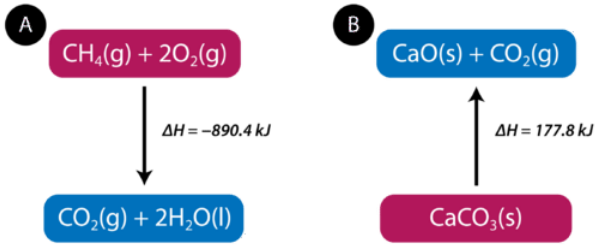


Figure 6.13.1*: (A) As reactants are converted to products in an exothermic reaction, enthalpy is released into the surroundings. The enthalpy change of the reaction is negative. (B) As reactants are converted to products in an endothermic reaction, enthalpy is absorbed from the surroundings. The enthalpy change of the reaction is positive.* (CC BY-NC; CK-12)

In the combustion of methane example, the enthalpy change is negative because heat is being released by the system. Therefore, the overall enthalpy of the system decreases. The **heat of reaction** is the enthalpy change for a chemical reaction. In the case above, the heat of reaction is -890.4 kJ. The thermochemical reaction can also be written in this way:

$$\mathrm{CH_4}\,(g) + 2\mathrm{O_2}\,(g) \rightarrow \mathrm{CO_2}\,(g) + 2\mathrm{H_2O}\,(l) \quad \Delta H = -890.4\ \mathrm{kJ}$$

Heats of reaction are typically measured in kilojoules. It is important to include the physical states of the reactants and products in a thermochemical equation, as the value of the ΔH depends on those states.

Endothermic reactions absorb energy from the surroundings as the reaction occurs. When 1 mol of calcium carbonate decomposes into 1 mol of calcium oxide and 1 mol of carbon dioxide, 177.8 kJ of heat is absorbed. The process is shown visually in the figure above (B). The thermochemical reaction is shown below.

$$\mathrm{CaCO_3}\,(s) + 177.8\ \mathrm{kJ} \rightarrow \mathrm{CaO}\,(s) + \mathrm{CO_2}\,(g)$$

Because the heat is absorbed by the system, the 177.8 kJ is written as a reactant. The heat of reaction is positive for an endothermic reaction.

$$\mathrm{CaCO_3}\,(s) \rightarrow \mathrm{CaO}\,(s) + \mathrm{CO_2}\,(g) \quad \Delta H = 177.8\ \mathrm{kJ}$$

The way in which a reaction is written influences the value of the enthalpy change for the reaction. Many reactions are reversible, meaning that the product(s) of the reaction are capable of combining and reforming the reactant(s). If a reaction is written in the reverse direction, the sign of the ΔH changes. For example, we can write an equation for the reaction of calcium oxide with carbon dioxide to form calcium carbonate:

$$\mathrm{CaO}\,(s) + \mathrm{CO_2}\,(g) \rightarrow \mathrm{CaCO_3}\,(s) + 177.8\ \mathrm{kJ}$$

The reaction is exothermic and thus the sign of the enthalpy change is negative.

$$\mathrm{CaO}\,(s) + \mathrm{CO_2}\,(g) \rightarrow \mathrm{CaCO_3}\,(s) \quad \Delta H = -177.8\ \mathrm{kJ}$$

Summary

- A thermochemical equation is a chemical equation that includes the enthalpy change of the reaction.
- The heat of reaction is the enthalpy change for a chemical reaction.

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6.14: Stoichiometric Calculations and Enthalpy Changes

There is a growing concern about damage to the environment done by emissions from manufacturing plants. Many companies are taking steps to reduce these harmful emissions by adding equipment that will trap the pollutants. In order to know what equipment (and the quantity) to order, studies are done to measure the amount of product currently produced. Since pollution is often both particulate and thermal, energy changes need to be determined in addition to the amounts of products released.

Stoichiometric Calculations and Enthalpy Changes

Chemistry problems that involve enthalpy changes can be solved by techniques similar to stoichiometry problems. Refer again to the combustion reaction of methane. Since the reaction of 1 mol of methane released 890.4 kJ, the reaction of 2 mol of methane would release $2 \times 890.4 \text{ kJ} = 1781 \text{ kJ}$. The reaction of 0.5 mol of methane would release $\frac{890,4 \text{ kJ}}{2} = 445.2 \text{ kJ}$. As with other stoichiometry problems, the moles of a reactant or product can be linked to mass or volume.

6.14.1 Example

Sulfur dioxide gas reacts with oxygen to form sulfur trioxide in an exothermic reaction, according to the following thermochemical equation.

$$2\text{SO}_2\,(g) + \text{O}_2\,(g) \rightarrow 2\text{SO}_3\,(g) + 198 \text{ kJ}$$

Calculate the enthalpy change that occurs when 58.0 g of sulfur dioxide is reacted with excess oxygen.

Solution:

Step 1: List the known quantities and plan the problem.

- Mass $\text{SO}_2 = 58.0$ g
- Molar mass $\text{SO}_2 = 64.07$ g/mol
- $\Delta H = -198$ kJ for the reaction of 2 mol SO_2

Unknown

The calculation requires two steps. The mass of SO_2 is converted to moles. Then the moles of SO_2 is multiplied by the conversion factor of $\left(\frac{-198 \text{ kJ}}{2 \text{ mol SO}_2}\right)$.

Step 2: Solve.

$$\Delta H = 58.0 \text{ g SO}_2 \times \frac{1 \text{ mol SO}_2}{64.07 \text{ g SO}_2} \times \frac{-198 \text{ kJ}}{2 \text{ mol SO}_2} = 89.6 \text{ kJ}$$

Step 3: Think about your result.

The mass of sulfur dioxide is slightly less than 1 mol. Since 198 kJ is released for every 2 mol of SO_2 that reacts, the heat released when about 1 mol reacts is one half of 198. The 89.6 kJ is slightly less than half of 198. The sign of ΔH is negative because the reaction is exothermic.

Summary

- Chemistry problems that involve enthalpy changes can be solved by techniques similar to stoichiometry problems.
- Calculations of energy changes in enthalpy equations are described.

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CHAPTER OVERVIEW

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7.1: Structure and Composition of the Atmosphere

Life as we know it on the Earth is entirely dependent on the tenuous layer of gas that clings to the surface of the globe, adding about 1% to its diameter and an insignificant amount to its total mass. And yet the atmosphere serves as the earth's window and protective shield, as a medium for the transport of heat and water, and as source and sink for exchange of carbon, oxygen, and nitrogen with the biosphere. The atmosphere acts as a compressible fluid tied to the earth by gravitation; as a receptor of solar energy and a thermal reservoir, it constitutes the working fluid of a heat engine that transports and redistributes matter and energy over the entire globe. The atmosphere is also a major temporary repository of a number of chemical elements that move in a cyclic manner between the hydrosphere, atmosphere, and the upper lithosphere. Finally, the atmosphere is a site for a large variety of complex photochemically initiated reactions involving both natural and anthropogenic substances.

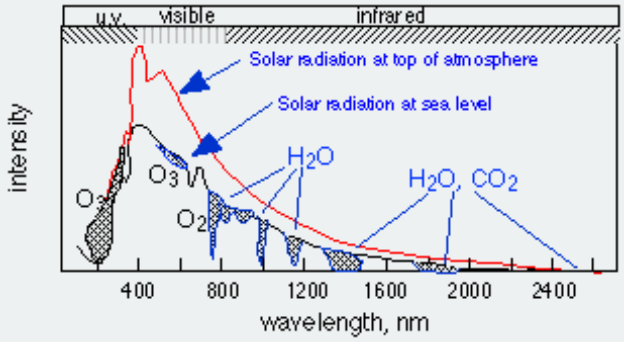
> *On the scale of cubic meters the air is a homogeneous mixture of its constituent gases, but on a larger scale the atmosphere is anything but uniform. Variations of temperature, pressure, and moisture content in the layers of air near the earth's surface give rise to the dynamic effects we know as the weather.*

Although the density of the atmosphere decreases without limit with increasing height, for most practical purposes one can roughly place its upper boundary at about 500 km. However, half the mass of the atmosphere lies within 5 km, and 99.99% within 80 km of the surface. The average atmospheric pressure at sea level is 1.01 x 10^5 pascals, or 1010 millibars. A 1-cm^2 cross section of the earth's surface supports a column weighing 1030 g; the total mass of the atmosphere is about 5.27 x 10^{21} g.

About 80% of the mass of the atmosphere resides in the first 10 km; this well-mixed region of fairly uniform composition is known as the *troposphere*.

Solar irradiation of the Earth

The gases ozone, water vapor, and carbon dioxide are only minor components of the atmosphere, but they exert a huge effect on the Earth by absorbing radiation in the ranges indicated by the shading. Ozone in the upper atmosphere filters out the ultraviolet light below about 360 nm that is destructive of life. O_2, H_2O, CO_2 and CH_4 are "greenhouse" gases that trap some of the heat absorbed from the Sun and prevent it from re-radiating back into space.

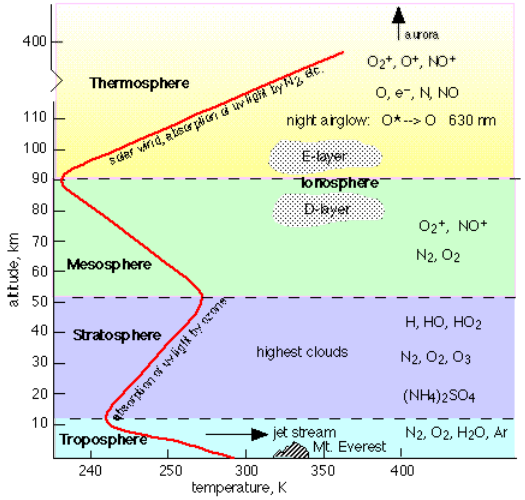


Structure of the atmosphere

We commonly think of gas molecules as moving about in a completely random manner, but the Earth's gravitational field causes downward motions to be very slightly favored so that the molecules in any thin layer of the air collide more frequently with those in the layer below. This gives rise to a pressure gradient that is the most predictable and well known structural characteristic of the atmosphere. This gradient is described by an exponential law which predicts that the atmospheric pressure should decrease by 50% for every 6 km increase in altitude. This law also predicts that the composition of a gas mixture will change with altitude, the lower-molecular weight components being increasingly favored at higher altitudes. However, this gravitational fractionation effect is completely obliterated below about 160 km owing to turbulence and convective flows (winds).

The atmosphere is divided vertically into several major regions which are distinguished by the sign of the temperature gradient. In the lowermost region, the troposphere, the temperature falls with increasing altitude. The major source of heat input into this part of the atmosphere is long-wave radiation from the earth's surface, while the major loss is radiation into space.

At higher elevations the temperature begins to rise with altitude as we move into a region in which heat is produced by exothermic chemical reactions, mainly the decomposition of ozone that is formed photochemically from dioxygen in the stratosphere. At still higher elevations the ozone gives out and the temperature begins to drop; this is the mesosphere, which is finally replaced by the thermosphere which consists largely of a plasma (gaseous ions). This outer section of the atmosphere which extends indefinitely to perhaps 2000 km is heated by absorption of intense u.v. radiation from the Sun and also from the solar wind, a continual rain of electrons, protons, and other particles emitted from the Sun's surface.



Structure of the atmosphere. *The main divisions of the atmosphere are defined by the elevations at which the sign of the temperature gradient changes. The chemical formulas at the right show the major species of interest in the various regions. The shaded D- and E-layers are regions of high ion concentrations that reflect radio waves and are important in long-distance communication.*

Composition of the atmosphere

Except for water vapor, whose atmospheric abundance varies from practically zero up to 4%, the fractions of the major atmospheric components N_2, O_2, and Ar are remarkably uniform below about 100 km. At greater heights, diffusion becomes the principal transport process, and the lighter gases become relatively more abundant. In addition, photochemical processes result in the formation of new species whose high reactivities would preclude their existence in significant concentrations at the higher pressures found at lower elevations.

The atmospheric gases fall into three abundance categories: major, minor, and trace. Nitrogen, the most abundant component, has accumulated over time as a result of its geochemical inertness; a very small fraction of it passes into the other phases as a result of biological activity and natural fixation by lightning. It is believed that denitrifying bacteria in marine sediments may provide the major route for the return of N_2 to the atmosphere. Oxygen is almost entirely of biological origin, and cycles through the hydrosphere, the biosphere, and sedimentary rocks. Argon consists mainly of Ar^{40} which is a decay product of K^{40} in the mantle and crust.

Table 1: Major components

nitrogen	N_2	78.08 %
oxygen	O_2	20.95 %
argon	Ar	0.93 %

The most abundant of the minor gases aside from water vapor is carbon dioxide, about which more will be said below. Next in abundance are neon and helium. Helium is a decay product of radioactive elements in the earth, but neon and the other inert gases are primordial, and have probably been present in their present relative abundances since the earth's formation. Two of the minor gases, ozone and carbon monoxide, have abundances that vary with time and location. A variable abundance implies an imbalance between the rates of formation and removal. In the case of carbon monoxide, whose major source is anthropogenic (a small amount

is produced by biological action), the variance is probably due largely to localized differences in fuel consumption, particularly in internal combustion engines. The nature of the carbon monoxide sink (removal mechanism) is not entirely clear; it may be partly microbial.

Table 2: Minor components

water	H_2O	0-4 %
carbon dioxide	CO_2	325 ppm
neon	Ne	18 ppm
helium	He	5 ppm
methane	CH_4	2 ppm
krypton	Kr	1 ppm
hydrogen	H_2	0.5 ppm
nitrous oxide	N_2O	0.3 ppm
carbon monoxide	CO	0.05-0.2 ppm
ozone	O_3	0.02 - 10 ppm
xenon	Xe	0.08 ppm

Table 3:Trace components

ammonia	NH_3	4 ppb
nitrogen oxide	NO	1 ppb
sulfur dioxide	SO_2	1 ppb
hydrogen sulfide	H_2S	0.05 ppb

Ozone

Ozone is formed by the reaction of O_2 with oxygen atoms produced photochemically. As a consequence the abundance of ozone varies with the time of day, the concentration of O atoms from other sources (photochemical smog, for example), and particularly with altitude; at 30 km, the ozone concentration reaches a maximum of 12 ppm.

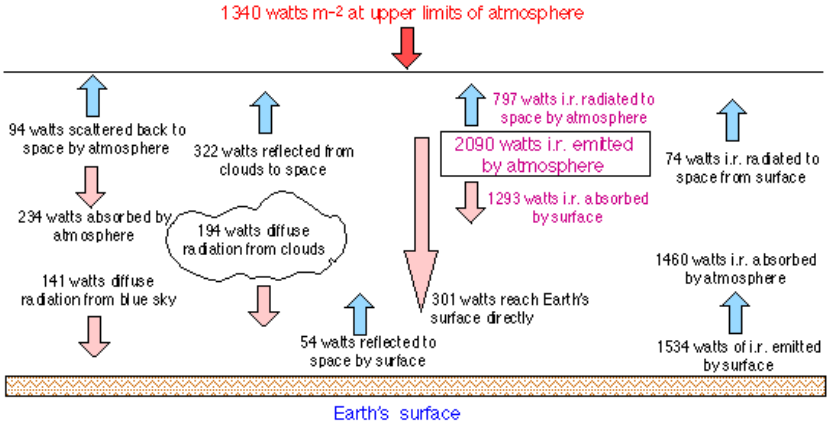
Carbon dioxide

The concentration of atmospheric carbon dioxide, while fairly uniform globally, is increasing at a rate of 0.2-0.7% per year as a result of fossil fuel burning. The present CO_2 content of the atmosphere is about 129 $\times 10^{18}$ g. Most of the CO^2, however, is of natural origin, and represents the smallest part of the total carbonate reservoir that includes oceanic CO_2, HCO_3^-, and carbonate sediments. The latter contain about 600 times as much CO_2 as the atmosphere, and the oceans contain about 50 times as much. These relative amounts are controlled by the rates of the reactions that interconvert the various forms of carbonate.

The surface conditions on the earth are sensitively dependent on the atmospheric CO_2 concentration. This is due mainly to the strong infrared absorption of CO_2, which promotes the absorption and trapping of solar heat (see below). Since CO_2 acts as an acid in aqueous solution, the pH of the oceans is also dependent on the concentration of CO_2 in the atmosphere; it has been estimated that if only 1% of the carbonate presently in sediments were still in the atmosphere, the pH of the oceans would be 5.9, instead of the present 8.2.

Energy balance of the atmosphere and earth

The amount of energy (the solar flux) impinging on the outer part of the atmosphere is 1367 watts m^{-2} . About 30% of this is reflected or scattered back into space by clouds, dust, and the atmospheric gas molecules themselves, and by the earth's surface. About 19% of the radiation is absorbed by clouds or the atmosphere (mainly by and O_3 , but not CO_2), leaving 51% of the incident energy available for absorption by the earth's surface. If one takes into account the uneven illumination of the earth's surface and the small flux of internal heat to the surface, the assumption of thermal equilibrium requires that the earth emit about 240 watts m^{-2}. This corresponds to the power that would be emitted by a black body at 255 K, or –18°C, which is the average temperature of the atmosphere at an altitude of 5 km. The observed mean global surface temperature of the earth is 13°C, and is presumably the temperature required to maintain thermal equilibrium between the earth and the atmosphere.



The greenhouse effect

The energy radiated by the earth has a longer wavelength (maximum 12m) than the incident radiation. Most gases absorb radiation in this range quite efficiently, including those gases such as CO_2 and N_2O that do not absorb the incident radiation. The energy absorbed by atmospheric gases is re-radiated in all directions; some of it therefore escapes into space, but a portion returns to the earth and is reabsorbed, thus raising its temperature.This is commonly called the greenhouse effect. If the amount of an infrared-absorbing gas such as carbon dioxide increases, a larger fraction of the incident solar radiation is trapped, and the mean temperature of the earth will increase.

Any significant increase in the temperature of the oceans would increase the atmospheric concentrations of both water and CO_2, producing the possibility of a runaway process that would be catastrophic from a human perspective. Fossil fuel combustion and deforestation during the last two hundred years have increased the atmospheric CO_2 concentration by 25%, and this increase is continuing. The same combustion processes responsible for the increasing atmospheric CO_2 concentration also introduce considerable quantities of particulate materials into the upper atmosphere. The effect of these would be to scatter more of the incoming solar radiation, reducing the amount that reaches and heats the earth's surface. The extent to which this process counteracts the greenhouse effect is still a matter of controversy; all that is known for sure is that the average temperature of the Earth is increasing.

Nitrous oxide

Carbon dioxide is not the only atmospheric gas of anthropogenic origin that can affect the heat balance of the earth; other examples are SO_2 and N_2O. Nitrous oxide is of particular interest, since its abundance is fairly high, and is increasing at a rate of about 0.5% per year. It is produced mainly by bacteria, and much of the increase is probably connected with introduction of increased nitrate into the environment through agricultural fertilization and sewage disposal. Besides being a strong infrared absorber, N_2O is photochemically active, and can react with ozone. Any significant depletion of the ozone content of the upper atmosphere would permit more ultraviolet radiation to reach the earth. This would have numerous deleterious effects on present life forms, as well as contributing to a temperature increase. The warming effect attributed to anthropogenic additions of greenhouse gases to the atmosphere is estimated to be about 2 watts per m^2 , or about 1.5% of the 150 watts per m^2trapped by clouds and atmospheric gases. This is a relatively large perturbation compared to the maximum variation in solar output of 0.5 watts per m^2 that has been observed during the past century. Continuation of greenhouse gas emission at present levels for another century could increase the atmospheric warming effect by 6-8 watts per m^2.

> *A less-appreciated side effect of the increase in atmospheric carbon dioxide (and of other plant nutrients such as nitrates) may be reduction in plant species diversity by selectively encouraging the growth of species which are ordinarly held in check by other species that are able to grow well with fewer nutrients. This effect, for which there is already some evidence, could be especially pronounced when the competing species utilize the C_3 and C_4 photosynthetic pathways that differ in their sensitivity to CO_2.*

Contributors and Attributions

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7.2: Origin and Evolution of the Atmosphere

Prebiotic atmosphere

The atmosphere of the Earth (and also of Venus and Mars) is generally believed to have its origin in relatively volatile compounds that were incorporated into the solids from which these planets accreted. Such compounds could include nitrides (a source of N_2), water (which can be taken up by silica, for example), carbides, and hydrogen compounds of nitrogen and carbon. Many of these compounds (and also some noble gases) can form clathrate complexes with water and some minerals which are fairly stable at low temperatures. The high temperatures developed during the later stages of accretion as well as subsequent heating produced by decay of radioactive elements presumably released these gases the surface. Even at the present time, large amounts of CO_2 , water vapor, N_2, HCl, SO_2 and H_2S are emitted from volcanos. The more reactive of these gases would be selectively removed from the atmosphere by reaction with surface rocks or dissolution in the ocean, leaving an atmosphere enriched in its present major components with the exception of oxygen which is discussed in the next section.

Any hydrogen present would tend to escape into space, causing the atmosphere to gradually became less reducing. However there is now some doubt that hydrogen and other volatiles (mainly the inert gases) were present in the newly accreted planets in anything like their cosmic abundance. The main evidence against this is the observation that gases such as helium, neon and argon, which are among the ten most abundant elements in the universe, are depleted on the earth by factors of 10^{-7} to 10^{-11} . This implies that there was a selective removal of these volatiles prior to or during the planetary accretion process.

The overall oxidation state of the earth's mantle is not consistent with what one would expect from equilibration with highly reduced volatiles, and there is no evidence to suggest that the composition of the mantle has not remained the same. If this is correct, then the primitive atmosphere may well have had about the same composition as the gases emitted by volcanos at the present time. These consist mainly of water and CO_2, together with small amounts of N_2, H_2, H_2S, SO_2, CO, CH_4, NH_3, HCl and HF. If water vapor was a major component of outgassing of the accreted earth, it must have condensed quite rapidly into rain. Any significant concentration of water vapor in the atmosphere would have led to a runaway greenhouse effect, resulting in temperatures as high as 400°C.

Origin of Atmospheric Oxygen

Free oxygen is never more than a trace component of most planetary atmospheres. Thermodynamically, oxygen is much happier when combined with other elements as oxides; the pressure of O_2 in equilibrium with basaltic magmas is only about 10^{-7} atm. Photochemical decomposition of gaseous oxides in the upper atmosphere is the major source of O_2 on most planets. On Venus, for example, CO_2 is broken down into CO and O_2 . On the earth, the major inorganic source of O_2 is the photolysis of water vapor; most of the resulting hydrogen escapes into space, allowing the O2 concentration to build up. An estimated 2 $\times$ 10^{11} g of O_2 per year is generated in this way. Integrated over the earth's history, this amounts to less than 3% of the present oxygen abundance. The partial pressure of O_2 in the prebiotic atmosphere is estimated to be no more than 10^{-3} atm, and may have been several orders of magnitude less. The major source of atmospheric oxygen on the earth is photosynthesis carried out by green plants and certain bacteria:

$$H_2O + CO_2 \longrightarrow (CH_2O)x + O_2 \tag{7.2.1}$$

A historical view of the buildup of atmospheric oxygen concentration since the beginning of the sedimentary record (3.7 $\times$ 10^9 ybp) can be worked out by making use of the fact that the carbon in the product of the above reaction has a slightly lower C^{13} content than does carbon of inorganic origin. Isotopic analysis of carbon-containing sediments thus provides a measure of the amounts of photosynthetic O_2 produced at various times in the past.

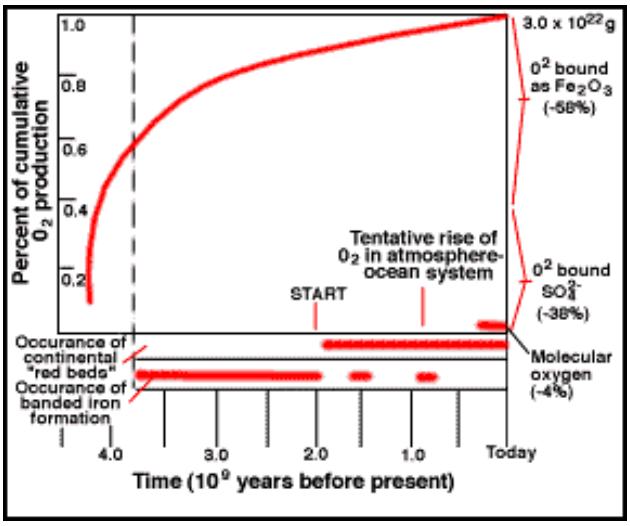


Figure 7.2.1: ***Evolution of atmospheric oxygen content.*** *Note carefully that the curve plots cumulative O_2 production, but that until a few hundred million years ago, most of this was taken up by Fe(II) compounds in the crust and by reduced sulfur; only after this massive "oxygen sink" became filled did free O_2 begin to accumulate in the atmosphere.*

Carbon Dioxide

Carbon dioxide has probably always been present in the atmosphere in the relatively small absolute amounts now observed (around 54 x 10^{15} mol = 54 Pmol). The reaction of CO_2 with silicate-containing rocks to form precambrian limestones suggest a possible moderating influence on its atmospheric concentration throughout geological time.

$$\mathrm{CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2} \tag{7.2.2}$$

About ten percent of the atmospheric CO_2 is taken up each year by photosynthesis. Of this, all except 0.05 percent is returned by *respiration*, almost entirely due to microorganisms. The remainder leaks into the slow part of the geochemical cycle, mostly as buried carbonate sediments.

Since the advent of the industrial revolution in 1860, the amount of CO_2 in the atmosphere has been increasing. Isotopic analysis shows that most of this has been due to fossil-fuel combustion; in recent years, the mass of carbon released to the atmosphere by this means has been more than ten times the estimated rate of natural removal into sediments. The large-scale destruction of tropical forests, which has accelerated greatly in recent years, is believed to exacerbate this effect by removing a temporary sink for CO_2.

The oceans have a large absorptive capacity for CO_2 owing to its reaction with carbonate:

$$\mathrm{CO_2 + CO_3^{2-} \rightleftharpoons 2\,HCO_3-} \tag{7.2.3}$$

There is about 60 times as much inorganic carbon in the oceans as in the atmosphere. However, efficient transfer takes place only into the topmost (100 m) wind-mixed layer of the ocean, which contains only about one atmosphere equivalent of CO_2. Further uptake is limited by the very slow transport of water into the deep ocean, which takes around 1000 years. For this reason, the buffering effect of the oceans on atmospheric CO_2 is not very effective; only about ten percent of the added CO_2 is taken up by the oceans.

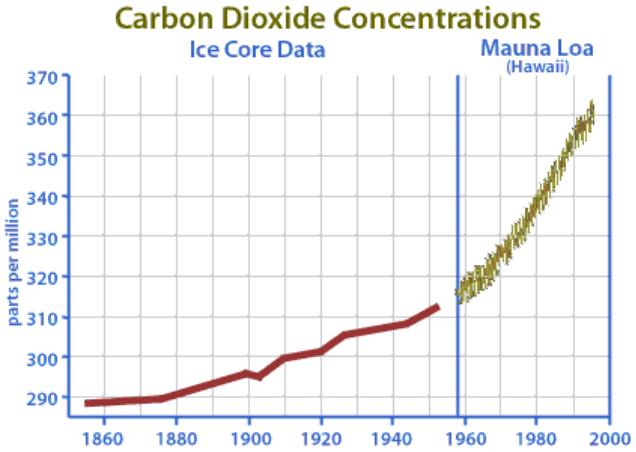


Figure. This set of plots, taken from an ETE page with data from NASA, shows the dramatic increase in atmospheric CO_2since the beginning of the industrial age. The "squiggles" on the Mauna Loa data reflect seasonal variations; more $CO_2$is taken up during the longer-daylight periods of the summer.

Contributors and Attributions

- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook

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7.3: Compressibility

When we pack to go on vacation, there seems to always be "one more" thing that we need to get in our suitcase. Maybe it's another bathing suit, pair of shoes, book—whatever the item, we need to get it in. Fortunately, we can usually squeeze things together somehow. Perhaps there is a little space between folds of clothing, or we can rearrange the shoes; somehow we can get that last item in and close the suitcase.

Compressibility

Scuba diving is a form of underwater diving in which a diver carries his own breathing gas, usually in the form of a tank of compressed air. The pressure in most commonly used scuba tanks ranges from 200 to 300 atmospheres. Gases are unlike other states of matter in that a gas expands to fill the shape and volume of its container. For this reason, gases can also be compressed so that a relatively large amount of gas can be forced into a small container. If the air in a typical scuba tank were transferred to a container at the standard pressure of 1 atm, the volume of that container would need to be about 2500 liters.

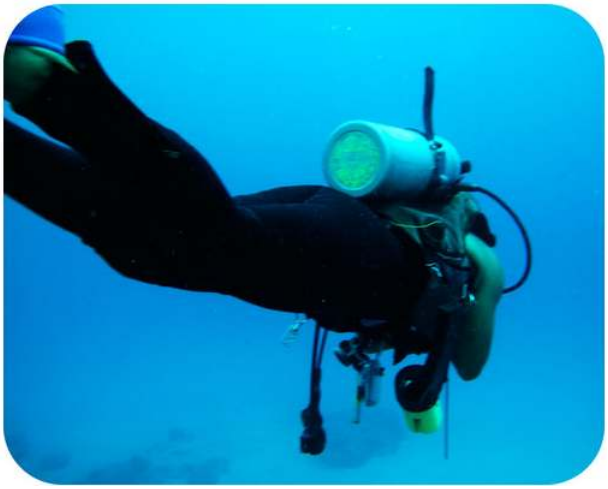


Figure 7.3.1: Scuba diver. (CC BY-NC; CK-12)

Compressibility is the measure of how much a given volume of matter decreases when placed under pressure. If we put pressure on a solid or a liquid, there is essentially no change in volume. The atoms, ions, or molecules that make up the solid or liquid are very close together. There is no space between the individual particles, so they cannot pack together.

The kinetic-molecular theory explains why gases are more compressible than either liquids or solids. Gases are compressible because most of the volume of a gas is composed of the large amounts of empty space between the gas particles. At room temperature and standard pressure, the average distance between gas molecules is about ten times the diameter of the molecules themselves. When a gas is compressed, as when the scuba tank is being filled, the gas particles are forced closer together.

Compressed gases are used in many situations. In hospitals, oxygen is often used for patients who have damaged lungs to help them breathe better. If a patient is having a major operation, the anesthesia that is administered will frequently be a compressed gas. Welding requires very hot flames produced by compressed acetylene and oxygen mixtures. Many summer barbeque grills are fueled by compressed propane.



Figure 7.3.2: *Oxygen tank.* (CC BY-NC; CK-12)

Summary

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7.4: Factors Affecting Gas Pressure

The pressure of the air in a basketball has to be adjusted so that the ball bounces to the correct height. Before a game, officials check the ball by dropping it from shoulder height and seeing how far back up it bounces. What would an official do if the ball did not bounce up high enough, or if it bounced too high?

The pressure inside a container is dependent on the amount of gas inside the container. If a basketball does not bounce high enough, an official could remedy the situation by using a hand pump and adding more air to the ball. Conversely, if it bounces too high, the official could let some air out of the ball.

Factors Affecting Gas Pressure

Recall from the kinetic-molecular theory that gas particles move randomly and in straight lines until they elastically collide with either other gas particles, or with one of the walls of the container. It is these collisions with the walls of the container that define the pressure of the gas. Four variables are used to describe the condition of a gas: pressure (P), volume (V), temperature (T), and the amount of the gas as measured by the number of moles (\left(n \right)\). We will examine separately how the volume, temperature, and amount of gas each affect the pressure of an enclosed gas sample.

Amount of Gas

The figure below shows what happens when air is added to a **rigid container**. A rigid container is one that is incapable of expanding or contracting. A steel canister is an example of a rigid container.

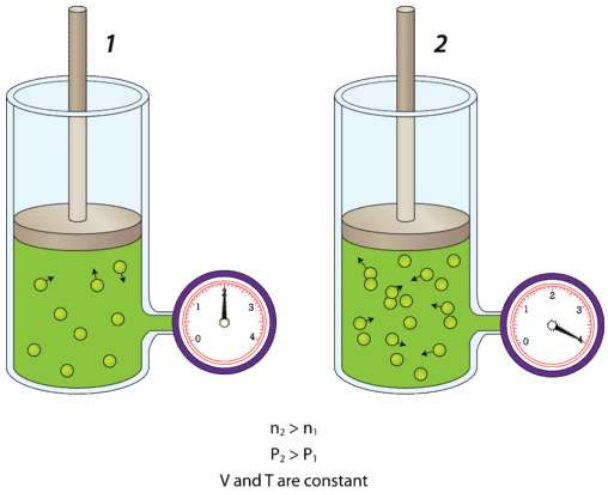


Figure 7.4.1: Increase in pressure with increase in number of gas particles. (CC BY-NC; CK-12)

The canister on the left contains a gas at a certain pressure. The attached air pump is then used to double the amount of gas in the canister. Since the canister cannot expand, the increased number of air molecules will strike the inside walls of the canister twice as frequently as they did before. The result is that the pressure inside the canister doubles. As you might imagine, if more and more air is continually added to a rigid container, it may eventually burst. Reducing the number of molecules in a rigid container has the opposite effect, and the pressure decreases.

Volume

Pressure is also affected by the volume of the container. If the volume of a container is decreased, the gas molecules have less space in which to move around. As a result, they will strike the walls of the container more often, and the pressure increases.

The figure below shows a cylinder of gas whose volume is controlled by an adjustable piston. On the left, the piston is pulled mostly out and the gauge reads a certain pressure. On the right, the piston has been pushed so that the volume of the enclosed portion of the container where the gas is located has been cut in half. The pressure of the gas doubles. Increasing the volume of the container would have the opposite effect, and the pressure of the gas would decrease.

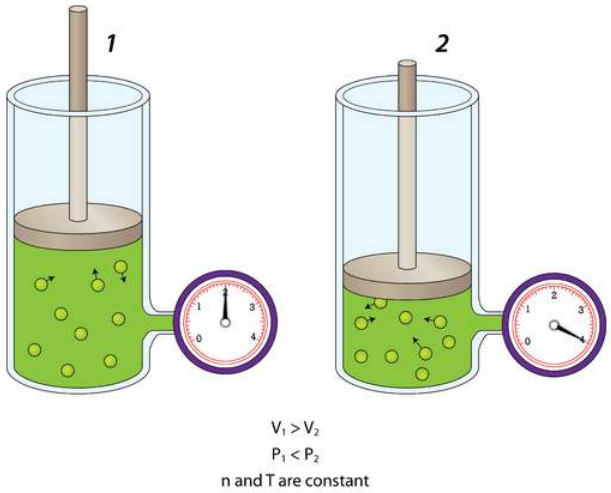


Figure 7.4.2: Decrease in gas volume produced increase in gas pressure. (CC BY-NC; CK-12)

Temperature

It would be very inadvisable to place a can of soup over a campfire without venting the can. As the can heats up, it may explode. The kinetic-molecular theory explains why. The air inside the rigid can of soup is given more kinetic energy by the heat coming from the campfire. The kinetic energy causes the air molecules to move faster; they impact the container walls more frequently and with more force. The increase in pressure inside may eventually exceed the strength of the can and it will explode. An additional factor is that the soup may begin boiling, which will then aid even more gas and more pressure to the inside of the can.

Shown in the figure below is a cylinder of gas (left) that is at room temperature (300 K). On the right, the cylinder has been heated until the Kelvin temperature has doubled to 600 K. The kinetic energy of the gas molecules increases, so collisions with the walls of the container are now more forceful than they were before. As a result, the pressure of the gas doubles. Decreasing the temperature would have the opposite effect, and the pressure of an enclosed gas would decrease.

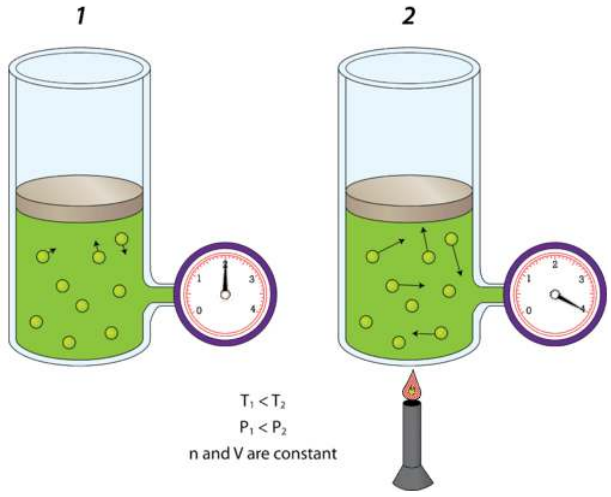


Figure 7.4.3: Increase in temperature produces increase in pressure. (CC BY-NC; CK-12)

Summary

- An increase in the number of gas molecules, while container volume stays constant, increases pressure.
- A decrease in container volume increases gas pressure.
- An increase in temperature of a gas in a rigid container increases the pressure.

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7.5: Mole Fraction

Sulfur dioxide is a by-product of many processes, both natural and human-made. Massive amounts of this gas are released during volcanic eruptions. Humans produce sulfur dioxide by burning coal. When in the atmosphere, the gas has a cooling effect by reflecting sunlight away from the earth. However, sulfur dioxide is also a component of smog and acid rain, both of which are harmful to the environment. Many efforts have been made to reduce SO_2 levels to lower acid rain production. However, SO_2 reduction efforts have an unforeseen complication: as we lower the concentration of this gas in the atmosphere, we lower its ability to cool, and consequently have global warming concerns.

Mole Fraction

One way to express relative amounts of substances in a mixture is with the mole fraction. **Mole fraction X** is the ratio of moles of one substance in a mixture to the total number of moles of all substances. For a mixture of two substances, A and B, the mole fractions of each would be written as follows:

$$X_A = \frac{\text{mol A}}{\text{mol A} + \text{mol B}} \quad \text{and} \quad X_B = \frac{\text{mol B}}{\text{mol A} + \text{mol B}}$$

If a mixture consists of 0.50 mol A and 1.00 mol B, then the mole fraction of A would be $X_A = \frac{0.5}{1.5} + 0.33$. Similarly, the mole fraction of B would be $X_B = \frac{1.0}{1.5} = 0.67$. Mole fraction is a useful quantity for analyzing gas mixtures in conjunction with Dalton's law of partial pressures. Consider the following situation... A 20.0 liter vessel contains 1.0 mol of hydrogen gas at a pressure of 600 mm Hg. Another 20.0 liter vessels contains 3.0 mol of helium at a pressure of 1800 mm Hg. These two gases are mixed together in an identical 20.0 liter vessel. Because each will exert its own pressure according to Dalton's law, we can express the partial pressures as follows:

$$P_{H_2} = X_{H_2} \times P_{\text{Total}} \quad \text{and} \quad P_{He} = X_{He} \times P_{\text{Total}}$$

The partial pressure of a gas in a mixture is equal to its mole fraction multiplied by the total pressure. For our mixture of hydrogen and helium:

$$X_{H_2} = \frac{1.0 \text{ mol}}{1.0 \text{ mol} + 3.0 \text{ mol}} = 0.25 \quad \text{and} \quad X_{He} = \frac{3.0 \text{ mol}}{1.0 \text{ mol} + 3.0 \text{ mol}} = 0.75$$

The total pressure according to Dalton's law is $600 \text{ mm Hg} + 1800 \text{ mm Hg} = 2400 \text{ mm Hg}$. So, each partial pressure will be:

$$P_{H_2} = 0.25 \times 2400 \text{ mm Hg} = 600 \text{ mm Hg}$$

$$P_{He} = 0.75 \times 2400 \text{ mm Hg} = 1800 \text{ mm Hg}$$

The partial pressures of each gas in the mixture do not change, since they were mixed into the same size vessel and the temperature was not changed.

7.5.1 Example

A flask contains a mixture of 1.24 moles of hydrogen gas and 2.91 moles of oxygen gas. If the total pressure is 104 kPa, what is the partial pressure of each gas?

Solution

Step 1: List the known quantities and plan the problem.

Known

- 1.24 mol H_2
- 2.91 mol O_2
- $P_{\text{Total}} = 104$ kPa

Unknown

- $P_{H_2} = ?$ kPa
- $P_{O_2} = ?$ kPa

First, the mole fraction of each gas can be determined. Then, the partial pressure can be calculated by multiplying the mole fraction by the total pressure.

Step 2: Solve.

$$X_{H_2} = \frac{1.24\ \text{mol}}{1.24\ \text{mol} + 2.91\ \text{mol}} = 0.299 \qquad X_{O_2} = \frac{2.91\ \text{mol}}{1.24\ \text{mol} + 2.91\ \text{mol}} = 0.701$$

$$P_{H_2} = 0.299 \times 104\ \text{kPa} = 31.1\ \text{kPa} \qquad P_{O_2} = 0.701 \times 104\ \text{kPa} = 72.9\ \text{kPa}$$

Step 3: Think about your result.

The hydrogen is slightly less than one third of the mixture, so it exerts slightly less than one third of the total pressure.

Summary

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7.6: Dalton's Law of Partial Pressures

The atmosphere of Venus is markedly different from that of Earth. The gases in the Venusian atmosphere are 96.5% carbon dioxide and 3% nitrogen. The atmospheric pressure on Venus is roughly 92 times that of Earth, so the amount of nitrogen on Venus contributes pressure well over 2700 mm Hg. And there is no oxygen present, so humans could not breathe there. Not that anyone would want to go to Venus—the surface temperature is usually over 460°C.

Dalton's Law of Partial Pressures

Gas pressure results from collisions between gas particles and the inside walls of their container. If more gas is added to a rigid container, the gas pressure increases. The identities of the two gases do not matter. John Dalton, the English chemist who proposed the atomic theory, also studied mixtures of gases. He found that each gas in a mixture exerts a pressure independently of every other gas in the mixture. For example, our atmosphere is composed of about 78% nitrogen and 21% oxygen, with smaller amounts of several other gases making up the rest. Since nitrogen makes up 78% of the gas particles in a given sample of air, it exerts 78% of the pressure. If the overall atmospheric pressure is 1.00 atm, then the pressure of just the nitrogen in the air is 0.78 atm. The pressure of the oxygen in the air is 0.21 atm.

The **partial pressure** of a gas is the contribution that gas makes to the total pressure when the gas is part of a mixture. The partial pressure of nitrogen is represented by P_{N_2}. **Dalton's law of partial pressures** states that the total pressure of a mixture of gases is equal to the sum of all of the partial pressures of the component gases. Dalton's law can be expressed with the following equation:

$$P_{\text{total}} = P_1 + P_2 + P_3 + \cdots$$

The figure below shows two gases that are in separate, equal-sized containers at the same temperature and pressure. Each exerts a different pressure, P_1 and P_2, reflective of the number of particles in the container. On the right, the two gases are combined into the same container, with no volume change. The total pressure of the gas mixture is equal to the sum of the individual pressures. If $P_1 = 300 \text{ mm Hg}$ and $P_2 = 500 \text{ mm Hg}$, then $P_{\text{total}} = 800 \text{ mm Hg}$.

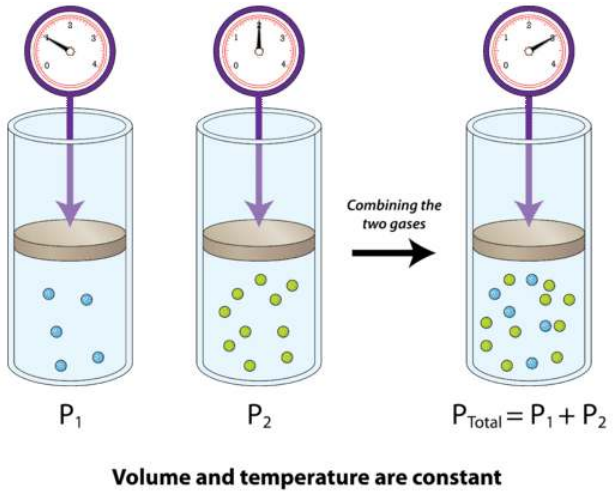


Figure 7.6.1: Dalton's law says that the pressure of a gas mixture is equal to the partial pressures of the combining gases. (CC BY-NC; CK-12)

Summary

- The partial pressure of a gas is the contribution that gas makes to the total pressure when the gas is part of a mixture.
- The total pressure in a system is equal to the sums of the partial pressures of the gases present, according to Dalton's Law of Partial Pressures.

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7.7: Structure of Water

In his well-known poem "The Rime of the Ancient Mariner", Samuel Coleridge wrote "water, water everywhere, nor any drop to drink." Coleridge was talking about being out on the ocean, but not having any water because he had killed an albatross (apparently bringing bad luck to everyone on the ship). About 75% of the Earth's surface is water. The major constituent of the human body (over 60%) is water. This simple molecule plays important roles in all kinds of processes.

Structure of Water

Water is a simple molecule consisting of one oxygen atom bonded to two different hydrogen atoms. Because of the higher **electronegativity** of the oxygen atom, the bonds are polar covalent (**polar bonds**). The oxygen atom attracts the shared electrons of the covalent bonds to a significantly greater extent than the hydrogen atoms. As a result, the oxygen atom acquires a partial negative charge $(\delta-)$, while the hydrogen atoms each acquire a partial positive charge $(\delta+)$. The molecule adopts a bent structure because of the two lone pairs of electrons on the oxygen atom. The $\mathrm{H-O-H}$ bond angle is about 105°, slightly smaller than the ideal 109.5^{o} of an sp^3 hybridized atomic orbital.

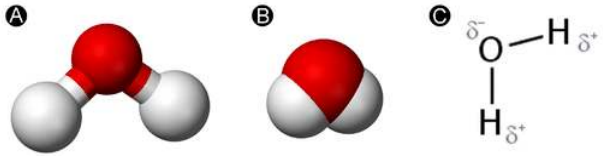


Figure 7.7.1: The water molecule, visualized three different ways: ball-and-stick model, space-filling model, and structural formula with partial charges.

The bent shape of the water molecule is critical because the polar $\mathrm{O-H}$ bonds do not cancel one another and the molecule as a whole is polar. The figure below illustrates the net polarity of the water molecule. The oxygen is the negative end of the molecule, while the area between the hydrogen atoms is the positive end of the molecule.

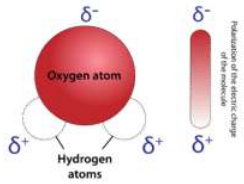


Figure 7.7.2: Water is a polar molecule, as greater electron density is found around the more electronegative oxygen atom.

Polar molecules attract one another by dipole-dipole forces, as the positive end of one molecule is attracted to the negative end of the nearby molecule. In the case of water, the highly polar $\mathrm{O-H}$ bonds results in very little electron density around the hydrogen atoms. Each hydrogen atom is strongly attracted to the lone-pair electrons on an adjacent oxygen atom. These are called hydrogen bonds and are stronger than conventional dipole-dipole forces.

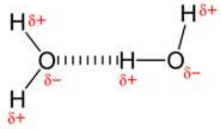


Figure 7.7.3: A hydrogen bond is the attraction between a lone pair of electrons on the oxygen atom of one molecule and the electron-deficient hydrogen atom of a nearby molecule.

Because each oxygen atom has two lone pairs, it can make hydrogen bonds to the hydrogen atoms of two separate other molecules. The figure below shows the result—an approximately tetrahedral geometry around each oxygen atom, consisting of two covalent bonds and two hydrogen bonds.

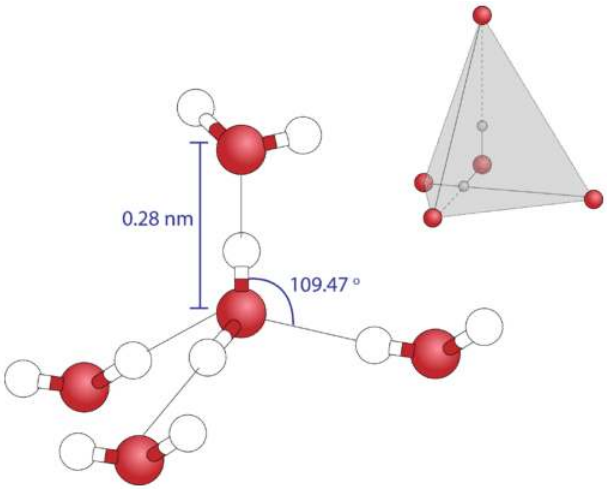


Figure 7.7.4: As a result of two covalent bonds and two hydrogen bonds, the geometry around each oxygen atom is approximately tetrahedral.

Summary

- Water is a molecular compound consisting of polar molecules that have a bent shape.
- The oxygen atom acquires a partial negative charge, while the hydrogen atom acquires a partial positive charge.

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7.8: Structure of Ice

Ice is an interesting and useful material. It can be used to cool food and keep it fresh. Ice can provide recreation, such as in the case of ice-skating. It can do great damage when it freezes—roads can buckle, houses can be damaged, water pipes can burst. All of this happens because of a unique property of water: when water freezes, it expands in volume as ice is formed.

Structure of Ice

Liquid water is a fluid. The hydrogen bonds in liquid water constantly break and reform as the water molecules tumble past one another. As water cools, its molecular motion slows and the molecules move gradually closer to one another. The **density** of any liquid increases as its temperature decreases. For most liquids, this continues as the liquid freezes; the solid state is denser than the liquid state. However, water behaves differently. It actually reaches its highest density at about $4^{\circ}\mathrm{C}$.

Table 7.8.1: Density of Water and Ice

Temperature $(^{\circ}\mathrm{C})$	**Density** $\left(\mathrm{g/cm^3}\right)$
100 (liquid)	0.9584
50	0.9881
25	0.9971
10	0.9997
4	1.0000
0 (liquid)	0.9998
0 (solid)	0.9168

Between $4^{\circ}\mathrm{C}$ and $0^{\circ}\mathrm{C}$, the density gradually decreases as the hydrogen bonds begin to form a network characterized by a generally **hexagonal** structure with open spaces in the middle of the hexagons (see figure below).

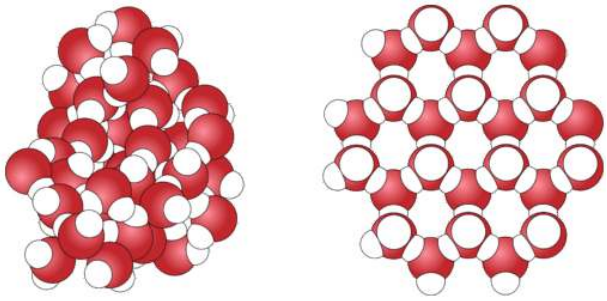


Figure 7.8.1: The structure of liquid water (left) consists of molecules connected by short-lived hydrogen bonds because water is a fluid. In ice (right), the hydrogen bonds become permanent, resulting in an interconnected hexagonally-shaped framework of molecules.

Ice is less dense than liquid water and so it floats. Ponds or lakes begin to freeze at the surface, closer to the cold air. A layer of ice forms, but does not sink as it would if water did not have this unique structure dictated by its shape, polarity, and hydrogen bonding. If the ice were to sink as it froze, entire lakes would freeze solid. Since the ice does not sink, liquid water remains under the ice all winter long. This is important, as fish and other organisms are capable of surviving through winter. Ice is one of few solids that is less dense than its liquid form.

Summary

- The density of any liquid increases as its temperature decreases. As an exception, ice is less dense than liquid water.
- The intermolecular structure of ice has spaces that are not present in liquid water.

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7.9: Physical Properties of Water

Water loss to the atmosphere is a significant problem in many parts of the world. When water supplies are low, anything that can be done to decrease water loss is important for farmers. An evaporation pan can be used to measure how fast water evaporates in a given location. This information can be used as part of project development to cut down on evaporation, and increase the amount of usable water in a region.

Properties of Water

Compared to other molecular compounds of relatively low molar mass, ice melts at a very high temperature. A great deal of energy is required to break apart the hydrogen-bonded network of ice and return it to the liquid state. Likewise, the boiling point of water is very high. Most molecular compounds of similar molar mass are gases at room temperature.

Surface Tension

Water has a high **surface tension** (attraction between molecules at the surface of a liquid) because of its hydrogen bonding. Liquids that cannot hydrogen bond do not exhibit nearly as much surface tension. Surface tension can be seen by the curved meniscus that forms when water is in a thin column, such as in a graduated cylinder or a buret.



Figure 7.9.1: The meniscus of water in a graduated cylinder forms because of water's hydrogen bonding.

Vapor Pressure

The **vapor pressure** of a liquid is the pressure of the vapor produced by evaporation of a liquid or solid above the liquid or solid in a closed container. The hydrogen bonding between liquid water molecules explains why water has an unusually low vapor pressure. Relatively few molecules of water are capable of escaping the surface of the liquid and entering the vapor phase. Evaporation is slow, and thus the vapor exerts a low pressure in a closed container. Low vapor pressure is an important physical property of water, since lakes, oceans, and other large bodies of water would otherwise evaporate much more quickly.

Vapor pressure is influenced by temperature. As the temperature increases, more molecules are released from the surface of the liquid. This increases movement above the liquid surface, increasing the pressure in the vapor stage. The image below illustrates the effect of temperature on vapor pressure.

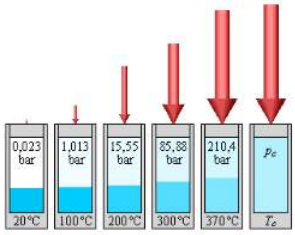


Figure 7.9.2: Vapor pressure of water at different temperatures.

Summary

- Water has high surface tension because of extensive hydrogen bonding.
- The vapor pressure of water is low due to hydrogen bonding.
- Vapor pressure increases as temperature increases.

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7.10: Solute and Solvent

In the winter, the temperature often gets well below the freezing point of water. This condition can create problems in car radiators. If the water freezes, water hoses will break, the engine block can crack, and significant damage can be done to the car.

Solute and Solvent

When one substance dissolves into another, a **solution** is formed. A solution is a homogeneous mixture consisting of a **solute** dissolved into a **solvent**. The solute is the substance that is being dissolved, while the solvent is the dissolving medium. Solutions can be formed with many different types and forms of solutes and solvents.

We know of many types of solutions. Check out a few examples in the table below.

Table 7.10.1: Types of Solutions

Type	Solvent	Solute	Example
gas/gas	nitrogen	oxygen	air
gas/liquid	water	carbon dioxide	soda pop
liquid/liquid	water	ethylene glycol	antifreeze
solid/liquid	water	salts	seawater

This section's focus is on solutions where the solvent is water. An aqueous solution is water that contains one or more dissolved substances. The dissolved substances in an aqueous solution many be solids, gases, or other liquids. Some examples are listed in the table above. Other examples include vinegar (acetic acid in water), alcoholic beverages (ethanol in water), and liquid cough medicines (various drugs in water).



Figure 7.10.1: Typical solution: clear and stable.

In order to be a true solution, a mixture must be stable. When sugar is fully dissolved into water, it can stand for an indefinite amount of time and the sugar will not settle out of the solution. Further, if the sugar-water solution is passed through a filter, it will be unchanged. The dissolved sugar particles will pass through the filter along with the water. This is because the dissolved particles in a solution are very small, usually less than 1 nm in diameter. Solute particles can be atoms, ions, or molecules, depending on the type of substance that has been dissolved.

Summary

- A solution is a homogeneous mixture of a solute in a solvent.
- A solute is the material present in the smaller amount in the solution.
- A solvent is the material present in the larger amount in the solution.

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7.11: Dissolving Process

Many people start their day with a cup of coffee (others drink coffee all day long). The coffee typically consumed is a type of solution—sometimes a very complex one. The coffee itself has been brewed so that material from the coffee bean will dissolve in hot water. Some people add sugar, while others add milk or cream. In some areas of the country, lattés are popular; one or more special flavors might be added along with the milk. Whatever the situation, the end result is an enjoyable solution to drink.

The Process of Dissolution

Water typically dissolves many ionic compounds and polar molecules. Nonpolar molecules such as those found in grease or oil do not dissolve in water. We will first examine the process that occurs when an ionic compound such as table salt (sodium chloride) dissolves in water.

Water molecules move about continuously due to their kinetic energy. When a crystal of sodium chloride is placed into water, the water's molecules collide with the crystal lattice. Recall that the crystal lattice is composed of alternating positive and negative ions. Water is attracted to the sodium chloride crystal because water is polar and has both a positive and a negative end. The positively charged sodium ions in the crystal attract the oxygen end of the water molecules because they are partially negative. The negatively charged chloride ions in the crystal attract the hydrogen end of the water molecules because they are partially positive. The action of the polar water molecules takes the crystal lattice apart (see image below).

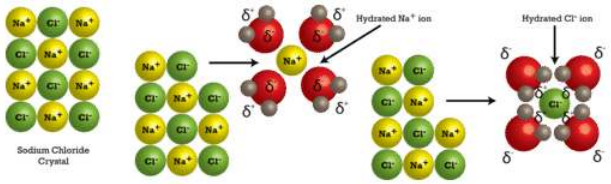


Figure 7.11.1: The dissolving of sodium chloride in water.

After coming apart from the crystal, the individual ions are then surrounded by solvent particles in a process called **solvation**. Note that the individual Na^{+} ions are surrounded by water molecules with the oxygen atom oriented near the positive ion. Likewise, the chloride ions are surrounded by water molecules with the opposite orientation. **Hydration** is the process of solute particles being surrounded by water molecules arranged in a specific manner. Hydration helps to stabilize aqueous solutions by preventing the positive and negative ions from coming back together and forming a precipitate.

Table sugar is sucrose $(\mathrm{C_{12}H_{22}O_{11}})$, and is an example of a molecular compound. Solid sugar consists of individual sugar molecules held together by intermolecular attractive forces. When water dissolves sugar, it separates the individual sugar molecules by disrupting the attractive forces, but does not break the covalent bonds between the carbon, hydrogen, and oxygen atoms. Dissolved sugar molecules are also hydrated, but without as distinct an orientation to the water molecules as in the case of the ions. The sugar molecules contain many $-\mathrm{OH}$ groups that can form hydrogen bonds with the water molecules, helping to form the sucrose solution.

Summary

- Motion of water molecules helps break up interactions between solid ions or molecules.
- Solvation involves surrounding ions with solvent particles.
- Ionic solute molecules are hydrated (surrounded by water molecules in a specific orientation).

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7.12: Electrolytes and Nonelectrolytes

People around the world jog for exercise. For the most part, jogging can be a healthy way to stay fit. However, problems can develop for those who jog in the heat. Excessive sweating can lead to electrolyte loss, which can be life-threatening. Early symptoms of electrolyte deficiency can include nausea, fatigue, and dizziness. If not treated, individuals can experience muscle weakness and increased heart rate (which could lead to a heart attack). Sports drinks can be consumed to restore electrolytes quickly in the body.

Electrolytes and Nonelectrolytes

An **electrolyte** is a compound that conducts an electric current when it is in an aqueous solution or melted. In order to conduct a current, a substance must contain mobile ions that can move from one electrode to the other. All ionic compounds are electrolytes. When ionic compounds dissolve, they break apart into ions which are then able to conduct a current (**conductivity**). Even insoluble ionic compounds such as $CaCO_3$ are electrolytes because they can conduct a current in the molten (melted) state.

A **nonelectrolyte** is a compound that does not conduct an electric current in either aqueous solution or in the molten state. Many molecular compounds, such as sugar or ethanol, are nonelectrolytes. When these compounds dissolve in water, they do not produce ions. The figure below illustrates the difference between an electrolyte and a nonelectrolyte.

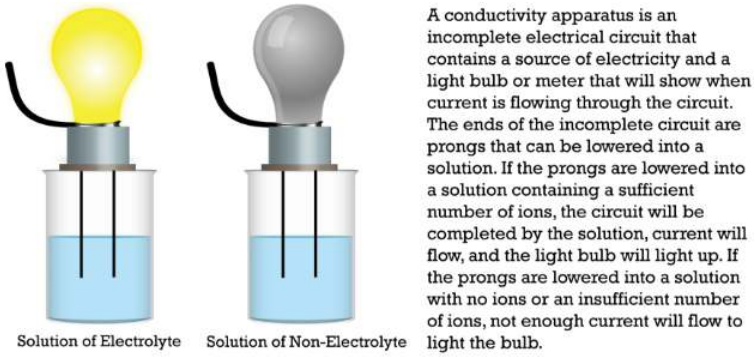


Figure 7.12.1: Conductivity apparatus.

Roles of Electrolytes in the Body

Several electrolytes play important roles in the body. Here are a few significant electrolytes:

1. Calcium - in bones and teeth. Also important for muscle contraction, blood clotting, and nerve function.
2. Sodium - found outside the cell. Mainly involved in water balance and nerve signaling.
3. Potassium - major cation inside the cell. Important for proper functioning of heart, muscles, kidneys, and nerves.
4. Magnesium - in bone and cells. Involved in muscle, bone, nervous system, and takes part in many biochemical reactions.

Summary

- Electrolytes conduct electric current when in solution or melted.
- Nonelectrolytes do not conduct electric current when in solution or melted.
- Some electrolytes play important roles in the body.

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7.13: Dissociation

In many areas, winter ice on the streets and sidewalks represents a serious walking and driving hazard. One common approach to melting the ice is to put some form of deicing salt on the surface. Materials such as sodium chloride or calcium chloride are frequently employed for this purpose. In order to be effective, the solid material must first dissolve and break up into the ions that make up the compound.

Dissociation

An ionic crystal lattice breaks apart when it is dissolved in water. **Dissociation** is the separation of ions that occurs when a solid ionic compound dissolves. It is important to be able to write dissociation equations. Simply undo the crisscross method that you learned when writing chemical formulas of ionic compounds. The subscripts for the ions in the chemical formulas become the coefficients of the respective ions on the product side of the equation. Shown below are dissociation equations for NaCl, $\mathrm{Ca(NO_3)_2}$, and $\mathrm{(NH_4)_3PO_4}$.

$$\mathrm{NaCl}\,(s) \rightarrow \mathrm{Na^+}\,(aq) + \mathrm{Cl^-}\,(aq)$$

$$\mathrm{Ca(NO_3)_2}\,(s) \rightarrow \mathrm{Ca^{2+}}\,(aq) + 2\mathrm{NO_3^-}\,(aq)$$

$$\mathrm{(NH_4)_3PO_4}\,(s) \rightarrow 3\mathrm{NH_4}\,(aq) + \mathrm{PO_4}\,(aq)$$

The formula unit of sodium chloride dissociates into one sodium ion and one chloride ion. The calcium nitrate formula unit dissociates into one calcium ion and two nitrate ions. This is because of the $2+$ charge of the calcium ion. Two nitrate ions, each with a $1-$ charge are required to make the equation balance electrically. The ammonium phosphate formula unit dissociates into three ammonium ions and one phosphate ion. Note that the polyatomic ions themselves do not dissociate further, but remain intact.

Do not confuse the subscripts of the atoms within the polyatomic ion for the subscripts that result from the crisscrossing of the charges that make up the original compound neutral. The 3 subscript of the nitrate ion and the 4 subscript of the ammonium ion are part of the polyatomic ion and simply remain as part of its formula after the compound dissociates. Notice that the compounds are solids (s) which then become ions in aqueous solution (aq).



Figure 7.13.1: Calcium nitrate is a typical ionic compound. In an aqueous solution, it dissociates into calcium ions and nitrate ions.

Nonelectrolytes do not dissociate when forming an aqueous solution. An equation can still be written that simply shows the solid going into solution. For the dissolution of sucrose:

$$\mathrm{C_{12}H_{22}O_{11}}\,(s) \rightarrow \mathrm{C_{12}H_{22}O_{11}}\,(aq)$$

Summary

- Dissociation is the separation of ions that occurs when a solid ionic compound dissolves.
- Nonionic compounds do not dissociate in water.

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7.14: Saturated and Unsaturated Solutions

When compounds are synthesized, contaminating materials are often mixed in with them. The process of recrystallization can be used to remove these impurities. The crystals are dissolved in a hot solvent, forming a solution. When the solvent is cooled, the compound is no longer as soluble and will precipitate out of solution, leaving contaminating materials still dissolved.

Saturated and Unsaturated Solutions

Table salt (NaCl) readily dissolves in water. Suppose that you have a beaker of water to which you add some salt, stirring until it dissolves. You add more and that dissolves. You keep adding more and more salt, eventually reaching a point at which no more of the salt will dissolve—no matter how long or how vigorously you stir it. Why? On the molecular level, we know that action of the water causes the individual ions to break apart from the salt crystal and enter the solution, where they remain hydrated by water molecules. What also happens is that some of the dissolved ions collide back again with the crystal and remain there. **Recrystallization** is the process of dissolved solute returning to the solid state. At some point, the rate at which the solid salt is dissolving becomes equal to the rate at which the dissolved solute is recrystallizing. When that point is reached, the total amount of dissolved salt remains unchanged. **Solution equilibrium** is the physical state described by the opposing processes of dissolution and recrystallization occurring at the same rate. The solution equilibrium for the dissolution of sodium chloride can be represented by one of two equations:

$$\mathrm{NaCl}\,(s) \rightleftharpoons \mathrm{NaCl}\,(aq)$$

While the above equation shows the change of state back and forth between solid and aqueous solution, the preferred equation also shows the dissociation that occurs as an ionic solid dissolves:

$$\mathrm{NaCl}\,(s) \rightleftharpoons \mathrm{Na}^{+}\,(aq) + \mathrm{Cl}^{-}\,(aq)$$

When the solution equilibrium point is reached and no more solute will dissolve, the solution is said to be saturated. A **saturated solution** is a solution that contains the maximum amount of solute that is capable of dissolving. At $20^{\circ}\mathrm{C}$, the maximum amount of NaCl that will dissolve in \100. \: \text{g}\) of water is $36.0\ \mathrm{g}$. If any more NaCl is added past this point, it will not dissolve, because the solution is saturated. What if more water is added to the solution instead? In that case, more NaCl would be capable of dissolving in the additional solvent. An **unsaturated solution** is a solution that contains less than the maximum amount of solute that is capable of being dissolved. The figure below illustrates the above process and shows the distinction between unsaturated and saturated.

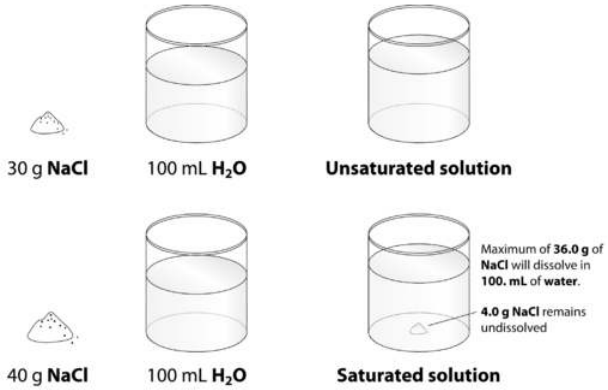


Figure 7.14.1: When 30.0 g of NaCl is added to 100 mL, it all dissolves, forming an unsaturated solution. When 40.0 g is added, 36.0 g dissolves and 4.0 g remains undissolved, forming a saturated solution.

How can you tell if a solution is saturated or unsaturated? If more solute is added and it does not dissolve, then the original solution was saturated. If the added solute dissolves, then the original solution was unsaturated. A solution that has been allowed to reach equilibrium, but which has extra undissolved solute at the bottom of the container, must be saturated.

Summary

- Recrystallization is the process of dissolved solute returning to the solid state.
- A saturated solution is a solution that contains the maximum amount of solute that is capable of dissolving.
- An unsaturated solution is a solution that contains less than the maximum amount of solute that is capable of being dissolved.

- Solution equilibrium exists when the rate of dissolution equals the rate of recrystallization.

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7.15: How Temperature Influences Solubility

Nuclear power plants require large amounts of water to generate steam for turbines and to cool equipment. They are usually situated near bodies of water to use that water as a coolant, returning the warmer water back to the lake or river. This increases the overall temperature of the water, which lowers the quantity of dissolved oxygen, affecting the survival of fish and other organisms.

How Temperature Influences Solubility

The **solubility** of a substance is the amount of that substance that is required to form a saturated solution in a given amount of solvent at a specified temperature. Solubility is often measured as the grams of solute per 100 g of solvent. The solubility of sodium chloride in water is 36.0 g per 100 g water at 20°C. The temperature must be specified because solubility varies with temperature. For gases, the pressure must also be specified. Solubility is specific for a particular solvent. In this section, we will consider solubility of material in water as solvent.

The solubility of the majority of solid substances increases as the temperature increases. However, the effect is difficult to predict and varies widely from one solute to another. The temperature dependence of solubility can be visualized with the help of a **solubility curve**, a graph of the solubility vs. temperature (see figure below).

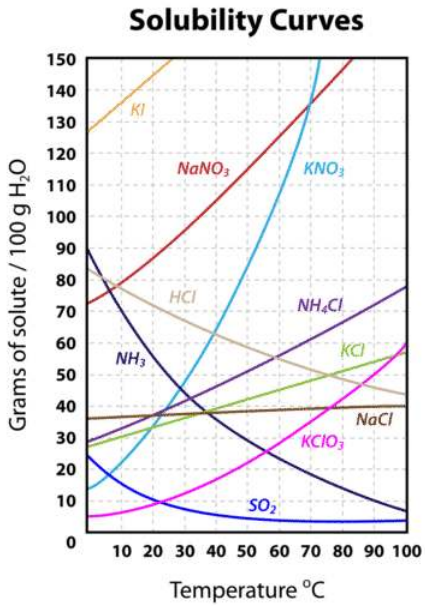


Figure 7.15.1: Solubility curves for several compounds.

Notice how the temperature dependence of NaCl is fairly flat, meaning that an increase in temperature has relatively little effect on the solubility of NaCl. The curve for KNO_3, on the other hand, is very steep, and so an increase in temperature dramatically increases the solubility of KNO_3.

Several substances—HCl, NH_3, and SO_2—have solubility that decreases as temperature increases. They are all gases at standard pressure. When a solvent with a gas dissolved in it is heated, the kinetic energy of both the solvent and solute increase. As the kinetic energy of the gaseous solute increases, its molecules have a greater tendency to escape the attraction of the solvent molecules and return to the gas phase. Therefore, the solubility of a gas decreases as the temperature increases.

Solubility curves can be used to determine if a given solution is saturated or unsaturated. Suppose that 80 g of KNO_3 is added to 100 g of water at 30°C. According to the solubility curve, approximately 48 g of KNO_3 will dissolve at 30°C. This means that the solution will be saturated since 48 g is less than 80 g. We can also determine that there will be $80 - 48 = 32$ g of undissolved KNO_3 remaining at the bottom of the container. In a second scenario, suppose that this saturated solution is heated to 60°C. According to the curve, the solubility of KNO_3 at 60°C is about 107 g. The solution, in this case, is unsaturated since it contains only the original 80 g of dissolved solute. Suppose in a third case, that the solution is cooled all the way down to 0°C. The solubility at 0°C is about 14 g, meaning that $80 - 14 = 66$ g of the KNO_3 will recrystallize.

Summary

- The solubility of a substance is the amount of that substance that is required to form a saturated solution in a given amount of solvent at a specified temperature.
- A solubility curve is a graph of the solubility vs. temperature
- The solubility of a solid in water increases with an increase in temperature.
- Gas solubility decreases as the temperature increases.

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7.16: Henry's Law

Having a soft drink in outer space poses some special problems. Under microgravity, the carbonation can quickly dissipate if not kept under pressure. You can't open the can, or you will lose carbonation. So, a special pressurized container has been developed to get around the problem of gas loss at low gravity.

Henry's Law

Pressure has very little effect on the solubility of solids or liquids, but has a significant effect on the solubility of gases. Gas solubility increases as the partial pressure of a gas above the liquid increases. Suppose a certain volume of water is in a closed container with the space above it occupied by carbon dioxide gas at standard pressure. Some of the $\mathrm{CO_2}$ molecules come into contact with the surface of the water and dissolve into the liquid. Now suppose that more $\mathrm{CO_2}$ is added to the space above the container, causing a pressure increase. In this case, more $\mathrm{CO_2}$ molecules are in contact with the water and so more of them dissolve. Thus, the solubility increases as the pressure increases. As with a solid, the $\mathrm{CO_2}$ that is undissolved reaches an equilibrium with the dissolved $\mathrm{CO_2}$, represented by the equation:

$$\mathrm{CO_2}\,(g) \rightleftharpoons \mathrm{CO_2}\,(aq)$$

At equilibrium, the rate of gaseous $\mathrm{CO_2}$ dissolution is equal to the rate of dissolved $\mathrm{CO_2}$ coming out of the solution.

When carbonated beverages are packaged, they are done so under high $\mathrm{CO_2}$ pressure so that a large amount of carbon dioxide dissolves in the liquid. When the bottle is open, the equilibrium is disrupted because the $\mathrm{CO_2}$ pressure above the liquid decreases. Immediately, bubbles of $\mathrm{CO_2}$ rapidly exit the solution and escape out of the top of the open bottle. The amount of dissolved $\mathrm{CO_2}$ decreases. If the bottle is left open for an extended period of time, the beverage becomes "flat" as more and more $\mathrm{CO_2}$ comes out of the liquid.

The relationship of gas solubility to pressure is described by Henry's law, named after English chemist William Henry (1774-1836). **Henry's Law** states that the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas above the liquid. Henry's law can be written as follows:

$$\frac{S_1}{P_1} = \frac{S_2}{P_2}$$

S_1 and P_1 are the solubility and the pressure at an initial set of conditions; S_2 and P_2 are the solubility and pressure at another changed set of conditions. The solubility of a gas is typically reported in $\mathrm{g/L}$.

7.16.1 Example

The solubility of a certain gas in water is $0.745\ \mathrm{g/L}$ at standard pressure. What is its solubility when the pressure above the solution is raised to $4.50\ \mathrm{atm}$? The temperature is constant at $20^{\circ}\mathrm{C}$.

Solution

Step 1: List the known quantities and plan the problem.

Known

- $S_1 = 0.745\ \mathrm{g/L}$
- $P_1 = 1.00\ \mathrm{atm}$
- $P_2 = 4.50\ \mathrm{atm}$

Unknown

Substitute into Henry's law and solve for S_2.

Step 2: Solve.

$$S_2 = \frac{S_1 \times P_2}{P_1} = \frac{0.745\ \mathrm{g/L} \times 4.50\ \mathrm{atm}}{1.00\ \mathrm{atm}} = 3.35\ \mathrm{g/L}$$

Step 3: Think about your result.

The solubility is increased to 4.5 times its original value, according to the direct relationship.

Summary

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7.17: Percent Solutions

There are human cultures that do not recognize numbers above three. Anything greater than that is simply referred to as "much" or "many". Although this form of calculation may seem very limited, American culture does the same thing to a certain degree. For example, there are several ways to express the amount of solute in a solution in a quantitative manner. The **concentration** of a solution is a measure of the amount of solute that has been dissolved in a given amount of solvent or solution. A **concentrated** solution is one that has a relatively large amount of dissolved solute. A **dilute** solution is one that has a relatively small amount of dissolved solute. However, those terms are vague, and it is often necessary to express concentration with numbers.

Percent Solutions

One way to describe the concentration of a solution is by the percent of a solute in the solvent. The percent can further be determined in one of two ways: (1) the ratio of the mass of the solute divided by the mass of the solution or (2) the ratio of the volume of the solute divided by the volume of the solution.

Mass Percent

When the solute in a solution is a solid, a convenient way to express the concentration is by mass percent $\left(\frac{\text{mass}}{\text{mass}}\right)$, which is the grams of solute per $100\ \text{g}$ of solution.

$$\text{Percent by mass} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$$

Suppose that a solution was prepared by dissolving $25.0\ \text{g}$ of sugar into $100\ \text{g}$ of water. The percent by mass would be calculated by:

$$\text{Percent by mass} = \frac{25\ \text{g sugar}}{125\ \text{g solution}} \times 100\% = 20\%\ \text{sugar}$$

Sometimes you may want to make up a particular mass of solution of a given percent by mass, and need to calculate what mass of the solvent to use. For example, you need to make $3000\ \text{g}$ of a 5% solution of sodium chloride. You can rearrange and solve for the mass of solute:

$$\text{mass of solute} = \frac{\text{percent by mass}}{100\%} \times \text{mass of solution} = \frac{5\%}{100\%} \times 3000\ \text{g} = 150\ \text{g NaCl}$$

You would need to weigh out $150\ \text{g}$ of NaCl and add it to $2850\ \text{g}$ of water. Notice that it was necessary to subtract the mass of the $\text{NaCl}\ (150\ \text{g})$ from the mass of solution $(3000\ \text{g})$ to calculate the mass of the water that would need to be added.

Volume Percent

The percentage of solute in a solution can more easily be determined by volume when the solute and solvent are both liquids. The volume of the solute divided by the volume of the solution, expressed as a percent, yields the percent by volume $\left(\frac{\text{volume}}{\text{volume}}\right)$ of the solution. If a solution is made by adding $40\ \text{mL}$ of ethanol to $200\ \text{mL}$ of water, the percent by volume is:

$$\begin{aligned}\text{Percent by volume} &= \frac{\text{volume of solute}}{\text{volume of solution}} \times 100\% \\ &= \frac{40\ \text{mL ethanol}}{240\ \text{mL solution}} \times 100\% \\ &= 16.7\%\ \text{ethanol}\end{aligned}$$

Frequently, ingredient labels on food products and medicines have amounts listed as percentages (see figure below).

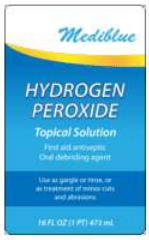


Figure 7.17.1: Hydrogen peroxide is commonly labeled as a 3% by volume solution for use as a disinfectant.

Summary

- The concentration of a solution is a measure of the amount of solute that has been dissolved in a given amount of solvent or solution.
- A concentrated solution has a relatively large amount of dissolved solute.
- A dilute solution has a relatively small amount of dissolved solute.
- Techniques for calculation of percent mass and percent volume solution concentrations are described.

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7.18: Molarity

Chemists deal with amounts of molecules every day. Chemical reactions are described as so many molecules of compound A reacting with so many molecules of compound B to form so many molecules of compound C. When we determine how much reagent to use, we need to know the number of molecules in a given volume of the reagent. Percent solutions only tell us the number of grams, not molecules. A $100\ \text{mL}$ solution of $2\%\ \text{NaCl}$ will have a very different number of molecules than a 2% solution of CsCl. So, we need another way to talk about numbers of molecules.

Molarity

Chemists primarily need the concentration of solutions to be expressed in a way that accounts for the number of particles that react according to a particular chemical equation. Since percentage measurements are based on either mass or volume, they are generally not useful for chemical reactions. A concentration unit based on moles is preferable. The **molarity** (M) of a solution is the number of moles of solute dissolved in one liter of solution. To calculate the molarity of a solution, divide the moles of solute by the volume of the solution expressed in liters:

$$\text{Molarity (M)} = \frac{\text{moles of solute}}{\text{liters of solution}} = \frac{\text{mol}}{\text{L}}$$

Note that the volume is in liters of solution and not liters of solvent. When a molarity is reported, the unit is the symbol M and is read as "molar". For example a solution labeled as $1.5\ \text{M}\ \text{NH}_3$ is read as "1.5 molar ammonia solution".

7.18.1 Example

A solution is prepared by dissolving $42.23\ \text{g}$ of NH_4Cl into enough water to make $500.0\ \text{mL}$ of solution. Calculate its molarity.

Solution

Step 1: List the known quantities and plan the problem.

Known

- Mass $= 42.23\ \text{g}\ \text{NH}_4\text{Cl}$
- Molar mass $\text{NH}_4\text{Cl} = 53.50\ \text{g/mol}$
- Volume solution $= 500.0\ \text{mL} = 0.5000\ \text{L}$

Unknown

The mass of the ammonium chloride is first converted to moles. Then the molarity is calculated by dividing by liters. Note that the given volume has been converted to liters.

Step 2: Solve.

$$42.23\ \text{g}\ \text{NH}_4\text{Cl} \times \frac{1\ \text{mol}\ \text{NH}_4\text{Cl}}{53.50\ \text{g}\ \text{NH}_4\text{Cl}} = 0.7893\ \text{mol}\ \text{NH}_4\text{Cl}$$

$$\frac{0.7893\ \text{mol}\ \text{NH}_4\text{Cl}}{0.5000\ \text{L}} = 1.579\ \text{M}$$

Step 3: Think about your result.

The molarity is $1.579\ \text{M}$, meaning that a liter of the solution would contain $1.579\ \text{mol}\ \text{NH}_4\text{Cl}$ Four significant figures are appropriate.

In a laboratory situation, a chemist must frequently prepare a given volume of solutions of a known molarity. The task is to calculate the mass of the solute that is necessary. The molarity equation can be rearranged to solve for moles, which can then be converted to grams.

7.18.2 Example

A chemist needs to prepare $3.00\ \text{L}$ of a $0.250\ \text{M}$ solution of potassium permanganate (KMnO_4). What mass of KMnO_4 does she need to make the solution?

Solution

Step 1: List the known quantities and plan the problem.

Known

- Molarity $= 0.250\ \text{M}$
- Volume $= 3.00\ \text{L}$
- Molar mass $\text{KMnO}_4 = 158.04\ \text{g/mol}$

Unknown

Moles of solute is calculated by multiplying molarity by liters. Then, moles is converted to grams.

Step 2: Solve.

$$\text{mol KMnO}_4 = 0.250\ \text{M KMnO}_4 \times 3.00\ \text{L} = 0.750\ \text{mol KMnO}_4$$

$$0.750\ \text{mol KMnO}_4 \times \frac{158.04\ \text{g KMnO}_4}{1\ \text{mol KMnO}_4} = 119\ \text{g KMnO}_4$$

Step 3: Think about your result.

When $119\ \text{g}$ of potassium permanganate is dissolved into water to make $3.00\ \text{L}$ of solution, the molarity is $0.250\ \text{M}$.

Summary

- The molarity (M) of a solution is the number of moles of solute dissolved in one liter of solution.
- Calculations using the concept of molarity are described.

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CHAPTER OVERVIEW

8: Biochemistry

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8.1: Monosaccharides

The brain is a marvelous organ. And it's a hungry one, too. The major fuel for the brain is glucose—a carbohydrate. The average adult brain represents about 2% of our body's weight, but uses 25% of the glucose in the body. Moreover, specific areas of the brain use glucose at different rates. If you are concentrating hard (taking a test, for example), certain parts of the brain need a lot of extra glucose, while other parts of the brain only use their normal amount.

Monosaccharides

Some foods that are high in carbohydrates include bread, pasta, and potatoes. Because carbohydrates are easily digested, athletes often rely on carbohydrate-rich foods to enable a high level of performance.



Figure 8.1.1: Foods that serve as carbohydrate sources.

The term carbohydrate comes from the fact that the majority contain carbon, hydrogen, and oxygen in a ratio of 1:2:1, making for an empirical formula of CH_2O. This is somewhat misleading, because the molecules are not actually hydrates of carbon at all. **Carbohydrates** are monomers and polymers of aldehydes and ketones that have multiple hydroxyl groups attached.

Carbohydrates are the most abundant source of energy found in most foods. The simplest carbohydrates, also called simple sugars, are plentiful in fruits. A **monosaccharide** is a carbohydrate consisting of one sugar unit. Common examples of simple sugars or monosaccharides are glucose and fructose. Both of these monosaccharides are referred to as hexoses, since they have six carbons. Glucose is abundant in many plant sources, and makes up sweeteners such as corn sugar and grape sugar. Fructose is found in many fruits, as well as in honey. These sugars are structural isomers of one another, with the difference being that glucose contains an aldehyde functional group, whereas fructose contains a ketone functional group.

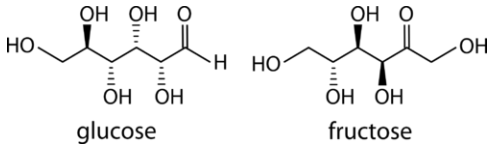


Figure 8.1.2: Glucose and fructose are monosaccharides, or simple sugars.

Glucose and fructose are both very soluble in water. In aqueous solution, the predominant forms are not the straight-chain structure shown above. Rather, they adopt a cyclic structure (see figure below). Glucose is six membered ring, while fructose is a five-membered ring. Both rings contain an oxygen atom.

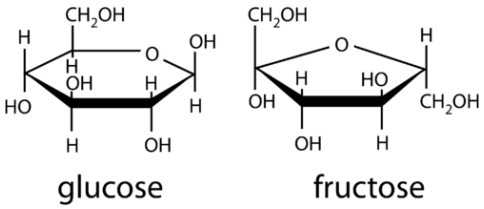


Figure 8.1.3: The cyclic form of sugars is the favored form in aqueous solution.

Another important group of monosaccharides are the pentoses, containing five carbons in the chain. Ribose and deoxyribose are two pentoses that are components of the structures of DNA and RNA.

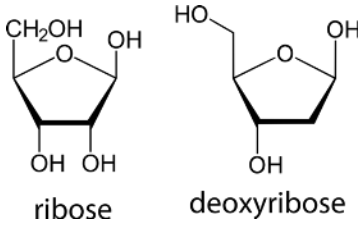


Figure 8.1.4: Ribose and deoxyribose.

Summary

- Carbohydrates are monomers and polymers of aldehydes and ketones that have multiple hydroxyl groups attached.
- A monosaccharide is a carbohydrate consisting of one sugar unit.
- Common examples of simple sugars or monosaccharides are glucose and fructose.
- Another important group of monosaccharides are the pentoses, containing five carbons in the chain; DNA and RNA are partly comprised of pentoses.

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8.2: Disaccharides

Milk is one of the basic foods needed for good nutrition, especially for growing children. It contains vitamins and minerals necessary for healthy development. Unfortunately, milk and other dairy products also contain lactose, a carbohydrate that can make some people very ill. Lactose intolerance is a condition in which the lactose in milk cannot be digested well in the small intestine. The undigested lactose then moves into the large intestine where bacteria attack it, forming large amounts of gas. Symptoms of lactose intolerance include bloating, cramps, nausea, and vomiting. Often, in the case of children, the individual will outgrow this problem. Avoidance of foods containing lactose is recommended for people who show signs of lactose intolerance. Since dairy products can provide many vital nutrients, tablets can be taken that provide the needed digestive materials in the small intestine. Lactose-free milk is also readily available.

Disaccharides

The simple sugars form the foundation of more complex carbohydrates. The cyclic forms of two sugars can be linked together by means of a condensation reaction. The figure below shows how a glucose molecule and a fructose molecule combine to form a sucrose molecule. A hydrogen atom from one molecule and a hydroxyl group from the other molecule are eliminated as water, with a resulting covalent bond linking the two sugars together at that point.

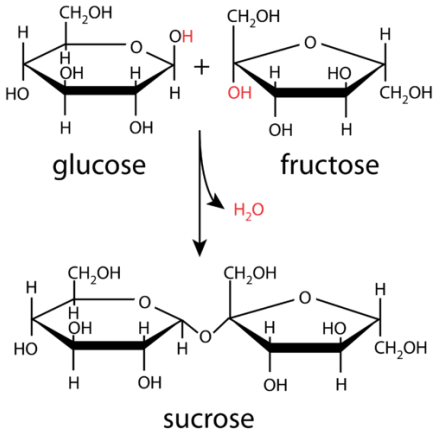


Figure 8.2.1: Glucose and fructose combine to produce the disaccharide sucrose in a condensation reaction.

Sucrose, commonly known as table sugar, is an example of a disaccharide. A **disaccharide** is a carbohydrate formed by the joining of two monosaccharides. Other common disaccharides include lactose and maltose. Lactose, a component of milk, is formed from glucose and galactose, while maltose is formed from two glucose molecules.

During digestion, these disaccharides are hydrolyzed in the small intestine to form the component monosaccharides, which are then absorbed across the intestinal wall and into the bloodstream to be transported to the cells.

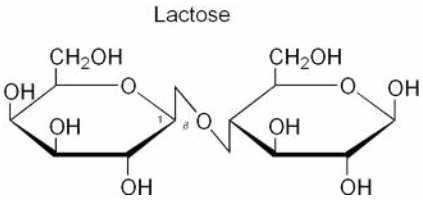


Figure 8.2.2: Lactose.

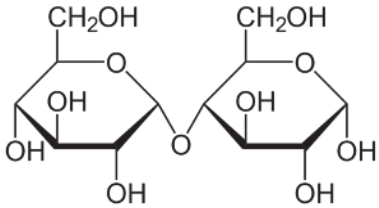


Figure 8.2.3: Maltose.

Summary

- A **disaccharide** is a carbohydrate formed by the joining of two monosaccharides.
- Common disaccharides include sucrose, lactose, and maltose.

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8.3: Polysaccharides

As the weather warms up, the runners come out. Not just the casual joggers, but also the really serious runners who actually enjoy running all 26.2 miles of a marathon. Prior to these races (and a lot of shorter ones), you hear a lot about carbo-loading. This practice involves eating a lot of starch in the days prior to the race. The starch is converted to glucose, which is normally used for biochemical energy. Excess glucose is stored as glycogen in liver and muscle tissue to be used when needed. If there is a lot of glycogen available, the muscles will have more biochemical energy to draw on when needed for the long run. Meanwhile, the rest of us will sit at the sidewalk restaurant, eating our spaghetti, and enjoying watching other people work hard.

Polysaccharides

Many simple sugars can combine by repeated condensation reactions until a very large molecule is formed. A **polysaccharide** is a complex carbohydrate polymer formed from the linkage of many monosaccharide monomers. One of the best known polysaccharides is starch, the main form of energy storage in plants. Starch is a staple in most human diets. Foods such as corn, potatoes, rice, and wheat have high starch contents. Starch is made of glucose monomers and occurs in both straight-chain and branched forms. Amylose is the straight-chain form, and consists of hundreds of linked glucose molecules. The branched form of starch is called amylopectin. In the small intestine, starch is hydrolyzed to form glucose. The glucose can then be converted to biochemical energy or stored for later use.

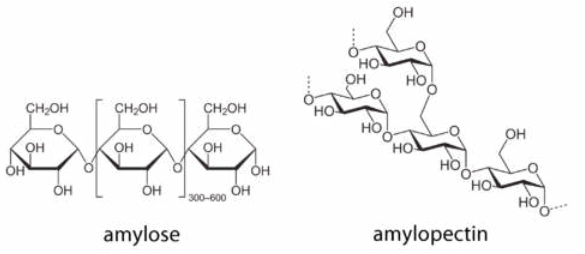


Figure 8.3.1: Amylose and amylopectin are the two most common components of naturally occurring starch. Both consist of many glucose monomers connected into a polymer. Starch serves as energy storage in plants.

Glycogen is an even more highly branched polysaccharide of glucose monomers that serves the function of energy storage in animals. Glycogen is made and stored primarily in the cells of the liver and muscles.

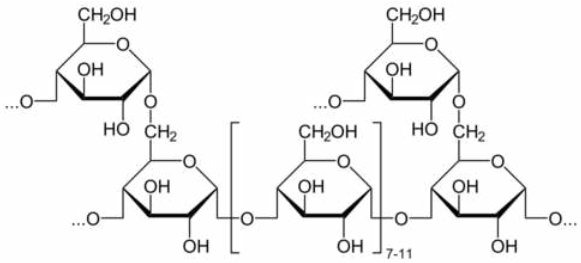


Figure 8.3.2: Glycogen is a branched polymer of glucose and serves as energy storage in animals.

Cellulose is another polymer of glucose, consisting of anywhere from hundreds to over ten thousand monomers. It is the structural component of the cell walls of green plants and is the single most common organic molecule on Earth. Roughly 33% of all plant matter is cellulose. The linkage structure in cellulose is different than that of starch, and cellulose is indigestible except by a few microorganisms that live in the digestive tracts of cattle and termites. The figure below shows a triple strand of cellulose. There is no branching and the fibers adopt a very stiff rod-like structure with numerous hydrogen bonds between the fibers adding to its strength. Cellulose is the main component of paper, cardboard, and textiles made from cotton, linen, and other plant fibers.

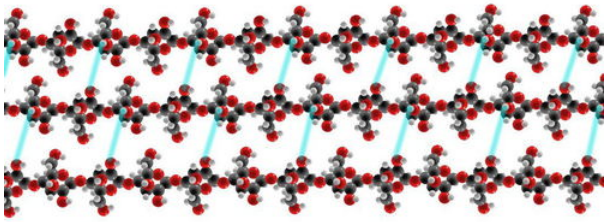


Figure 8.3.3: Cellulose is composed of very long strands of glucose monomers that are hydrogen bonded to one another. Cellulose is largely indigestible and comprises the cell walls of plants.

Summary

- A polysaccharide is a complex carbohydrate polymer formed from the linkage of many monosaccharide monomers.
- One of the best known polysaccharides is starch, the main form of energy storage in plants.
- Glycogen is an even more highly branched polysaccharide of glucose monomers that serves the function of storing energy in animals.
- Cellulose is another polymer of glucose; it is the structural component of the cell walls of green plants.

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8.4: Amino Acids

Athletics are very competitive these days at all levels, from school sports to the pros. Everybody is looking for that edge that will make them faster, stronger, and more physically fit. One approach taken by many athletes is the use of amino acid supplements. The theory is that the increase in amino acids in the diet will lead to increased protein for muscles. However, the only real benefit comes to the people who make and sell the pills. Studies have not shown any advantage obtained by the athletes themselves; they are better off just maintaining a healthy diet.

Amino Acids

An **amino acid** is a compound that contains both an amine group $(-NH_2)$ and a carboxyl group $(-COOH)$ in the same molecule. While any number of amino acids can be imagined, biochemists generally reserve the term for a group of 20 amino acids which are formed and used by living organisms. The figure below shows the general structure of an amino acid.

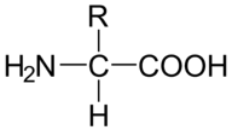


Figure 8.4.1: An amino acid is an organic molecule that contains an amine group, a carboxyl group, and a side chain (R), all bonded to a central carbon atom.

The amino acid and carboxyl group of an amino acid are both covalently bonded to a central carbon atom. That carbon atom is also bonded to a hydrogen atom and an R group. It is this R group which varies from one amino acid to another and is called the amino acid side chain.

The nature of the side chains accounts for the variability in physical and chemical properties of the different amino acids. Some side chains consist of nonpolar aliphatic or aromatic hydrocarbons. Other side chains are polar, while some are acidic or basic.

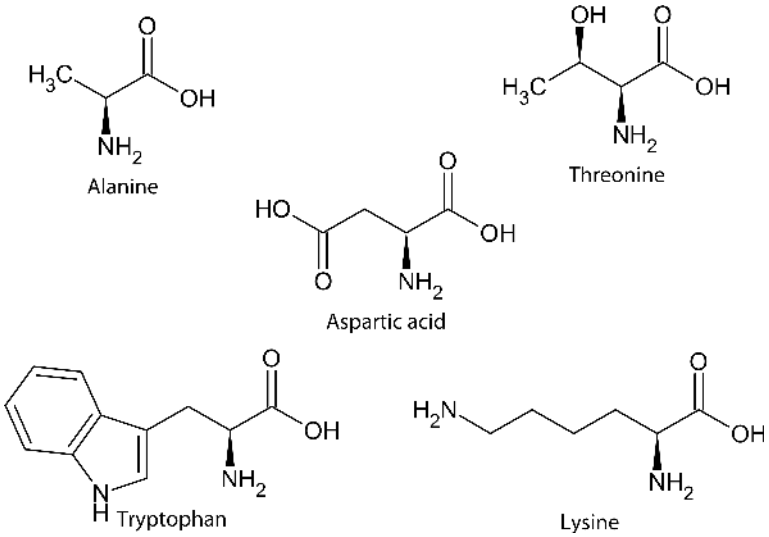


Figure 8.4.2: Five of the twenty biologically relevant amino acids, each having a distinct side chain (R). Alanine's side chain is nonpolar, while threonine's is polar. Tryptophan is one of several amino acids whose side chain is aromatic. Aspartic acid has an acidic side chain, while lysine has a basic side chain.

The table below lists the names of the 20 naturally occurring amino acids along with a three-letter abbreviation which is used to describe sequences of linked amino acids.

Table 8.4.1: Amino acids and Abbreviations

Amino Acid	Abbreviation	Amino Acid	Abbreviation
Alanine	Ala	Leucine	Leu
Arginine	Arg	Lysine	Lys
Asparagine	Asp	Methionine	Met

Amino Acid	Abbreviation	Amino Acid	Abbreviation
Aspartic acid	Asp	Phenylalanine	Phe
Cysteine	Cys	Proline	Pro
Glutamine	Gln	Serine	Ser
Glutamic acid	Glu	Threonine	Thr
Glycine	Gly	Tryptophan	Trp
Histidine	His	Tyrosine	Tyr
Isoleucine	Ile	Valine	Val

Another more recent set of abbreviations employs only one letter. Leucine would be designated by L, serine by S, tyrosine by Y. The advantage of this system comes when listing the amino acid sequence of a protein that may contain over 100 amino acids in its chain.

Summary

- An amino acid is a compound that contains both an amine group $(-NH_2)$ and a carboxyl group $(-COOH)$ in the same molecule.
- The nature of an amino acid's side chain accounts for the variability in chemical and physical properties of amino acids.
- There are 20 amino acids formed and used by living organisms.

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8.5: Peptides

Cells in our bodies have an intricate mechanism for the manufacture of proteins. Humans have to use other techniques in order to synthesize the same proteins in a lab. The chemistry of peptide synthesis is complicated. Both active groups on an amino acid can react, and the amino acid sequence must be a specific one in order for the protein to function. Robert Merrifield developed the first synthetic approach for making proteins in the lab, a manual approach which was lengthy and tedious. Merrifield won the Nobel Prize in Chemistry in 1984 for his work. Today, however, automated systems can crank out a peptide in a very short period of time.

Peptides

A **peptide** is a combination of amino acids in which the amine group of one amino acid has undergone a reaction with the carboxyl group of another amino acid. The reaction is a condensation reaction, forming an amide group $(\mathrm{CO{-}N})$, shown below.

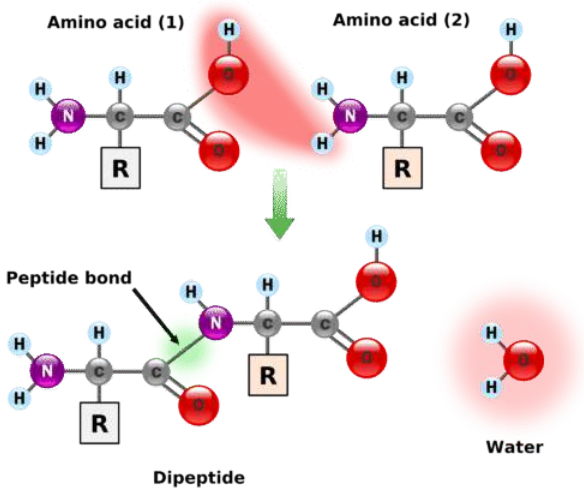


Figure 8.5.1: Amino acids join together to form a molecule called a dipeptide. The $\mathrm{C{-}N}$ bond is called a peptide bond. The order of amino acids is, by convention, shown with the free amine group on the left and the free carboxyl group on the right.

A **peptide bond** is the amide bond that occurs between the amine nitrogen of one amino acid and the carboxyl carbon of another amino acid. The resulting molecule is called a dipeptide. Notice that the particular side chains of each amino acid are irrelevant since the R groups are not involved in the peptide bond.

The dipeptide has a free amine group on one end of the molecule and a free carboxyl group on the other end. Each is capable of extending the chain through the formation of another peptide bond. The particular sequence of amino acids in a longer chain is called an amino acid sequence. By convention, the amino acid sequence is listed in the order such that the free amine group is on the left end of the molecule, and the free carboxyl group is on the right end of the molecule. For example, suppose that a sequence of the amino acids glycine, tryptophan, and alanine is formed with the free amine group as part of the glycine and the free carboxyl group as part of the alanine. The amino acid sequence can be easily written using the abbreviations as Gyl-Trp-Ala. This is a different sequence from Ala-Trp-Gly, because the free amine and carboxyl groups would be on different amino acids in that case.

Summary

- A peptide is a combination of amino acids in which the amine group of one amino acid has undergone a reaction with the carboxyl group of another amino acid.
- A peptide bond is the amide bond that occurs between the amine nitrogen of one amino acid and the carboxyl carbon of another amino acid.

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8.6: Proteins

Hemoglobin is a complex protein which has a quaternary structure and contains iron. There are four subunits in the hemoglobin molecule: two alpha subunits and two beta subunits. Each subunit contains one iron ion, whose oxidation state changes from $+2$ to $+3$ and back again, depending upon the environment around the iron. When oxygen binds to the iron, the three-dimensional shape of the molecule changes. Upon release of the oxygen to the cells, the shape changes again.

With hemoglobin of normal structure, this shift in conformation does not present any problems. However, individuals with hemoglobin S do experience serious complications. This hemoglobin has one amino acid in the two beta chains that is different from the amino acid at that point in the primary structure of normal hemoglobin. The result of this one structural change is aggregation of the individual protein molecules when oxygen is released. Adjacent hemoglobin molecules come in contact with one another and clump up, causing the red cells to deform and break.

This abnormality, known as sickle cell, is genetic in nature. A person may inherit the gene from one parent and have sickle cell trait (only some of the hemoglobin is hemoglobin S), which is usually not life-threatening. Inheriting the gene from both parents, however, will result in sickle cell disease—a very serious condition.

Proteins

A **polypeptide** is a sequence of amino acids between ten and one hundred in length. A **protein** is a peptide that is greater than one hundred amino acids in length. Proteins are very prevalent in living organisms. Hair, skin, nails, muscles, and the hemoglobin in red blood cells are some important parts of the human body that are made of different proteins. The wide array of chemical and physiological properties of proteins is a function of their amino acid sequences. Since proteins generally consist of one hundred or more amino acids, the number of amino acid sequences that are possible is virtually limitless.

The three-dimensional structure of a protein is very critical to its function. This structure can be broken down into four levels. The **primary structure** is the amino acid sequence of the protein. The amino acid sequence of a given protein is unique and defines the function of the protein. The **secondary structure** is a highly regular sub-structure of the protein. The two most common types of protein secondary structure are the alpha helix and the beta sheet. An alpha helix consists of amino acids that adopt a spiral shape. A beta sheet is alternating rows of amino acids that line up in a side-by-side fashion. In both cases, the secondary structures are stabilized by extensive hydrogen bonding between the side chains. The interaction of the various side chains in the amino acid, specifically the hydrogen bonding, leads to the adoption of a particular secondary structure.

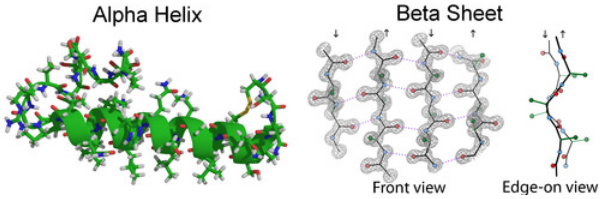


Figure 8.6.1: Secondary structure: alpha helix and beta sheet.

The **tertiary structure** is the overall three-dimensional structure of the protein. A typical protein consists of several sections of a specific secondary structure (alpha helix or beta sheet), along with other areas in which a more random structure occurs. These areas combine to produce the tertiary structure.

Some protein molecules consist of multiple protein subunits. The **quaternary structure** of a protein refers to the specific interaction and orientation of the subunits of that protein. Hemoglobin is a very large protein found in red blood cells, whose function is to bind and carry oxygen throughout the bloodstream. As pictured below, hemoglobin consists of four subunits—two α subunits (yellow) and two β subunits (gray)—which then come together in a specific and defined way through interactions of the side chains. Hemoglobin also contains four iron atoms, located in the middle of each of the four subunits. The iron atoms are part of a structure called a porphyrin, shown in red in the figure.

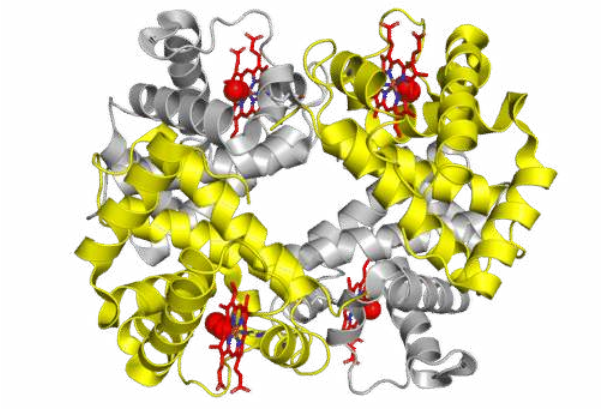


Figure 8.6.2: Hemoglobin.

Some proteins consist of only one subunit and thus do not have a quaternary structure. The figure below diagrams the interaction of the four levels of protein structure.

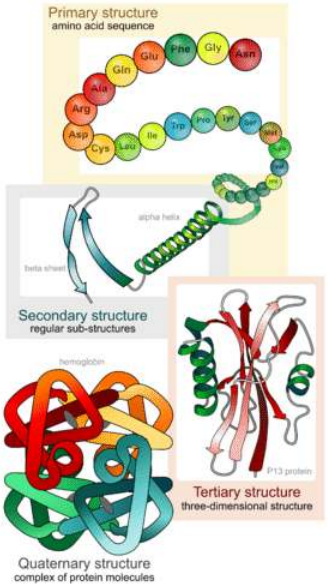


Figure 8.6.3: The four levels of protein structure.

Summary

- A polypeptide is a sequence of amino acids between ten and one hundred in length.
- A protein is a peptide that is greater than one hundred amino acids in length.
- The primary structure is the amino acid sequence of the protein (unique to each protein).
- The secondary structure is a highly regular sub-structure of the protein; the two most common types being the alpha helix and the beta sheet.
- The tertiary structure is the overall three-dimensional structure of the protein.
- The quaternary structure of a protein refers to the specific interaction and orientation of the subunits of that protein.

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8.7: Enzymes

The first enzyme to be isolated was discovered in 1926 by American chemist James Sumner, who crystallized the protein. The enzyme was urease, which catalyzes the hydrolytic decomposition of urea, a component of urine, into ammonia and carbon dioxide.

$$\mathrm{H_2NCONH_2}\,(aq) + \mathrm{H_2O}\,(l) \overset{\text{urease}}{\rightarrow} 2\mathrm{NH_3}\,(g) + \mathrm{CO_2}\,(g)$$

His discovery was ridiculed at first, because nobody believed that enzymes would behave the same way that other chemicals did. Sumner was eventually proven right and won the Nobel Prize in Chemistry in 1946.

Enzymes

An **enzyme** is a protein that acts as a biological catalyst. Recall that a catalyst is a substance that increases the rate of a chemical reaction without itself being consumed in the reaction. Cellular processes consist of many chemical reactions that must occur quickly in order for the cell to function properly. Enzymes catalyze most of the chemical reactions that occur in a cell. A **substrate** is the molecule or molecules on which the enzyme acts. In the urease catalyzed reaction above, urea is the substrate. The figure below diagrams a typical enzymatic reaction.

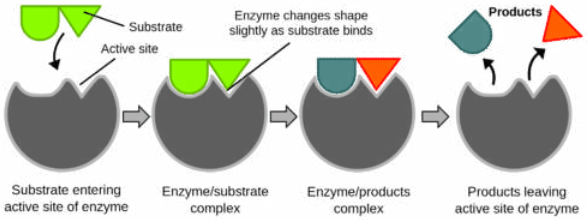


Figure 8.7.1: The sequence of steps for a substrate binding to an enzyme in its active site, reacting, then being released as products.

The first step in the reaction is that the substrate binds to a specific part of the enzyme molecule. The binding of the substrate is dictated by the shape of each molecule. Side chains on the enzyme interact with the substrate in a specific way, resulting in the making and breaking of bonds. The **active site** is the place on an enzyme where the substrate binds. An enzyme binds in such a way that it typically has one active site, usually a pocket or crevice formed by the folding pattern of the protein. Because the active site of an enzyme has such a unique shape, only one particular substrate is capable of binding to that enzyme. In other words, each enzyme catalyzes only one chemical reaction with only one substrate. Once the enzyme/substrate complex is formed, the reaction occurs, and the substrate is transformed into products. Finally, the product molecule or molecules are released from the active site. Note that the enzyme is left unaffected by the reaction and is now capable of catalyzing the reaction of another substrate molecule.

Inhibitors

An **inhibitor** is a molecule which interferes with the function of an enzyme, either by slowing or stopping the chemical reaction. Inhibitors can work in a variety of ways, but one of the most common is illustrated in the figure below.

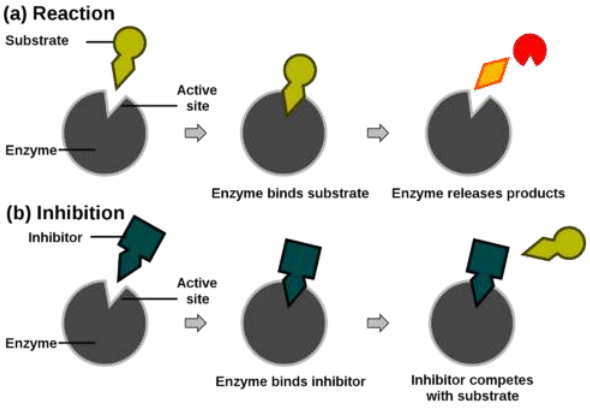


Figure 8.7.2: A competitive inhibitor is a molecule that binds to the active site of an enzyme without reacting, thus preventing the substrate from binding.

The competitive inhibitor binds competitively at the active site and blocks the substrate from binding. Since no reaction occurs with the inhibitor, the enzyme is prevented from catalyzing the reaction. Cyanide is a potent poison which acts as a competitive inhibitor. It binds to the active site of the enzyme *cytochrome c oxidase* and interrupts cellular respiration. The binding of the cyanide to the enzyme is irreversible and the affected organism dies quickly.

Non-competitive Inhibition

A non-competitive inhibitor does not bind at the active site. It attaches at some other site on the enzyme, and changes the shape of the protein. This shift in three-dimensional structure alters the shape of the active site so that the substrate will no longer fit in the site properly (see figure below).

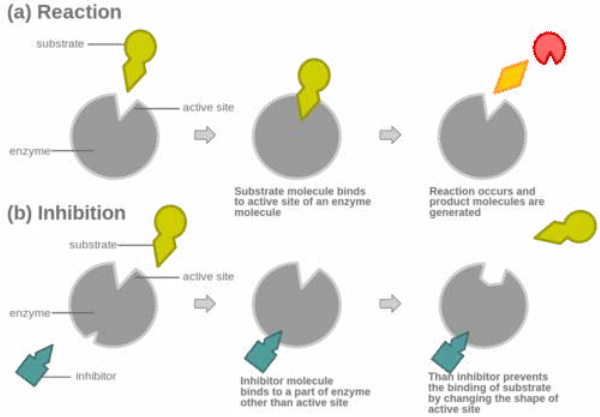


Figure 8.7.3: Non-competitive inhibitors.

Cofactors

Some enzymes require the presence of a non-protein molecule called a cofactor on order to function properly. Cofactors can be inorganic metal ions or small organic molecules. Many vitamins, such as B vitamins, act as cofactors. Some metal ions which function as cofactors for various enzymes include zinc, magnesium, potassium, and iron.

Summary

- An enzyme is a protein that acts as a biological catalyst.
- A substrate is the molecule or molecules on which the enzyme acts.
- The active site is the place on an enzyme where the substrate binds.
- Each enzyme catalyzes only one chemical reaction with only one substrate.
- An inhibitor is a molecule which interferes with the function of an enzyme, either by slowing or stopping the chemical reaction.
- A competitive inhibitor is a molecule that binds to the active site of an enzyme without reacting, thus preventing the substrate from binding.
- A non-competitive inhibitor does not bind at the active site; it attaches at some other site on the enzyme.
- Some enzymes require the presence of a non-protein molecule called a cofactor on order to function properly.

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8.8: Triglycerides

There is a lot of interest these days in healthy diets, as well as concerns about heart problems. There is also a strong market for the sales of omega-3 fatty acids, which are said to help lower triglyceride (fat) levels in blood. But too many people rely on the supplements to help their hearts and don't understand the chemistry behind it all. Yes, taking omega-3 fatty acids will give you some of the fatty acids your body requires. No, this is not a substitute for eating a healthy diet and exercising. You can't sit in front of the TV set, eat a large pizza, and expect these pills to keep you healthy. It's important to eat healthfully and get exercise.

Triglycerides

A **lipid** is a member of a class of water-insoluble compounds that includes oils, fats, and waxes. Oils and fats are based on the same general structure, but fats are solids at room temperature, while oils are liquids. Butter is an example of a fat and is derived from animals. Some oils include olive oil and canola oil, which are obtained from plants. Lipids are an essential part of a healthy diet, though excess dietary fat can be harmful. Lipids store energy in the body and are also needed to keep cell membranes healthy.

One type of lipid is called a **triglyceride**, an ester derived from glycerol combined with three fatty acid molecules.

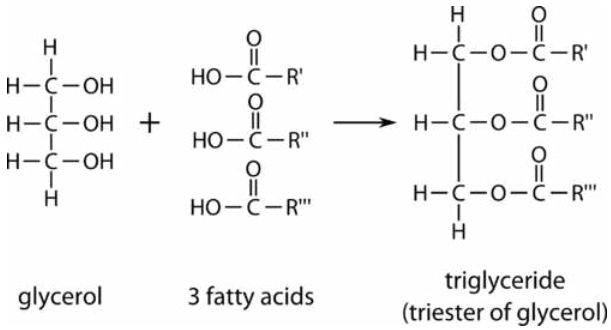


Figure 8.8.1: Triglyceride components.

Glycerol is a triol, an alcohol which contains three hydroxyl functional groups. A fatty acid is a long carbon chain, generally 12 to 24 carbons in length, with an attached carboxyl group. Each of the three fatty acid molecules undergoes an esterification with one of the hydroxyl groups of the glycerol molecule. The result is a large triester molecule referred to as a triglyceride.

Triglycerides function as a long-term storage form of energy in the human body. Because of the long carbon chains, triglycerides are nearly nonpolar molecules and thus do not dissolve readily in polar solvents such as water. Instead, oils and fats are soluble in nonpolar organic solvents such as hexane and ethers.

Fats may be either saturated or unsaturated. A **saturated fat** is a fat that consists of triglycerides whose carbon chains consist entirely of carbon-carbon single bonds. Therefore, the carbon chains are saturated with the maximum number of hydrogen atoms possible. An **unsaturated fat** is a fat that consists of triglycerides whose carbon chains contain one or more carbon-carbon double bonds. A fat with one double bond is called monounsaturated, while a fat with multiple double bonds is called polyunsaturated (see figure below).

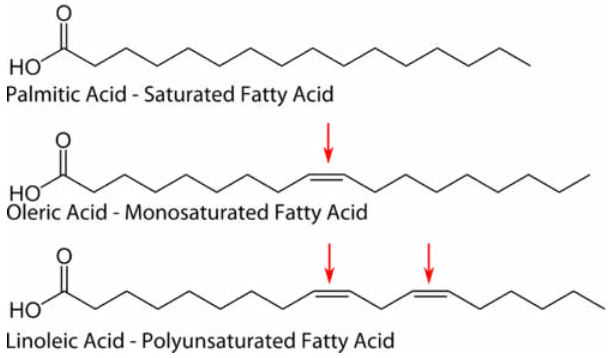


Figure 8.8.2: Saturated and unsaturated fatty acids.

High consumption of saturated fats is linked to an increased risk of cardiovascular disease. Some examples of foods with high concentrations of saturated fats include butter, cheese, lard, and some fatty meats. Foods with higher concentrations of unsaturated

fats include nuts, avocado, and vegetable oils such as canola oil and olive oil. The figure below shows the percentages of fat types in some common foods.

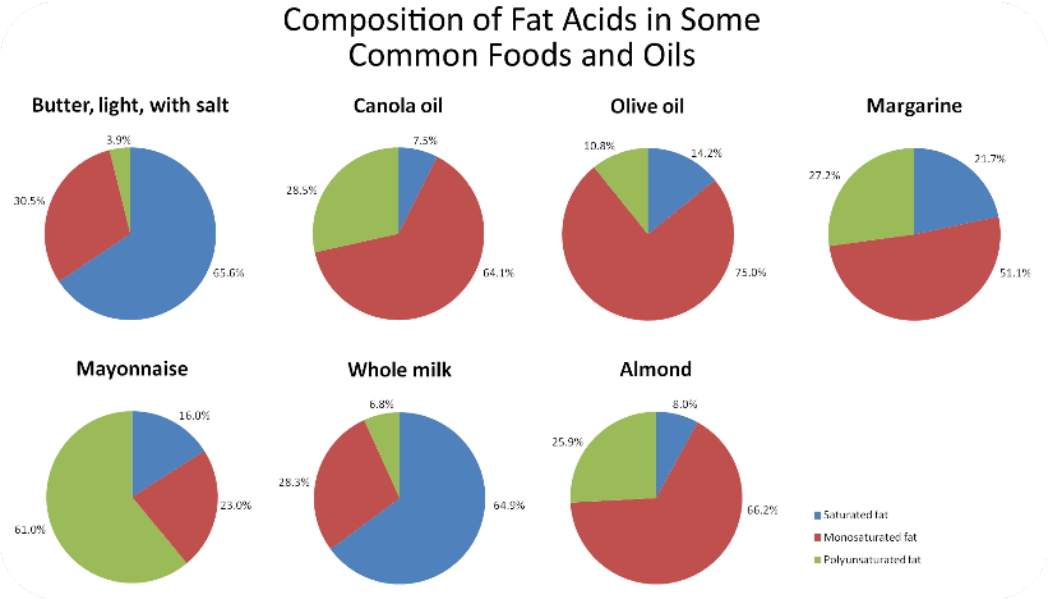


Figure 8.8.3: Some common foods and oils along with their percentages of saturated, monounsaturated, and polyunsaturated fats.

Summary

- A lipid is a member of a class of water-insoluble compounds that includes oils, fats, and waxes.
- One type of lipid is called a **t**riglyceride, an ester derived from glycerol combined with three fatty acid molecules.
- A saturated fat is a fat that consists of triglycerides whose carbon chains consist entirely of carbon-carbon single bonds.
- An unsaturated fat is a fat that consists of triglycerides whose carbon chains contain one or more carbon-carbon double bonds.

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8.9: Phospholipids

If you were to go to the dentist to get a tooth pulled, you would not want to feel any pain. The dentist would inject an anesthetic into your gum to numb it. One theory as to why anesthetics work deals with the movement of ions across the cell membrane. The anesthetic gets into the membrane structure and causes shifts in how ions move across the membrane. If ion movement is disrupted, nerve impulses will not be transmitted and you will not sense pain—at least, not until the anesthetic wears off.

Phospholipids

A **phospholipid** is a lipid that contains a phosphate group and is a major component of cell membranes. A phospholipid consists of a hydrophilic (water-loving) head and hydrophobic (water-fearing) tail (see figure below). The phospholipid is essentially a triglyceride in which a fatty acid has been replaced by a phosphate group of some sort.

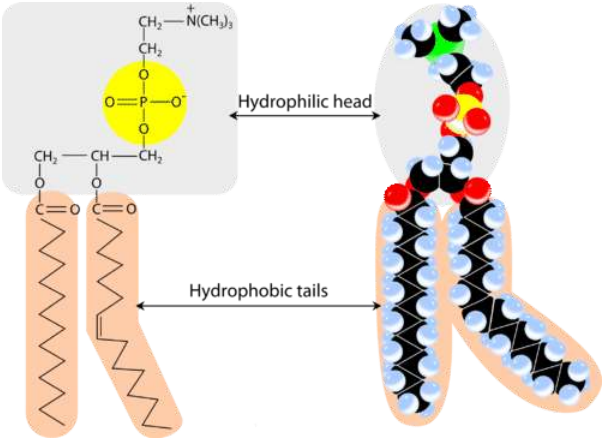


Figure 8.9.1: A phospholipid consists of a head and a tail. The "head" of the molecule contains the phosphate group and is hydrophilic, meaning that it will dissolve in water. The "tail" of the molecule is made up of two fatty acids, which are hydrophobic and do not dissolve in water.

Following the rule of "like dissolves like", the hydrophilic head of the phospholipid molecule dissolves readily in water. The long fatty acid chains of a phospholipid are nonpolar, and thus avoid water because of their insolubility. In water, phospholipids spontaneously form a double layer called a lipid bilayer, in which the hydrophobic tails of phospholipid molecules are sandwiched between two layers of hydrophilic heads (see figure below). In this way, only the heads of the molecules are exposed to the water, while the hydrophobic tails interact only with each other.

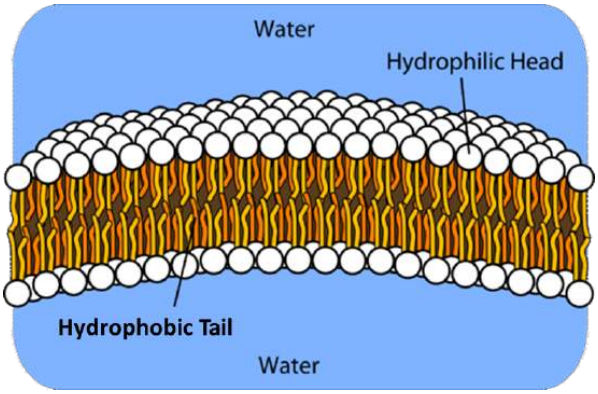


Figure 8.9.2: In a water solution, phospholipids form a bilayer where the hydrophobic tails point towards each other on the interior and only the hydrophilic heads are exposed to the water.

Phospholipid bilayers are critical components of cell membranes. The lipid bilayer acts as a barrier to the passage of molecules and ions into and out of the cell. However, an important function of the cell membrane is to allow selective passage of certain substances into and out of cells. This is accomplished by the embedding of various protein molecules in and through the lipid bilayer (see figure below). These proteins form channels through which certain specific ions and molecules are able to move. Many membrane proteins also contain attached carbohydrates on the outside of the lipid bilayer, allowing it to form hydrogen bonds with water.

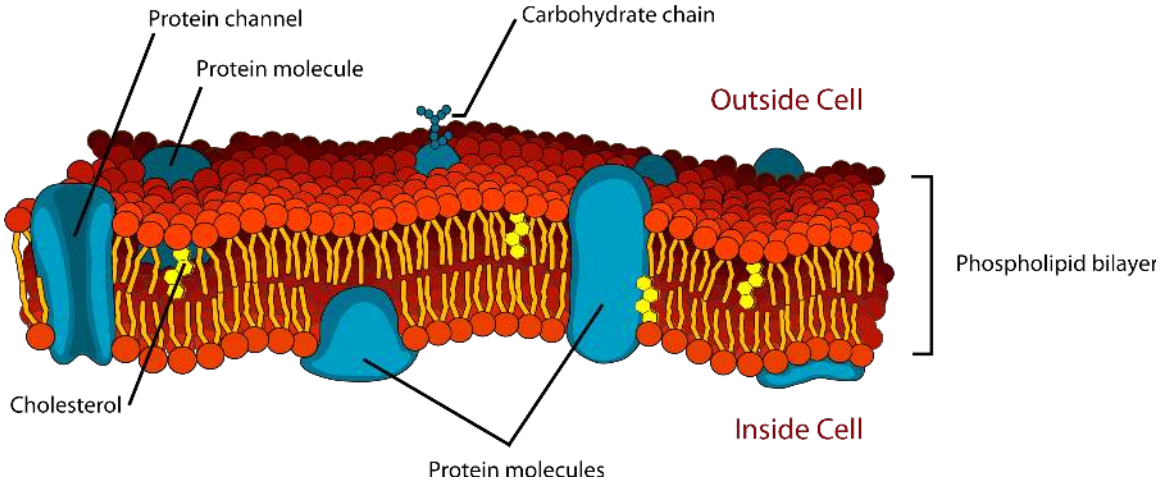


Figure 8.9.3: The phospholipid bilayer of a cell membrane contains embedded protein molecules, which allow for selective passage of ions and molecules through the membrane.

Summary

- A phospholipid is a lipid that contains a phosphate group.
- A phospholipid consists of a hydrophilic (water-loving) head and hydrophobic (water-fearing) tail.
- In water, phospholipids spontaneously form a double layer called a lipid bilayer, in which the hydrophobic tails of phospholipid molecules are sandwiched between two layers of hydrophilic heads.
- Phospholipid bilayers are critical components of cell membranes.

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8.10: Waxes

From the 1700s up to the late 1900s, whalers searched the ocean for the sperm whale. Whaling was a dangerous occupation—the prey averaged about fifty feet in length. But when successful, the search was worth it. One large whale could produce up to 500 gallons of oil, valuable for making candles, ointments, cosmetic creams, and industrial lubricants. In 1988, sperm whales (and other whale species) were placed under international protection because their numbers were diminishing rapidly. Today, various vegetable oils are used in place of whale oils.

Waxes

Another category of lipid molecule is waxes. **Waxes** are esters of long-chain fatty acids and long-chain alcohols. Waxes are soft solids with generally low melting points and are insoluble in water. The figure below shows the structure of cetyl palmitate, a natural wax present in sperm whales.

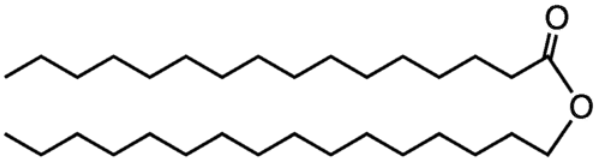


Figure 8.10.1: Cetyl palmitate belongs to the category of compounds called waxes. It is derived from a fatty acid that is 15 carbons in length and an alcohol that contains 16 carbon atoms.

One of the best known natural waxes is beeswax, though many other animals and plants synthesize waxes naturally. Waxes can be found on leaves of plants and on the skin, hair, or feathers of animals, where they function to keep these structures pliable and waterproof. Humans take advantage of the protective properties of natural and synthetic waxes in such applications as floor polish and car wax. Other common waxes include jojoba, carnauba, and wool wax, which is also known as lanolin.

Summary

- Waxes are esters of long-chain fatty acids and long-chain alcohols.
- Humans take advantage of the protective properties of natural and synthetic waxes in such applications as floor polish and car wax.

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8.11: Nucleic Acids

Cancer treatment is a complex and challenging effort. Cancer cells grow without the usual controls that act on normal cells. One approach to treating cancer is to alter the structure of the DNA in order to slow down or stop the growth of the abnormal cells. Compounds that structurally resemble the normal building blocks of DNA have been shown to be very effective in stopping some forms of cancer from spreading throughout the body.

Nucleic Acids

The Swiss biochemist Friedrich Miescher first discovered nitrogen-containing compounds in the nuclei of cells in 1869. The term nucleic acid was used to describe these molecules because of their discovery within the cell nucleus, and because of the presence of phosphate groups and their relationship to phosphoric acid. A **nucleic acid** is a large biopolymer consisting of many nucleotides. The two primary nucleic acids which are found in cells are deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). DNA is the carrier of genetic information and is ultimately responsible for how cells produce proteins in order to carry out all the functions necessary for life. RNA is a related molecule that is involved in the mechanism by which the information stored in DNA is eventually converted into protein molecules.

The basic components of nucleic acids are nucleotides. A **nucleotide** is a molecule that contains a five-carbon sugar, a phosphate group, and a nitrogen-containing base. The five-carbon sugar is either ribose, in the case of RNA, or deoxyribose, in the case of DNA. The only difference between the two molecule is the presence of a hydroxyl group attached to one member of the carbon ring in RNA. In DNA, that same carbon atom is attached only to a hydrogen atom (see figure below). Note that in drawing the structure of organic molecules, the single hydrogen atoms are not shown in the structure, but are understood to be attached at each carbon point unless another molecule is shown.

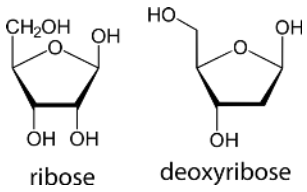


Figure 8.11.1: The sugars ribose and deoxyribose are components of RNA and DNA respectively.

The nucleotides form the backbone of RNA and DNA. Each nucleotide consists of a base, a pentose (either ribose or deoxyribose) and phosphate groups (see figure below). Three of the bases in RNA and DNA are identical (adenine, cytosine, and guanine). Thymine is found in DNA, while uracil is found in RNA.

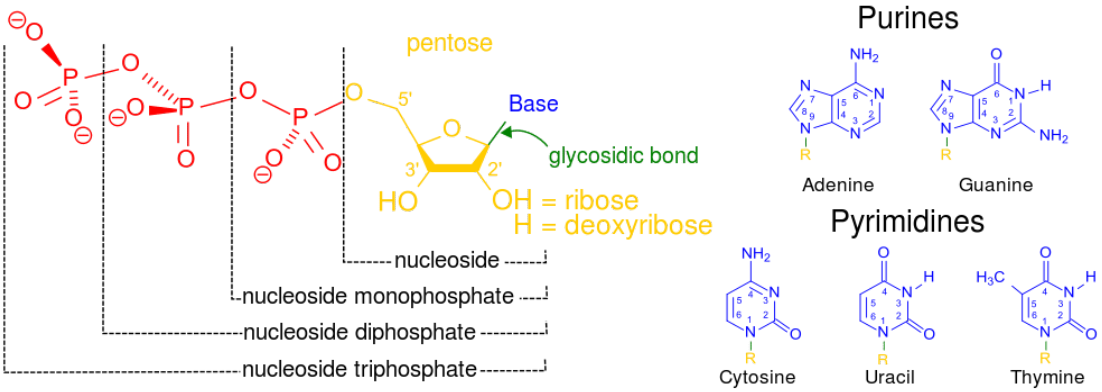


Figure 8.11.2: Nucleotides.

Summary

- A nucleic acid is a large biopolymer consisting of many nucleotides.
- The two primary nucleic acids which are found in cells are deoxyribonucleic acid (DNA) and ribonucleic acid (RNA).
- A nucleotide is a molecule that contains a five-carbon sugar, a phosphate group, and a nitrogenous base.

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8.12: DNA and RNA

Linus Pauling was one of the greatest scientists of the twentieth century. Pauling was a two-time Nobel Prize winner (in chemistry in 1954, and the peace prize in 1962). However, he didn't always come in first. In the 1950s, there was a great deal of interest in the structure of DNA. Pauling spent some time on this puzzle, although he was primarily interested in proteins. He proposed a DNA structure where the bases were on the outside and the phosphate groups were on the inside. This idea turned out to be incorrect, but it certainly did not take away from his outstanding scientific reputation.

DNA and RNA

The three parts of a DNA nucleotide are assembled as shown in the figure below.

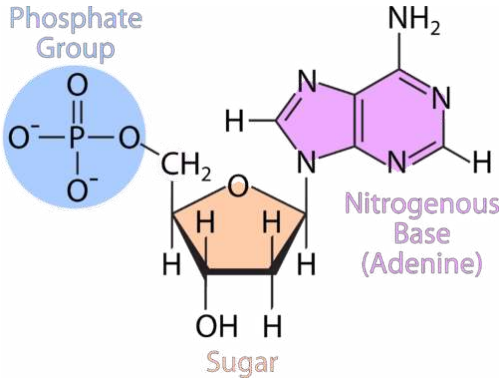


Figure 8.12.1: Nucleotides are composed of a phosphate group, a sugar, and one of five different nitrogenous bases.

Every DNA and RNA polymer consists of multiple nucleotides strung together into extremely long chains. The only variation in each nucleotide is the identity of the nitrogenous base. The figure above shows one example of a nitrogenous base, called adenine. There are only five different nitrogenous bases found in all nucleic acids. The four bases of DNA are adenine, thymine, cytosine, and guanine, abbreviated A, T, C, and G respectively. In RNA, the base thymine is not found and is instead replaced by a different base called uracil, abbreviated U. The other three bases are present in both DNA and RNA.

The specific structure of DNA proved elusive to scientists for many years. In 1953, James Watson and Francis Crick proposed that the structure of DNA consists of two side-by-side polynucleotide chains wrapped into the shape of a **double helix**. One aspect of this structure is that each nitrogenous base on one of the DNA strands must be paired up with another base on the opposite strand. The figure below illustrates the base pairing. Each adenine base is always paired with a thymine, while each cytosine is paired with a guanine. The bases fit together perfectly from one strand to the other and are also held together by hydrogen bonds. The A-T pairing contains two hydrogen bonds, while the C-G pairing contains three hydrogen bonds. The ends of each strand are labeled either with 3' or 5', based on a numbering of the deoxyribose sugar ring.

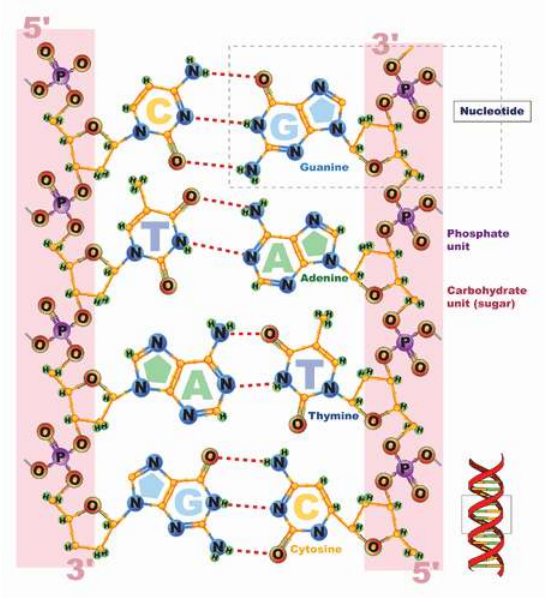


Figure 8.12.2: Base pairing in DNA.

The double helical structure of DNA is shown in the figure below.

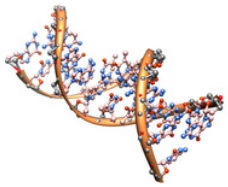


Figure 8.12.3: The DNA double helix.

Summary

- Every DNA and RNA polymer consists of multiple nucleotides strung together into extremely long chains.
- The only variation in each nucleotide is the identity of the nitrogenous base.
- The four bases of DNA are adenine, thymine, cytosine, and guanine, abbreviated A, T, C, and G respectively. In RNA, the base thymine is not found and is instead replaced by a different base called uracil, abbreviated U; the other three bases are present in both DNA and RNA.
- James Watson and Francis Crick proposed that the structure of DNA consists of two side-by-side polynucleotide chains wrapped into the shape of a double helix.

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8.13: Genetic Code

The Human Genome Project started in 1990 with the lofty goal of sequencing the complete set of human DNA. This project was completed in April 2003, ahead of schedule and under the budget set for it (a rare occurrence for a government project). With this knowledge, we can now identify genetic disorders quickly and personalize treatment for many diseases. However, much work still remains to fully understand the connections between specific DNA sequences and specific diseases.

The Genetic Code

Each particular organism contains many protein molecules that are specific to that organism. The particular base sequence of DNA is responsible for the production of all of the different proteins that are present in each and every living thing that has ever inhabited the Earth. How does that work? Cells use the unique sequence of DNA bases to decide which proteins to synthesize. A **gene** is a segment of DNA that carries a code for making a specific polypeptide chain. The cell essentially decodes the DNA in order to make whatever peptides and proteins are needed by that organism.

The **genetic code** works as a series of three-letter codes. Each sequence of three letters, called a triplet, corresponds to one of the twenty common amino acids. The triplets are read by the cell, one after the other, in the process of protein synthesis. The table below shows all of the possible triplets and the amino acids that result from each three-letter code.

Table 8.13.1: DNA Triplet Codes for Amino Acids

AAA	Lys	GAA	Glu	TAA	Stop	CAA	Gln
AAG	Lys	GAG	Glu	TAG	Stop	CAG	Gln
AAT	Asn	GAT	Asp	TAT	Tyr	CAT	His
AAC	Asn	GAC	Asp	TAC	Tyr	CAC	His
AGA	Arg	GGA	Gly	TGA	Stop	CGA	Arg
AGG	Arg	GGG	Gly	TGG	Trp	CGG	Arg
AGT	Ser	GGT	Gly	TGT	Cys	CGT	Arg
AGC	Ser	GGC	Gly	TGC	Cys	CGC	Arg
ATA	Ile	GTA	Val	TTA	Leu	CTA	Leu
ATG	Met	GTG	Val	TTG	Leu	CTG	Leu
ATT	Ile	GTT	Val	TTT	Phe	CTT	Leu
ATC	Ile	GTC	Val	TTC	Phe	CTC	Leu
ACA	Thr	GCA	Ala	TCA	Ser	CCA	Pro
ACG	Thr	GCG	Ala	TCG	Ser	CCG	Pro
ACT	Thr	GCT	Ala	TCT	Ser	CCT	Pro
ACC	Thr	GCC	Ala	TCC	Ser	CCC	Pro

The DNA code word GCA corresponds to the amino acid arginine, while the DNA code word TCG corresponds to the amino acid serine. Most amino acids are represented by more than one possible triplet code, but each triplet code yields only one particular amino acid. Three of the DNA code words (TAA, TAG, and TGA) are stop or termination code words. The translation of a DNA base sequence begins with a start code word and runs until a stop code word is reached.

Even with only four different bases, the number of possible nucleotide sequences in a DNA chain is virtually limitless. The particular DNA sequence of an organism constitutes the genetic blueprint for that organism. This genetic blueprint is found in the nucleus of each cell of the organism, and is passed on from parents to offspring. The incredible diversity of life on Earth stems from the differences in the genetic code of every living thing.

Summary

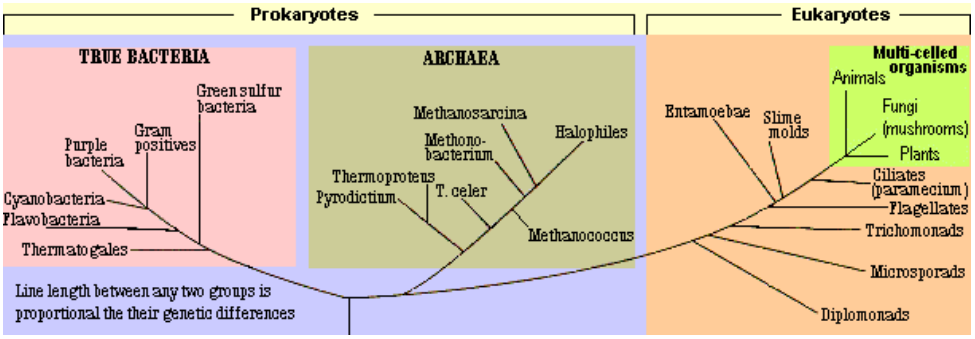
- The particular base sequence of DNA is responsible for the production of all of the different proteins that are present in each and every living thing that has ever inhabited the Earth.
- A gene is a segment of DNA that carries a code for making a specific polypeptide chain.
- The genetic code works as a series of three-letter codes.

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8.14: Chemistry and Energetics of the Life Process

The biosphere comprises the various regions near the earth's surface that contain and are dynamically affected by the metabolic activity of the approximately 1.5 million animal species and 0.5 million plant species that are presently known and are still being discovered at a rate of about 10,000 per year. The biosphere is the youngest of the dynamical systems of the earth, having had its genesis about 2 billion years ago. It is also the one that has most profoundly affected the other major environmental systems, particularly the atmosphere and the hydrosphere.



"The tree of life"

About a third of the chemical elements cycle through living organisms, which are responsible for massive deposits of silicon, iron, manganese, sulfur, and carbon. Large quantities of methane and nitrous oxide are introduced into the atmosphere by bacterial action, and plants alone inject about 400,000 tons of volatile substances (including some metals) into the atmosphere annually.

> It has been suggested that biological activity might be responsible for the deficiency of hydrogen on Earth, compared to its very high relative abundance in the solar system as a whole. Bacteria capable of reducing hydrogen compounds into H_2 transform this element into a form in which it can escape from the earth; such bacteria may have been especially active in the reducing atmosphere of the early planet.
>
> A second mechamism might be the microbial production of methane, which presently injects about 10^9 T of CH_4 into the atmosphere each year. Some of this reaches the stratosphere, where it is oxidized to CO_2 and H_2O. The water vapor is photolyzed to H_2, which escapes into space. This may be the major mechanism by which water vapor (and thus hydrogen) is transported to the upper atmosphere; the low temperature of the upper atmosphere causes most of the water originating at lower levels to condense before it can migrate to the top of the atmosphere.

The increase in the abundance of atmospheric oxygen from its initial value of essentially zero has without question been the most important single effect of life on earth, and the time scale of this increase parallels the development of life forms from their most primitive stages up to the appearance of the first land animals about 0.5 billion years ago.

Bioenergetics

All life processes involve the uptake and storage of energy, and its subsequent orderly release in small steps during the metabolic process. This energy is taken up in the combination of ADP with inorganic phosphate to form ATP, in which form the energy is stored and eventually delivered to sites where it can provide the free energy needed for driving non-spontaneous reactions such as protein and carbohydrate synthesis.

$ADP + PO_4^{3-} \rightarrow ATP\ \Delta G° = +30\ kJ$

The three main metabolic processes are glycolysis, respiration, and photosynthesis. The first two of these extract free energy from glucose by breaking it up into smaller, more thermodynamically stable fragments. Photosynthesis reverses this process by capturing the energy of sunlight into ATP which then drives the buildup of glucose from CO_2.

Glycolysis and fermentation.

As its name implies, this most primitive (and least efficient) of all metabolic processes is based on the breakdown of a sugar into fragments having a smaller total free energy. Thus the 6-carbon sugar glucose can be broken down into two 3-carbon lactic acid units, or into three 2-carbon ethanol units.

$C_6H_{12}O_6 \rightarrow 2\ CH_3CHOHCOOH\ \Delta G° = -197$ kJ

In this process, two molecules of ATP are produced, thus capturing 61 kJ of free energy. Since the standard free energy of glucose (with respect to its elements) is –2870 kJ, this represents an overall efficiency of about 2 percent.

The net reaction of glycolysis is essentially a rearrangement of the atoms initially present in the energy source. This is a form of fermentation, which is defined as the enzymatic breakdown of organic molecules in which other organic compounds serve as electron acceptors. Since there is no need for an external oxidizing or reducing agent, there is no change in the oxidation state of the environment.

Respiration

When the enzymatic degradation of organic molecules is accompanied by transfer of electrons to an external (and usually better) electron acceptor, the process is known as respiration. The overall reaction of respiration is the oxidation of glucose to carbon dioxide:

$C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O\ \Delta G° = -2380$ kJ

In this process, 36 molecules of ADP are converted into ATP, thus capturing 1100 kJ of free energy: an efficiency of 38 percent.

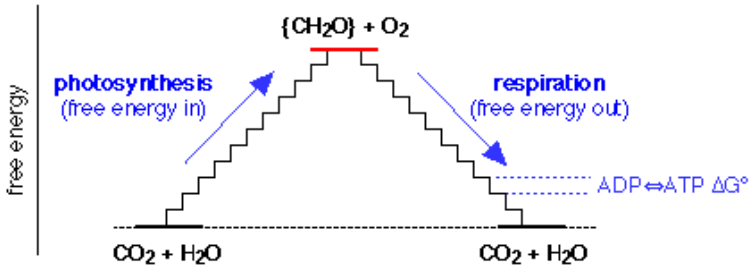
The oxidizing agent (electron sink) need not be oxygen; some bacteria reduce nitrates to NO or to N_2, and sulfates or sulfur to H_2S. These metabolic products can have far-reaching localized environmental effects, particularly if hydrogen ions are involved. Falling down the respiratory ladder presents a succinct picture of oxidation-reduction and the role of non-O_2 electron sinks in biological energy capture.

Photosynthesis

The energy of sunlight is trapped in the form of an intermediate which is able to deliver electrons to successively lower free-energy levels through the mediation of various molecules (mainly cytochromes) comprising an electron-transport chain. The free energy thus gained is utilized in part to reduce CO_2 to glucose, which is then available to supply metabolic energy by glycolysis or respiration. In green plants and eukaryotic algae, the source of hydrogen is water, the net reaction being

$6\ CO_2 + 6\ H_2O \rightarrow C_6H_{12}O_6 + 6\ O_2\ \Delta G° = +2830$ kJ

For every CO_2 molecule fixed in this way, 469 kJ of free energy must be supplied. Red light of 680 nm wavelength has an energy of 168 kJ/mol; this implies that about three photons must be absorbed for every carbon atom taken up, but experiment indicates that about ten seem to be required.



The photosynthetic - respiration cycle.

Photosynthesis utilizes the energy of red light to add hydrogen (from H_2O) and electrons (from the O in H_2O) to CO_2, reducing it to **carbohydrate**. **Respiration** is the reverse of this process; electrons are removed from the carbohydrate (food is "burned") in small steps, each one releasing a small amount of energy. Some of this energy is liberated as heat, but part of it is used to add a phosphate group to ADP, converting it into ATP. **ATP** (adenosine triphosphate) is to an organism's energy needs as money is to our material needs; it circulates to wherever it is required in order to bring about energy-requiring reactions or to make muscle cells contract. Each increment of energy given up by ATP converts it back to ADP and phosphate, ready to repeat the cycle.

Green plants are able to operate in both modes during the daylight hours, reverting to respiration-only at night. **Animals** carry out only the right side of the cycle and thus require as source of carbohydrate ("**food**") either directly (by eating plants), or indirectly by eating other animals that eat plants.

There are many kinds of photosynthetic bacteria, but with one exception (cyanobacteria) they are incapable of using water as a source of hydrogen for reducing carbon dioxide. Instead, they consume hydrogen sulfide or other reduced sulfur compounds,

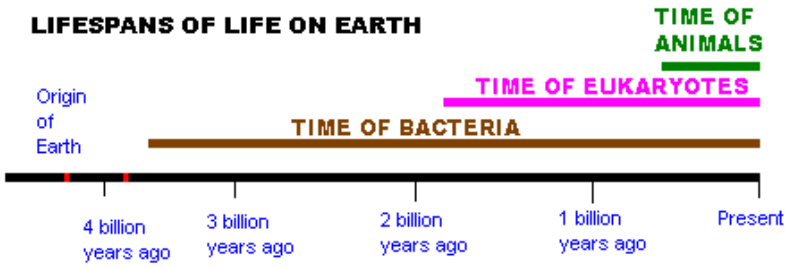
organic molecules, or elemental hydrogen itself, excreting the reducing agent in an oxidized state. Green plants, cyanobacteria, green filamentous bacteria and the purple nonsulfur bacteria utilize glucose by respiration during periods of darkness, while the green sulfur bacteria and the purple sulfur bacteria are strictly anaerobic.

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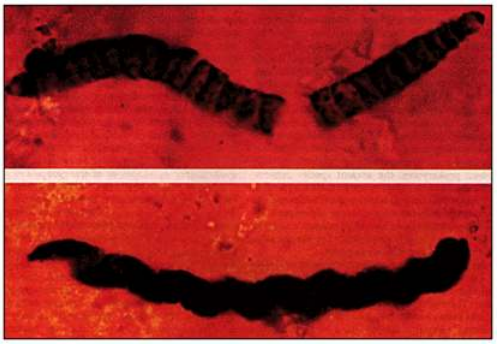
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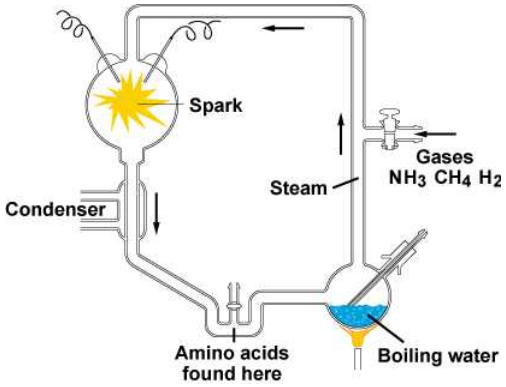
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These bacterial forms were likely the dominant form of life for several hundred million years. Eventually, due perhaps to the failing supply of H_2S, plants capable of mediating the photochemical extraction of hydrogen from water developed. This represented a large step in biochemical complexity; it takes 10 times as much energy to abstract hydrogen from water than from hydrogen sulfide, but the supply is virtually limitless.

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Superimposed on this, however, is an even more fundamental division between the procaryotes and eucaryotes.

Procaryotes

In this group are primitive organisms whose single cells contain no nucleus; the gene-bearing structure is a single long DNA chain that is folded irregularly throughout the cell. Procaryotic cells usually reproduce by budding or division; where sexual reproduction does occur, there is a net transfer of some genetic material from one cell to another, but there is never an equal contribution from both parents.

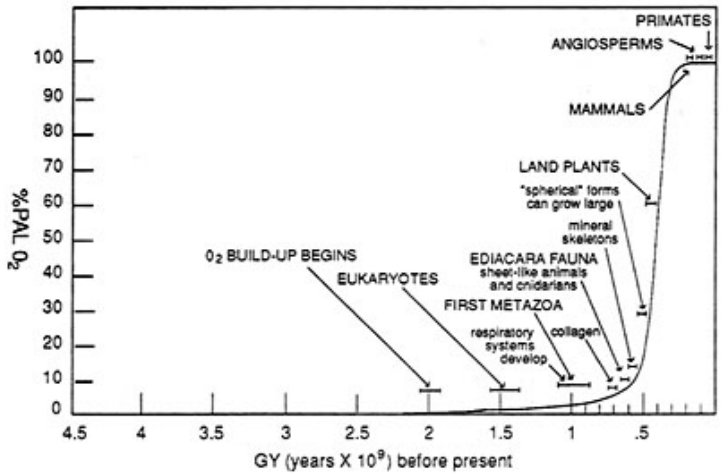
In spite of their primitive nature, procaryotes constitute the majority of organisms in the biosphere. The division between bacteria and archaea within the procaryotic group is a fairly recent one. Archaea are now believed to be the most primitive of all organisms, and include the so-called extremophiles that occupy environmental niches in which life was at one time thought to be impossible; they have been found in sedimentary rocks, hot springs, and highly saline environments.

Eucaryotes.

All other organisms— seaweeds (algae), protozoa, molds, fungi, animals and plants, are composed of eucaryotic cells. These all have a membrane-bound nucleus, and with a few exceptions they all reproduce by mitosis, in which the chromosomes split longitudinally and move toward opposite poles. Other organelles unique to eucaryotes are mitochondria, ribosomes, and structural elements such as microtubules.

Oxygen and biogeochemical evolution

Oxygen is poisonous to all forms of life in the absence of enzymes that can reduce the highly reactive byproducts of oxidation and oxidative metabolism (peroxides, superoxides, etc.). All organic compounds are thermodynamically unstable in the presence of oxygen; carbon-carbon double bonds in lipids are subject to rapid attack. Prebiotic chemical evolution leading to the development of biopolymers was possible only under the reducing, anoxic conditions of the primitive atmosphere.



The rise of atmospheric oxygen. *Once organisms existed that could use water as a hydrogen source for the reduction of carbon dioxide, O_2began to be introduced into the atmosphere. The widespread occurrence of ferrous compounds in surface rocks and sediments provided a sink for this oxygen that probably did not become saturated until about 2 billion years ago, when the atmospheric oxygen abundance first rose above about 1 percent.Illustration from All about entropy, the laws of thermdynamics, and order from disorder. There is lots of good stuff here!*

As the oxygen concentration began to rise, organisms in contact with the atmosphere had to develop protective mechanisms in order to survive. One indication of such adaptation is the discovery of fossil microbes whose cell walls are unusually thick. A more useful kind of adaptation was the synthesis of compounds that would detoxify oxygen by reacting rapidly either with O_2 itself or with peroxides and other active species derived from it. Isoprenoids (the precursors of steroids) and porphyrins are examples of two general classes of compounds that are found in nearly all organisms, and which may have originated in this way. Later, highly efficient oxygen mediating enzymes such as peroxidase and catalase developed. The widespread phenomenon of bioluminescence may be the result of a very early adaptation to oxygen. The compound luciferin is a highly efficient oxygen detoxifier, which also happens to be able to emit light under certain conditions. Bioluminescence probably developed as a by-product in early procaryotic organisms, but was gradually lost as more efficient detoxifying mechanisms became available.

Development of the eucaryotes

In spite of the deleterious effects of oxygen on cell biomolecules, O_2 is nevertheless an excellent electron sink, capable of releasing large quantities of energy through the oxidation of glucose. This energy can be efficiently captured through oxidative phosphorylation, the key process in respiration.

A cell that utilizes oxygen must have a structural organization that isolates the oxygen-consuming respiratory centers from the other parts of the cell that would be poisoned by oxygen or its reaction products. Some procaryotic organisms have developed in this way; a number of cyanobacteria and other species are facultative anaerobes which can survive both in the presence and absence of oxygen.

It is in the eucaryotic cell, however, that this organization is fully elaborated; here, respiration occurs in membrane-bound organelles called mitochondria. With only a few exceptions, all eucaryotic organisms are obligate aerobes; they can rarely survive and can never reproduce in the absence of oxygen. Mitotic cell division depends on the contractile properties of the protein actomyosin, which only forms when oxygen is present.

The development of the eucaryotic cell about 1.4 billion years ago is regarded as the most significant event in the evolution of the earth and of the biosphere since the appearance of photosynthesis and the origin of life itself. How did it come about? The present belief, supported by an increasing amount of evidence, suggests that it began when one species of organism engulfed another. The ingested organism possessed biochemical machinery not present in the host, but which was retained in such a way that it conferred a selective evolutionary advantage on the host. Eventually the two organisms became able to reproduce as one, and so effectively became a single organism. This process is known as *endosymbiosis*

According to this view, mitochondria represent the remains of a primitive oxygen-tolerant organism that was incorporated into one that could produce the glucose fuel for the oxygen to burn. Chloroplasts were once free-living photosynthesizing procaryotes similar to present-day cyanobacteria. It is assumed that some of these began parasitising respiratory organisms, conferring upon them the ability to synthesize their carbohydrate food during daylight. The immense selective advantage of this arrangement is evident in the extent of the plant kingdom.

Consequences of the oxygen increase

It is interesting that an atmospheric oxygen concentration of about 1 percent, known as the *Pasteur point* is both the maximum that obligate anaerobes can tolerate, and the minimum required for oxidative phosphorylation.

> *Louis Pasteur discovered that some bacteria are anaerobic and unable to tolerate oxygen above 1% concentration.*

As was mentioned previously, the oxygen produced by the first photosynthetic organisms was taken up by ferrous iron in sediments and surface minerals. The widespread deposits known as banded iron formations consist of alternating layers of Fe(III)-containing oxides (hematite and magnetite) that were laid down between 1 and 2 billion years ago; the layering may reflect changing climatic or other environmental conditions that brought about a cycling of the organism population.

During the buildup of oxygen, an equivalent amount of carbon had to be deposited in sediments in order to avoid the thermodynamically spontaneous back reaction which would consume the O_2through oxidation of the organic matter. Thus the present levels of atmospheric oxygen are due to a time lag in the geochemical cycling of photosynthetic products.

As the oxygen concentration increased, evolution seems to have speeded up; this may reflect both the increased metabolic efficiency and the greater biochemical complexity of the eucaryotic cell. The oldest metazoan (multiple-celled) fossils are coelenterates that appeared about 700 million years ago. Modern representatives of this group such as marine worms and jellyfish can tolerate oxygen concentrations as low as 7%, thus placing a lower boundary on the atmospheric oxygen content of that era. The oldest fossil organisms believed to have possessed gills, which function only above 10% oxygen concentration, appeared somewhat later.Carbon dioxide decreased as oxygen increased, as indicated by the prevalence of dolomite over limestone in early marine sediments.

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CHAPTER OVERVIEW

9: Biogeochemical Cycles

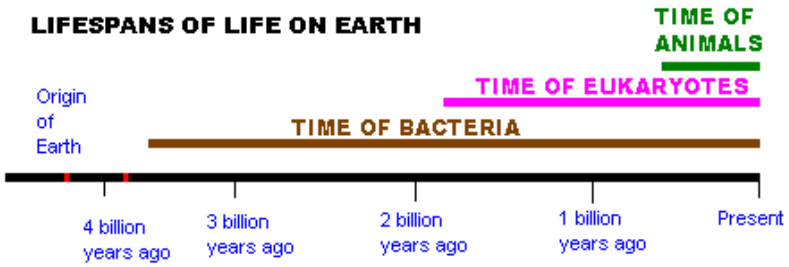
9.1: Biogeochemical Evolution
9.2: Water, Water Everywhere...
9.3: Chemical budgets of oceanic elements
9.4: Chemistry and geochemistry of the oceans
9.5: The hydrosphere and the oceans

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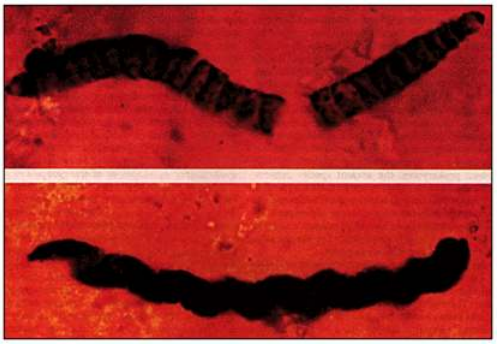
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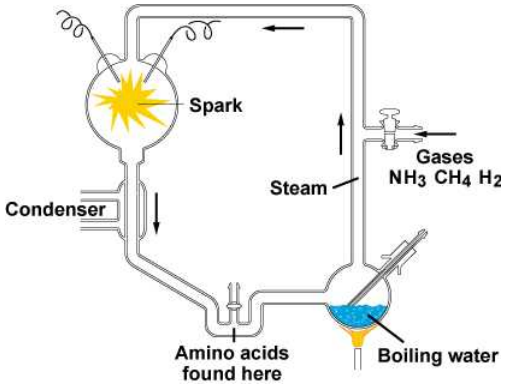
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In this group are primitive organisms whose single cells contain no nucleus; the gene-bearing structure is a single long DNA chain that is folded irregularly throughout the cell. Procaryotic cells usually reproduce by budding or division; where sexual reproduction does occur, there is a net transfer of some genetic material from one cell to another, but there is never an equal contribution from both parents.

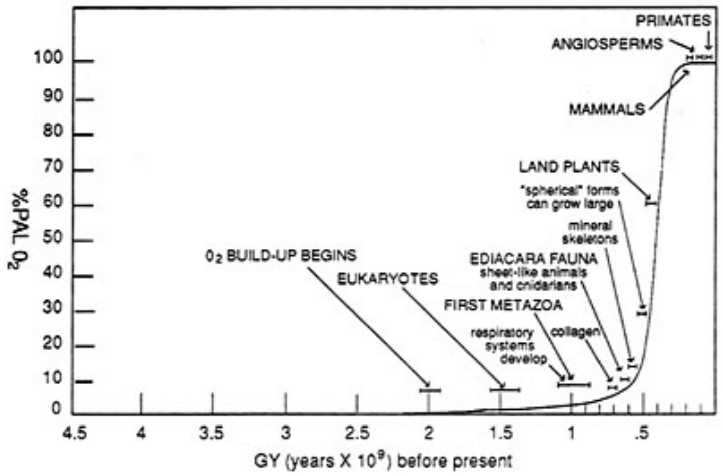
In spite of their primitive nature, procaryotes constitute the majority of organisms in the biosphere. The division between bacteria and archaea within the procaryotic group is a fairly recent one. Archaea are now believed to be the most primitive of all organisms, and include the so-called extremophiles that occupy environmental niches in which life was at one time thought to be impossible; they have been found in sedimentary rocks, hot springs, and highly saline environments.

Eucaryotes.

All other organisms— seaweeds (algae), protozoa, molds, fungi, animals and plants, are composed of eucaryotic cells. These all have a membrane-bound nucleus, and with a few exceptions they all reproduce by mitosis, in which the chromosomes split longitudinally and move toward opposite poles. Other organelles unique to eucaryotes are mitochondria, ribosomes, and structural elements such as microtubules.

Oxygen and biogeochemical evolution

Oxygen is poisonous to all forms of life in the absence of enzymes that can reduce the highly reactive byproducts of oxidation and oxidative metabolism (peroxides, superoxides, etc.). All organic compounds are thermodynamically unstable in the presence of oxygen; carbon-carbon double bonds in lipids are subject to rapid attack. Prebiotic chemical evolution leading to the development of biopolymers was possible only under the reducing, anoxic conditions of the primitive atmosphere.



The rise of atmospheric oxygen. *Once organisms existed that could use water as a hydrogen source for the reduction of carbon dioxide, O_2began to be introduced into the atmosphere. The widespread occurrence of ferrous compounds in surface rocks and sediments provided a sink for this oxygen that probably did not become saturated until about 2 billion years ago, when the atmospheric oxygen abundance first rose above about 1 percent.Illustration from All about entropy, the laws of thermdynamics, and order from disorder. There is lots of good stuff here!*

As the oxygen concentration began to rise, organisms in contact with the atmosphere had to develop protective mechanisms in order to survive. One indication of such adaptation is the discovery of fossil microbes whose cell walls are unusually thick. A more useful kind of adaptation was the synthesis of compounds that would detoxify oxygen by reacting rapidly either with O_2 itself or with peroxides and other active species derived from it. Isoprenoids (the precursors of steroids) and porphyrins are examples of two general classes of compounds that are found in nearly all organisms, and which may have originated in this way. Later, highly efficient oxygen mediating enzymes such as peroxidase and catalase developed. The widespread phenomenon of bioluminescence may be the result of a very early adaptation to oxygen. The compound luciferin is a highly efficient oxygen detoxifier, which also happens to be able to emit light under certain conditions. Bioluminescence probably developed as a by-product in early procaryotic organisms, but was gradually lost as more efficient detoxifying mechanisms became available.

Development of the eucaryotes

In spite of the deleterious effects of oxygen on cell biomolecules, O_2 is nevertheless an excellent electron sink, capable of releasing large quantities of energy through the oxidation of glucose. This energy can be efficiently captured through oxidative phosphorylation, the key process in respiration.

A cell that utilizes oxygen must have a structural organization that isolates the oxygen-consuming respiratory centers from the other parts of the cell that would be poisoned by oxygen or its reaction products. Some procaryotic organisms have developed in this way; a number of cyanobacteria and other species are facultative anaerobes which can survive both in the presence and absence of oxygen.

It is in the eucaryotic cell, however, that this organization is fully elaborated; here, respiration occurs in membrane-bound organelles called mitochondria. With only a few exceptions, all eucaryotic organisms are obligate aerobes; they can rarely survive and can never reproduce in the absence of oxygen. Mitotic cell division depends on the contractile properties of the protein actomyosin, which only forms when oxygen is present.

The development of the eucaryotic cell about 1.4 billion years ago is regarded as the most significant event in the evolution of the earth and of the biosphere since the appearance of photosynthesis and the origin of life itself. How did it come about? The present belief, supported by an increasing amount of evidence, suggests that it began when one species of organism engulfed another. The ingested organism possessed biochemical machinery not present in the host, but which was retained in such a way that it conferred a selective evolutionary advantage on the host. Eventually the two organisms became able to reproduce as one, and so effectively became a single organism. This process is known as *endosymbiosis*

According to this view, mitochondria represent the remains of a primitive oxygen-tolerant organism that was incorporated into one that could produce the glucose fuel for the oxygen to burn. Chloroplasts were once free-living photosynthesizing procaryotes similar to present-day cyanobacteria. It is assumed that some of these began parasitising respiratory organisms, conferring upon them the ability to synthesize their carbohydrate food during daylight. The immense selective advantage of this arrangement is evident in the extent of the plant kingdom.

Consequences of the oxygen increase

It is interesting that an atmospheric oxygen concentration of about 1 percent, known as the *Pasteur point* is both the maximum that obligate anaerobes can tolerate, and the minimum required for oxidative phosphorylation.

> *Louis Pasteur discovered that some bacteria are anaerobic and unable to tolerate oxygen above 1% concentration.*

As was mentioned previously, the oxygen produced by the first photosynthetic organisms was taken up by ferrous iron in sediments and surface minerals. The widespread deposits known as banded iron formations consist of alternating layers of Fe(III)-containing oxides (hematite and magnetite) that were laid down between 1 and 2 billion years ago; the layering may reflect changing climatic or other environmental conditions that brought about a cycling of the organism population.

During the buildup of oxygen, an equivalent amount of carbon had to be deposited in sediments in order to avoid the thermodynamically spontaneous back reaction which would consume the O_2through oxidation of the organic matter. Thus the present levels of atmospheric oxygen are due to a time lag in the geochemical cycling of photosynthetic products.

As the oxygen concentration increased, evolution seems to have speeded up; this may reflect both the increased metabolic efficiency and the greater biochemical complexity of the eucaryotic cell. The oldest metazoan (multiple-celled) fossils are coelenterates that appeared about 700 million years ago. Modern representatives of this group such as marine worms and jellyfish can tolerate oxygen concentrations as low as 7%, thus placing a lower boundary on the atmospheric oxygen content of that era. The oldest fossil organisms believed to have possessed gills, which function only above 10% oxygen concentration, appeared somewhat later.Carbon dioxide decreased as oxygen increased, as indicated by the prevalence of dolomite over limestone in early marine sediments.

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9.2: Water, Water Everywhere...

Water is the most abundant substance at the earth's surface. Almost all of it is in the oceans, which cover 70% of the surface area of the earth. However, the amounts of water present in the atmosphere and on land (as surface runoff, lakes and streams) is great enough to make it a significant agent in transporting substances between the lithosphere and the oceans. Water interacts with both the atmosphere and the lithosphere, acquiring solutes from each, and thus provides the major chemical link between these two realms. The various transformations undergone by water through the different stages of the hydrologic cycle act to transport both dissolved and particulate substances between different geographic locations.

Reservoir	Volume / 10^6, km^3	Percent of total
Oceans	1370	97.25
Ice caps and glaciers	39	2.05
Deep groundwater	5.3	0.38
Shallow groundwater	4.3	0.30
Lakes	0.125	0.01
Soil moisture	0.065	0.005
Atmosphere	0.013	0.001
Rivers	0.0017	0.0001
Biosphere	0.0006	0.00004
Total	**1408.7**	**100**

Composition of Seawater

The composition of the ocean has attracted the attention of some of the more famous names in science, including Robert Boyle, Antoine Lavoisier and Edmund Halley. Their early investigations tended to be difficult to reproduce, owing to the different conditions under which they crystallized the various salts. As many as 54 salts, double salts and hydrated salts can be obtained by evaporating seawater to dryness. At least 73 elements are now known to be present in seawater.

Table 1: Major ions of seawater: These values, expressed in parts per thousand, are for seawater of 35% salinity.

cations	g/kg	anions	g/kg
Na^+	10.77	Cl^-	19.354
Mg^{2+}	1.29	SO_4^{2-}	2.712
Ca^{2+}	0.412	Br^-	0.087
K^+	0.399		
Sr^{2+}	0.0079		
Al^{3+}	0.005		

The best way of characterizing seawater is in terms of its ionic content, shown above. The remarkable thing about seawater is the constancy of its relative ionic composition. The overall salt content, known as the salinity (grams of salts contained in 1 kg of seawater), varies slightly within the range of 32-37.5%, corresponding to a solution of about 0.7% salt content. The ratios of the concentrations of the different ions, however, are quite constant, so that a measurement of Cl^- concentration is sufficient to determine the overall composition and total salinity. Although most elements are found in seawater only at trace levels, marine organisms may selectively absorb them and make them more detectable. Iodine, for example, was discovered in marine algae (seaweeds) 14 years before it was found in seawater. Other elements that were not detected in seawater until after they were found

in marine organisms include barium, cobalt, copper, lead, nickel, silver and zinc. Si^{32}, presumably deriving from cosmic ray bombardment of Ar, has been discovered in marine sponges.

pH balance. Reflecting this constant ionic composition is the pH, which is usually maintained in the narrow range of 7.8-8.2, compared with 1.5 to 11 for fresh water. The major buffering action derives from the carbonate system, although ion exchange between Na+ in the water and H^+ in clay sediments has recently been recognized to be a significant factor.

Conservative and non-conservative substances

The major ionic constituents whose concentrations can be determined from the salinity are known as conservative substances. Their constant relative concentrations are due to the large amounts of these species in the oceans in comparison to their small inputs from river flow. This is another way of saying that their residence times are very large.

Table 2: Replacement time with respect to river addition for some components of seawater. Concentrations in micromols/L

component	concentration in river water	concentration in seawater	residence time, 10^6 y
Cl^-	250	558,000	87
Na^+	315	479,000	55
Mg^{2+}	150	54,300	13
SO_4^{2-}	120	28,900	8.7
Ca^{2+}	367	10,500	1
K^+	36	10,400	10
HCO_3^-	870	2000	0.083
H_4SiO_4	170	100	0.021
NO_3^-	10	20	0.072
$H_2PO_4^-$	0.7	1	0.080

A number of other species, mostly connected with biological activity, are subject to wide variations in concentration. These include the nutrients NO_3^-, NO_2^-, NH_4^+, and HPO_4^{2-}, which may become depleted near the surface in regions of warmth and light. As was explained in the preceding subsection on coastal upwelling, offshore prevailing winds tend to drive Western coastal surface waters out to sea, causing deeper and more nutrient-rich water to be drawn to the surface. This upwelled water can support a large population of phytoplankton and thus of zooplankton and fish. The best-known example of this is the anchovy fishery off the coast of Peru, but the phenomenon occurs to some extent on the West coasts of most continents, including our own.

Other non-conservative components include Ca^{2+} and SiO_4^{2-}. These ions are incorporated into the solid parts of marine organisms, which sink to greater depths after the organisms die. The silica gradually dissolves, since the water is everywhere undersaturated in this substance. Calcium carbonate dissolves at intermediate depths, but may reprecipitate in deep waters owing to the higher pressure. Thus the concentrations of Ca and of SiO_4^{2-} tend to vary with depth. The gases O_2 and CO_2, being intimately involved with biological activity, are also non-conservative, as are N_2O and CO.

Organic matter

Most of the organic carbon in seawater is present as dissolved material, with only about 1-2% in particulates. The total organic carbon content ranges between 0.5 mg/L in deep water to 1.5 mg/L near the surface. There is still considerable disagreement about the composition of the dissolved organic matter; much of it appears to be of high molecular weight, and may be polymeric. Substances qualitatively similar to the humic acids found in soils can be isolated. The greenish color that is often associated with coastal waters is due to a mixture of fluorescent, high molecular weight substances of undetermined composition known as *"Gelbstoffe"*. It is likely that the significance of the organic fraction of seawater may be much greater than its low abundance would suggest. For one thing, many of these substances are lipid-like and tend to adsorb onto surfaces. It has been shown that any particle entering the ocean is quickly coated with an organic surface film that may influence the rate and extent of its dissolution or decomposition. Certain inorganic ions may be strongly complexed by humic-like substances. The surface of the ocean is mostly

covered with an organic film, only a few molecular layers thick. This is believed to consist of hydrocarbons, lipids, and the like, but glycoproteins and proteoglycans have been reported. If this film is carefully removed from a container of seawater, it will quickly be reconstituted. How significant this film is in its effects on gas exchange with the atmosphere is not known.

Regulation of ocean composition

The salinity of the ocean appears to have been about the same for at least the last 200 million years. There have been changes in the relative amounts of some species, however; the ratio of Na/K has increased from about 1:1 in ancient ocean sediments to its present value of 28:1. Incorporation of calcium into sediments by the action of marine organisms has depleted the Ca/Mg ratio from 1:1 to 1:3.

Table: Mass balance of P, C, and Ca for the oceans

element	input to ocean	dissolved in seawater	in dead organisms	loss to sediments	residence time, y
phosphorus	1 (erosion)	1	1	1 (organic)	10,000
carbon	100 as CO_2 500 as carbonate	1000	125	100 (organic) 600 (carbonate)	165,000
calcium	500 (erosion)	5000	25	500 (as $CaCO_3$)	10^6

If the composition of the ocean has remained relatively unchanged with time, the continual addition of new mineral substances by the rivers and other sources must be exactly balanced by their removal as sediment, possibly passing through one or more biological systems in the process.

Where does the Salt Come From?

In 1715 Edmund Halley suggested that the age of the ocean (and thus presumably of the world) might be estimated from the rate of salt transport by rivers. When this measurement was actually carried out in 1899, it gave an age of only 90 million years.

> *This is somewhat better than the calculation made in 1654 by James Ussher, the Anglican Archbishop of Armagh, Ireland, based on his interpretation of the Biblical book of Genesis, that the world was created at 9 A.M. on October 23, 4004 BC, but it is still far too recent, being about when the dinosaurs became extinct. What Halley actually described was the residence time, which is about right for Na but much to long for some of the minor elements of seawater.*

The commonly stated view that the salt content of the oceans derives from surface runoff that contains the products of weathering and soil leaching is not consistent with the known compositions of the major river waters (See Table). The halide ions are particularly over-represented in seawater, compared to fresh water. These were once referred to as “excess volatiles”, and were attributed to volcanic emissions. With the discovery of plate tectonics, it became apparent that the locations of seafloor spreading at which fresh basalt flows up into the ocean from the mantle are also sources of mineral-laden water. Some of this may be seawater that has cycled through a hot porous region and has been able to dissolve some of the mineral material owing to the high temperature. Much of the water, however, is “juvenile” water that was previously incorporated into the mantle material and has never before been in the liquid phase. The substances introduced by this means (and by volcanic activity) are just the elements that are “missing” from river waters. Estimates of what fraction of the total volume of the oceans is due to juvenile water (most of it added in the early stages of mantle differentiation that began a billion years ago) range from 30 to 90%.

Geochemical processes involving the oceans

The oceans can be regarded as a product of a giant acid-base titration in which the carbonic acid present in rain reacts with the basic materials of the lithosphere. The juvenile water introduced at locations of ocean-floor spreading is also acidic, and is partly neutralized by the basic components of the basalt with which it reacts. Surface rocks mostly contain aluminum, silicon and oxygen combined with alkali and alkaline-earth metals, mainly potassium, sodium and calcium. The CO_2 and volcanic gases in rainwater react with this material to form a solution of the metal ion and HCO_3^-, in which is suspended some hydrated SiO^2. The solid material left behind is a clay such as kaolinite, $Al_2Si_2O_5(OH)_4$. This first forms as a friable coating on the surface of the weathered

rock; later it becomes a soil material, then an alluvial deposit, and finally it may reach the sea as a suspended sediment. Here it may undergo a number of poorly-understood transformations to other clay sediments such as illites. Sea floor spreading eventually transports these sediments to a subduction region under a continental block, where the high temperatures and pressures permit reactions that transform it into hard rock such as granite, thus completing the geochemical cycle.

Deep-sea hydrothermal vents are now recognized to be another significant route for both the addition and removal of ionic substances from seawater.

Distribution and cycling of elements in the oceans

Although the relative concentrations of most of the elements in seawater are constant throughout the oceans, there are certain elements that tend to have highly uneven distributions vertically, and to a lesser extent horizontally. Neglecting the highly localized effects of undersea springs and volcanic vents, these variations are direct results of the removal of these elements from seawater by organisms; if the sea were sterile, its chemical composition would be almost uniform.

Plant life can exist only in the upper part of the ocean where there is sufficient light available to drive photosynthesis. These plants, together with the animals that consume them, extract nutrients from the water, reducing the concentrations of certain elements in the upper part of the sea. When these organisms die, they fall toward the lower depths of the ocean as particulate material. On the way down, some of the softer particles, deriving from tissue, may be consumed by other animals and recycled. Eventually, however, the nutrient elements that were incorporated into organisms in the upper part of the ocean will end up in the colder, dark, and essentially lifeless lower part.

Mixing between the upper and lower reservoirs of the ocean is quite slow, owing to the higher density of the colder water; the average residence time of a water molecule in the lower reservoir is about 1600 years. Since the volume of the upper reservoir is only about 1/20 of that of the lower, a water molecule stays in the upper reservoir for only about 80 years.

Except for dissolved oxygen, all elements required by living organisms are depleted in the upper part of the ocean with respect to the lower part. In the case of the major nutrients P, N and Si, the degree of depletion is sufficiently complete (around 95%) to limit the growth of organisms at the surface. These three elements are said to be biolimiting. A few other biointermediate elements show partial depletion in surface waters: Ca (1%), C (15%), Ba (75%).

The organic component of plants and animals has the average composition $C_{80}N_{15}P$. It is remarkable that the ratio of N:P in seawater (both surface and deep) is also 15:1; this raises the interesting question of to what extent the ocean and life have co-evolved.

In the deep part of the ocean the elemental ratio corresponds to $C_{800}N_{15}P$, but of course with much larger absolute amounts of these elements. Eventually some of this deeper water returns to the surface where the N and P are quickly taken up by plants. But since plants can only utilize 80 out of every 800 carbon atoms, 90 percent of the carbon will remain in dissolved form, mostly as HCO_3^-.

> *To work out the balance of Ca and Si used in the hard parts of organisms, we add these elements to the average composition of the lower reservior to get $Ca_{3200}Si_{50}C_{800}N_{15}P$. Particulate carbon falls into the deep ocean in the ratio of about two atoms in organic tissue to one atom in the form of calcite. This makes the overall composition of detrital material something like $C_{120}N_{15}P$; i.e., 80 organic C's and 40 in $CaCO_3$. Accompanying these 40 calcite units will be 40 Ca atoms, but this represents a minor depletion of the 3200 Ca atoms that eventually return to the surface, so this element is only slightly depleted in the upper waters. Silicon, being far less abundant, is depleted to a much greater extent.*

The oceanic sediments

The particulate shower

A continual rain of particulate material from dead organisms falls through the ocean. This shower is comprised of three major kinds of material: calcite ($CaCO_3$), silica (SiO_2), and organic matter. The first two come from the hard parts of both plants and animals (mainly microscopic animals such as foraminifera and radiolarians). The organic matter is derived mainly from the soft tissues of

organisms, and from animal fecal material. Some of this solid material dissolves before it reaches the ocean floor, but not usually before it enters the deep ocean where it will remain for about 1600 years.

The remainder of this material settles onto the floor of the sea, where it forms one component of a layer of sediments that provide important information about the evolution of the sea and of the earth. Over a short time scale of months to years, these sediments are in quasi-equilibrium with the seawater. On a scale of millions of years, the sediments are merely way-stations in the geochemical cycling of material between the earth's surface and its interior.

The oceanic sediments have three main origins:

- **Detrital** material is derived largely from particles deposited in the ocean by rivers and also directly by the wind. These materials are mostly aluminosilicates (clays), along with some quartz. These substances accumulate on the deep ocean floor at a rate of about 0.3 g cm^{-2} per 1000 years.
- **Authigenic** materials are formed by precipitation within the ocean or by crystallization within the sediment itself. These constitute only a small fraction of the total sediment.
- **Biogenic** components consist mainly of the calcium carbonate and silica that make up the hard parts of organisms. Scavenging by other organisms is so efficient that only about 0.3 % of the total deep sea sediment consists of actual organic material.

Our main interest lies with the silica and calcium carbonate, since these substances form a crucial part of the biogeological cycle. Also, their distributions in the ocean are not uniform- a fact that must tell us something.

The skeletons of diatoms and radiolarians are the principal sources of silica sediments. Since the ocean is everywhere undersaturated with respect to silica, only the most resistant parts of these skeletons reach the bottom of the deep ocean and get incorporated into sediments. Silica sediments are less common in the Atlantic ocean, owing to the lower content of dissolved silica.

The parts of the ocean where these sediments are increasing most rapidly correspond to regions of upwelling, where deep water that is rich in dissolved silica rises to the surface where the silica is rapidly fixed by organisms. Where upwelling is absent, the growth of the organisms is limited, and little silica is precipitated. Since deep waters tend to flow from the Atlantic into the Pacific ocean where most of the upwelling occurs, Atlantic waters are depleted in silica, and silica sediments are not commonly found in this ocean.

For calcium carbonate, the situation is quite different. In the first place, surface waters are everywhere supersaturated with respect to both calcite and aragonite, the two common crystal forms of $CaCO_3$. Secondly, Ca^{2+} and HCO_3^- are never limiting factors in the growth of the coccoliths (plants) and forams (animals) that precipitate $CaCO_3$; their production depends on the availability of phosphate and nitrogen. Because these elements are efficiently recycled before they fall into the deep ocean, their supply does not depend on upwelling, and so the production of solid is more uniformly distributed over the world's oceans.

More importantly, however, the chances that a piece of carbonate skeleton will end up as sediment will be highly dependent on both the local CO_3^{2-} concentration and the depth of the ocean floor. These factors give rise to small-scale variations in the production of carbonate sediments that can be quite wide-ranging.

Ocean sediments and continental drift

New crust is being generated and moving away from the crests of the mid-ocean ridges at a rate of a few centimetres per year. Although the crests of these ridges are relatively high points, projecting to within about 3000 m of the surface, the continual injection of new material prevents sediments from accumulating in these areas. Farther from the crests, carbonate sediments do build up, eventually reaching a depth of about 500 m, but by this time the elevation has dropped off below the saturation horizon, so from this point on the carbonate sediments are overlaid by red clay.

If we drill a hole down through a part of the ocean floor that is presently below the saturation horizon, the top part of the drill core will consist of clay, followed by $CaCO_3$ at greater depths. The core may also contain regions in which silica predominates. Since silica production is very high in equatorial regions, the appearance of such a layer suggests that this particular region of the oceanic crust has moved across the equator.

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9.3: Chemical budgets of oceanic elements

To the extent that the composition of the ocean remains constant, the rate at which any one element is introduced into seawater must equal the rate of its removal. A listing of the various routes of addition and removal, together with the estimated rate of each process, constitutes the budget for a given element. If that budget is greatly out of balance and no other transport routes are apparent, then it is likely that the ocean is not in a steady state with respect to that element, at least on a short time scale. It is important to understand, however, that short-term deviations from constant composition are not necessarily inconsistent with a long-term steady state. Deviations from the latter condition are most commonly inferred from geological evidence.

The major input of elements to the oceans is river water. Groundwater seepage constitutes a very small secondary source. These were considered the only sources until the 1970's, when the existence of hydrothermal springs at sites of seafloor spreading became known. There are presently no reliable estimates of the magnitude of this source. Pollution represents an additional input, mainly dissolved in river water, but also sometimes in rain and by dry deposition.

Routes of removal are formation and burial of sediments, formation of evaporite deposits, direct input to the atmosphere by sea-salt aerosol transfer associated with bubble-breaking, and burial with sediments, either in interstitial water or adorbed onto active surfaces. Reaction with newly-formed basalt associated with undersea volcanic activity appears to be an important removal mechanism for some elements.

Table 7: Input and output rates of major elements in seawater by two routes. The units are Tg y–1. The other major routes involve interaction with the seafloor through hyrothermal vents and incorporation into sediments, but only river input and loss to the atmosphere are quantifiable with any degree of accuracy.

Species	Addition from Rivers	Loss to Atmosphere
Cl^-	308	40
Na^+	269	21
S (mostly SO_4^{2-})	143	4
Mg^{2+}	137	3
K^+	52	1
Ca^{2+}	550	0.5
HCO^{3-}	1980	
H_4SiO_4	180	

Phosphorus

The major elements undergoing steady-state dynamic change in the ocean are connected with biological processes. The key limiting element in the development of oceanic biomass is phosphorus, in the form of the phosphate ion. For terrestrial plant life, nitrogen is more commonly the limiting element, where it is taken up in the form of the nitrate ion. In the ocean, however, the ratio of the nitrate ion concentration to that of phosphorus has been found to be everywhere the same; this implies that the concentration of one controls that of the other. The source of nitrate ion is atmospheric N_2, which is freely soluble in water and is thus always present in abundance. The conversion of N_2 to NO_3^- is presumed to be biologically mediated, probably by bacteria. The constancy of the NO_3^-/P concentration ratio implies that the phosphorus concentration controls the activity of the nitrogen-fixing organisms, and thus the availability of nitrogen to oceanic life.

Photosynthetic activity in the upper part of the ocean causes inorganic phosphate to be incorporated into biomass, reducing the concentration of phosphorus; in warm surface waters, phosphate may become totally depleted. A given phosphorus atom may be traded several times among the plant, animal and bacterial populations before it eventually finds itself in biodebris (a dead organism or a fecal pellet) that falls into the deep part of the sea. Only about 1% of the phosphorus atoms that descend into deeper waters actually reach the bottom, where they are incorporated into sediments and permanently removed from circulation. The other 99% are released in the form of soluble phosphate, which is eventually brought to the surface in regions of upwelling. An average phosphorus atom will undergo one cycle of this circulation in about 1000 years; only a few months of this cycle will be spent in biomass. After an average of 100 such cycles, the atom will be removed from circulation and locked into the bottom sediment, and a new one will have entered the sea with river or juvenile water.

Phosphorus is unique in that its major source of input to the oceans derives ultimately from pollution; in the long term, this represents a transfer of land-based phosphate deposits to the oceans. About half of the phosphorus input is in the form of suspended material, both organic and inorganic, the latter being in a variety of forms including phosphates adsorbed onto clays and iron oxide paticles, and calcium phosphate (apatatite) eroded from rocks. These various particulates are known to dissolve to some extent once they reach the ocean, but there is considerable uncertainty about the rates of these processes under various conditions.

The major sink for oceanic phosphorus is burial with organic matter; this accounts for about two-thirds of the phosphorus removed. Most of the remainder is due to deposition with $CaCO_3$. A minor removal route is through reaction with Fe(II) formed when seawater attacks hot basalt, and in the formation of evaporite deposits. However, there is more phosphorus in evaporite deposits in the Western U.S. than in all of the ocean, so it is apparent that the long-term phosphorus budget is still not clearly understood.

Carbon

Carbon enters the ocean from both the atmosphere (as CO_2) and river water, in which the principal species is HCO_3^-. Once in solution, the carbonate species are in equilibrium with each other and with H_3O^+, and the concentrations of all of these are influenced by the partial pressure of atmospheric CO_2. The mass budget for calcium is linked to that of carbon through solubility equilibria with the various solid forms of $CaCO_3$ (mainly calcite). During photosynthesis, C^{12} is taken up slightly more readily than the rare isotope C^{13}. Since the rate of photosynthesis is controlled by the phosphate concentration, the C^{13}/C^{12} ratio in the dissolved carbon dioxide of surface waters is slightly higher than in the ocean as a whole. Observations of carbon isotope ratios in buried sediments have been useful in tracking historical changes in phosphate concentrations.

The C:P ratio and the regulation of atmospheric CO_2

The ratio of carbon to phosphorus in sea salt is about eight times greater than the same ratio measured in organic debris. This implies that in exhausting the available phosphate, the living organisms in the upper ocean consume only 12.5% of the dissolved carbon. Even this relatively small withdrawal of carbon from the carbonate system is sufficient to noticeably reduce the partial pressure of gaseous CO_2 in equilibrium with the ocean; it has been estimated that if all life in the ocean should suddenly cease, the atmospheric CO_2 content would rise to about three times its present level. The regulation of atmospheric CO_2 pressure by the oceans also works the other way: since the amount of dissolved carbonate in the oceans is so much greater than the amount of CO_2 in the atmosphere, the oceans act to buffer the effects of additions of CO_2 to the atmosphere. Calculations indicate that about half of the CO_2 that has been produced by burning fossil fuel since the Industrial Revolution has ended up in the oceans.

Bicarbonate

This is of course the major carbonate species in the ocean. Although it is interconvertible with CO_2 and is thus coupled to the carbon and photosynthetic cycles, itself can neither be taken up nor produced by organisms, and so it can be treated somewhat independently of biological activity. In this sense the only major input of into the oceans is river water. The two removal mechanisms are formation of CO_2

$$H^+ + HCO_3^- \rightarrow H_2O + CO^2 \tag{9.3.1}$$

and the (biologically mediated) formation of $CaCO_3^:$

$$Ca^{2+} + HCO_3^- \rightarrow CaCO_3 + H^+ \tag{9.3.2}$$

Since the pH of the oceans does not change, H^+ is conserved and the removal of HCO_3^- by biogenic secretion of $CaCO_3$ can be expressed by the sum of these reactions:

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O \tag{9.3.3}$$

whose reverse direction represents the dissolution of the skeletal remains of dead organisms as they fall to lower depths.

Calcite

The upper parts of the ocean tend to be supersaturated in $CaCO_3$. Solid $CaCO_3$, in the form of calcite, is manufactured by a large variety of organisms such as foraminifera. A constant rain of calcite falls through the ocean as these organisms die. The solubility of increases with pressure, so only that portion of the calcite that falls to shallow regions of the ocean floor is incorporated into sediments and removed from circulation; the remainder dissolves after reaching a depth known as the lysolcline. At the present time, the amounts of carbonate and Ca^{2+} supplied by erosion and volcanism appear to be only about one-third as great as the amount of calcite produced by organisms. As the carbonate concentration in a given region of the ocean becomes depleted due to higher calcite production, the lysocline moves up, tending to replenish the carbonate, and reducing the amount that is withdrawn by burial in sediments. Organic residues that fall into the deep sea are mostly oxidized to CO_2, presumably by bacterial activity.

Other Elements

Calcium

Calcium is removed from seawater solely by biodeposition as $CaCO_3$, a process whose rate can be determined quite accurately both at the present and in the past.

Table 9.3.1: Present-day budget for oceanic calcium (Tg Ca/yr).

inputs		outputs	
rivers	550	$CaCO_3$ into shallow water	520
volcanic basalt	191	$CaCO_3$ into deep water	440
cation exchange	37		
total	**778**		**960**

As is explained above, the upper part of the ocean is supersaturated in calcite but the lower ocean is not. For this reason, less than 20% of the $CaCO_3$ that is formed ends up as sediment and is eventually buried.

The main questions about the calcium budget tend to focus on the rates and locales at which dissolution of skeletal carbonates occurs, and on how to interpret the various kinds of existing carbonate sediments. For example, the crystalline form aragonite is less stable than calcite, and will presumably dissolve at a higher elevation. The absence of aragonite-containing pteropod shells in deeper deposits seems to confirm this, but in the absence of rate data is it difficult to know at what elevations these particular organisms originated.

The data in the above Table indicate that at the present time there is a net removal of calcium from the oceans. This is due to the rise in sea level since the decline of the more recent glacial epoch during the past 11,000 years. The additional water has covered the continental shelves, increasing the amount of shallow ocean where the growth of organisms is most intense. Over the more distant past (25 million years) the calcium budget appears to be well balanced.

Chloride

Evidence from geology and peleontology indicates that the salinity, and hence the chloride concentration of sewater has been quite constant for about 600 million years. There have been periods when climatic conditions and coastal topography have led to episodes of evaporite formation, but these have evidently been largely compensated by the eventual return of the evaporite deposits to the sea. The natural input of chloride from rivers is about 215 Tg/yr, but the present input is about half again as great (Table 7 on page 33), due to pollution. Also, there are presently no significant areas where seawater is evaporating to dryness. Thus the oceanic chloride budget is considerably out of balance. However, the replacement time of Cl^- in the oceans is so long (87 million years) that this will probably have no long-term effect.

Sodium

Although sodium is tied to chloride, it is also involved in the formation of silicate minerals, the weathering of rocks, and in cation exchange with clay sediments. Its short-term budget is quite out of balance for the same reasons as is that of chloride. On a longer time scale, removal of sodium by reaction with hot basalt associated with undersea volcanic activity may be of importance.

Sulfate

Considerably more sulfate is being added to seawater than is being removed by the major mechanisms of sediment formation (mainly $CaSO_4$ and pyrites). The natural river input is 82 Tg of S per year, while that due to pollution is 61 Tg/yr from rivers and 17 Tg/yr from rain and dry deposition.

Magnesium

This element is unusual in that its river-water input is balanced mostly by reaction with volcanic basalt; removal through biogenic formation of magnesian calcite (dolomite) accounts for only 11% of its total removal from the ocean. The present-day magnesium budget seems to have been balanced for the past 100 million years. However, most of the extensive dolomite deposits were formed prior to this time, so the longer-term magnesium budget is poorly understood.

Potassium

The potassium budget of the ocean is not well understood. The element is unusual in that only about 60% of its input is by rivers; the remainder is believed to come from newly formed undersea basalt. The big question about potassium is how it is removed; fixation by ion-exchange with illite clays seems to be a major mechanism, and its uptake by basalt (at lower temperatures than are required for its release) is also believed to occur.

Silica

About 85% of the silicon input to the oceans comes from river water in the form of silicic acid, H_4SiO_4. The remainder probably comes from basalt. It is removed by biogenic deposition as opaline silica, $SiO_2 \cdot n\ H_2O$ produced mainly by planktonic organisms (radiolaria and diatoms). Unlike the case for $CaCO_3$, the ocean is everywhere undersaturated in silica, especially near the surface where these organisms deplete it with greater efficiency than any other element.

Because opaline silica dissolves so rapidly, only a small fraction makes it to the bottom. The major deposits occur in shallower waters where coastal upwelling provides a good supply of N and P nutrients for siliceous organisms. Thus over half of the biogenic silica deposits are found in the Antarctic ocean.

In spite of the fact that dissolved silica has the shortest replacement time (21,000 years) of any major element in the ocean, its concentration appears to have been remarkably constant during geological time. This is taken as an indication of the ability of siliceous organisms to respond quickly to changes in local concentrations of dissolved silica.

Nitrogen

This element is complicated by its biologically-mediated exchange with atmospheric nitrogen, and by its existence in several oxidation states, all of which are interconvertible. Unlike the other major elements, nitrogen does not form extensive sedimentary deposits; most of the nitrogen present in dead organic material seems to be removed before it can be buried. Through this mechanism there is extensive cycling of nitrogen between the shallow and deep parts of the oceans.

The real difficulty in constructing a budget for oceanic nitrogen is the very large uncertainty in the rates of the major input (fixation) and output. Both of these processes are biologically mediated, but little is known about what organisms are responsible, where they thrive and how they are affected by local nutrient supply and other conditions.

Contributors and Attributions

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9.4: Chemistry and geochemistry of the oceans

Composition of seawater

The composition of the ocean has attracted the attention of some of the more famous names in science, including Robert Boyle, Antoine Lavoisier and Edmund Halley. Their early investigations tended to be difficult to reproduce, owing to the different conditions under which they crystallized the various salts.

As many as 54 salts, double salts and hydrated salts can be obtained by evaporating seawater to dryness. At least 73 elements are now known to be present in seawater.

Major ions of seawater These values, expressed in parts per thousand, are for seawater of 35% salinity.

cations	g/kg	anions	g/kg
Na^+	10.77	Cl^-	19.354
Mg^{2+}	1.29	SO_4^{2-}	2.712
Ca^{2+}	0.412	Br^-	0.087
K^+	0.399		
Sr^{2+}	0.0079		
Al^{3+}	0.005		

The best way of characterizing seawater is in terms of its ionic content, shown above. The remarkable thing about seawater is the constancy of its relative ionic composition. The overall salt content, known as the salinity (grams of salts contained in 1 kg of seawater), varies slightly within the range of 32-37.5%, corresponding to a solution of about 0.7% salt content. The ratios of the concentrations of the different ions, however, are quite constant, so that a measurement of Cl^- concentration is sufficient to determine the overall composition and total salinity. Although most elements are found in seawater only at trace levels, marine organisms may selectively absorb them and make them more detectable. Iodine, for example, was discovered in marine algae (seaweeds) 14 years before it was found in seawater. Other elements that were not detected in seawater until after they were found in marine organisms include barium, cobalt, copper, lead, nickel, silver and zinc. Si^{32}, presumably deriving from cosmic ray bombardment of Ar, has been discovered in marine sponges.

pH balance. Reflecting this constant ionic composition is the pH, which is usually maintained in the narrow range of 7.8-8.2, compared with 1.5 to 11 for fresh water. The major buffering action derives from the carbonate system, although ion exchange between Na+ in the water and H^+ in clay sediments has recently been recognized to be a significant factor.

Conservative and non-conservative substances

The major ionic constituents whose concentrations can be determined from the salinity are known as conservative substances. Their constant relative concentrations are due to the large amounts of these species in the oceans in comparison to their small inputs from river flow. This is another way of saying that their residence times are very large.

Ion	Concentration in river water micromols/L	Concentration in sea water micromols/L	Residence time/10^6 years
Cl^-	250	558,000	87
Na^+	315	479,000	55
Mg^{2+}	150	54,300	13
SO_4^{2-}	120	28,900	8.7
Ca^{2+}	367	10,500	1
K^+	36	10,400	10
HCO_3^-	870	2000	0.083

Ion	Concentration in river water micromols/L	Concentration in sea water micromols/L	Residence time/10^6 years
H_4SiO_4	170	100	0.021
NO_3^-	10	20	0.072
$H_2PO_4^-$	0.7	1	0.080

Replacement time with respect to river addition for some components of seawater

A number of other species, mostly connected with biological activity, are subject to wide variations in concentration. These include the nutrients NO_3^-, NO_2^-, NH_4^+, and HPO_4^{2-}, which may become depleted near the surface in regions of warmth and light. As was explained in the preceding subsection on coastal upwelling, offshore prevailing winds tend to drive Western coastal surface waters out to sea, causing deeper and more nutrient-rich water to be drawn to the surface. This upwelled water can support a large population of phytoplankton and thus of zooplankton and fish. The best-known example of this is the anchovy fishery off the coast of Peru, but the phenomenon occurs to some extent on the West coasts of most continents, including our own.

Other non-conservative components include Ca^{2+} and SiO_4^{2-}. These ions are incorporated into the solid parts of marine organisms, which sink to greater depths after the organisms die. The silica gradually dissolves, since the water is everywhere undersaturated in this substance. Calcium carbonate dissolves at intermediate depths, but may reprecipitate in deep waters owing to the higher pressure. Thus the concentrations of Ca and of SiO_4^{2-} tend to vary with depth. The gases O_2 and CO_2, being intimately involved with biological activity, are also non-conservative, as are N_2O and CO.

Organic matter

Most of the organic carbon in seawater is present as dissolved material, with only about 1-2% in particulates. The total organic carbon content ranges between 0.5 mg/L in deep water to 1.5 mg/L near the surface. There is still considerable disagreement about the composition of the dissolved organic matter; much of it appears to be of high molecular weight, and may be polymeric. Substances qualitatively similar to the humic acids found in soils can be isolated. The greenish color that is often associated with coastal waters is due to a mixture of fluorescent, high molecular weight substances of undetermined composition known as *"Gelbstoffe"*. It is likely that the significance of the organic fraction of seawater may be much greater than its low abundance would suggest. For one thing, many of these substances are lipid-like and tend to adsorb onto surfaces. It has been shown that any particle entering the ocean is quickly coated with an organic surface film that may influence the rate and extent of its dissolution or decomposition. Certain inorganic ions may be strongly complexed by humic-like substances. The surface of the ocean is mostly covered with an organic film, only a few molecular layers thick. This is believed to consist of hydrocarbons, lipids, and the like, but glycoproteins and proteoglycans have been reported. If this film is carefully removed from a container of seawater, it will quickly be reconstituted. How significant this film is in its effects on gas exchange with the atmosphere is not known.

Regulation of ocean composition

The salinity of the ocean appears to have been about the same for at least the last 200 million years. There have been changes in the relative amounts of some species, however; the ratio of Na/K has increased from about 1:1 in ancient ocean sediments to its present value of 28:1. Incorporation of calcium into sediments by the action of marine organisms has depleted the Ca/Mg ratio from 1:1 to 1:3.

Mass balance of P, C, and Ca for the oceans

Element	input to ocean	dissolved in seawater	in dead organisms	loss to sediments	residence time, y
phosphorus	1 (erosion)	1	1	1 (organic)	10,000
carbon	100 as CO_2 500 as carbonate	1000	125	100 (organic) 600 (carbonate)	165,000
calcium	500 (erosion)	5000	25	500 (as $CaCO_3$)	10^6

If the composition of the ocean has remained relatively unchanged with time, the continual addition of new mineral substances by the rivers and other sources must be exactly balanced by their removal as sediment, possibly passing through one or more biological systems in the process.

Where does the salt come from?

In 1715 Edmund Halley suggested that the age of the ocean (and thus presumably of the world) might be estimated from the rate of salt transport by rivers. When this measurement was actually carried out in 1899, it gave an age of only 90 million years.

> *This is somewhat better than the calculation made in 1654 by James Ussher, the Anglican Archbishop of Armagh, Ireland, based on his interpretation of the Biblical book of Genesis, that the world was created at 9 A.M. on October 23, 4004 BC, but it is still far too recent, being about when the dinosaurs became extinct. What Halley actually described was the residence time, which is about right for Na but much to long for some of the minor elements of seawater.*

The commonly stated view that the salt content of the oceans derives from surface runoff that contains the products of weathering and soil leaching is not consistent with the known compositions of the major river waters (See Table). The halide ions are particularly over-represented in seawater, compared to fresh water. These were once referred to as “excess volatiles”, and were attributed to volcanic emissions. With the discovery of plate tectonics, it became apparent that the locations of seafloor spreading at which fresh basalt flows up into the ocean from the mantle are also sources of mineral-laden water. Some of this may be seawater that has cycled through a hot porous region and has been able to dissolve some of the mineral material owing to the high temperature. Much of the water, however, is “juvenile” water that was previously incorporated into the mantle material and has never before been in the liquid phase. The substances introduced by this means (and by volcanic activity) are just the elements that are “missing” from river waters. Estimates of what fraction of the total volume of the oceans is due to juvenile water (most of it added in the early stages of mantle differentiation that began a billion years ago) range from 30 to 90%.

Geochemical processes involving the oceans

The oceans can be regarded as a product of a giant acid-base titration in which the carbonic acid present in rain reacts with the basic materials of the lithosphere. The juvenile water introduced at locations of ocean-floor spreading is also acidic, and is partly neutralized by the basic components of the basalt with which it reacts. Surface rocks mostly contain aluminum, silicon and oxygen combined with alkali and alkaline-earth metals, mainly potassium, sodium and calcium. The CO_2 and volcanic gases in rainwater react with this material to form a solution of the metal ion and HCO_3^-, in which is suspended some hydrated SiO^2. The solid material left behind is a clay such as kaolinite, $Al_2Si_2O_5(OH)_4$. This first forms as a friable coating on the surface of the weathered rock; later it becomes a soil material, then an alluvial deposit, and finally it may reach the sea as a suspended sediment. Here it may undergo a number of poorly-understood transformations to other clay sediments such as illites. Sea floor spreading eventually transports these sediments to a subduction region under a continental block, where the high temperatures and pressures permit reactions that transform it into hard rock such as granite, thus completing the geochemical cycle.

Deep-sea hydrothermal vents are now recognized to be another significant route for both the addition and removal of ionic substances from seawater.

Distribution and cycling of elements in the oceans

Although the relative concentrations of most of the elements in seawater are constant throughout the oceans, there are certain elements that tend to have highly uneven distributions vertically, and to a lesser extent horizontally. Neglecting the highly localized effects of undersea springs and volcanic vents, these variations are direct results of the removal of these elements from seawater by organisms; if the sea were sterile, its chemical composition would be almost uniform.

Plant life can exist only in the upper part of the ocean where there is sufficient light available to drive photosynthesis. These plants, together with the animals that consume them, extract nutrients from the water, reducing the concentrations of certain elements in the upper part of the sea. When these organisms die, they fall toward the lower depths of the ocean as particulate material. On the way down, some of the softer particles, deriving from tissue, may be consumed by other animals and recycled. Eventually,

however, the nutrient elements that were incorporated into organisms in the upper part of the ocean will end up in the colder, dark, and essentially lifeless lower part.

Mixing between the upper and lower reservoirs of the ocean is quite slow, owing to the higher density of the colder water; the average residence time of a water molecule in the lower reservoir is about 1600 years. Since the volume of the upper reservoir is only about 1/20 of that of the lower, a water molecule stays in the upper reservoir for only about 80 years.

Except for dissolved oxygen, all elements required by living organisms are depleted in the upper part of the ocean with respect to the lower part. In the case of the major nutrients P, N and Si, the degree of depletion is sufficiently complete (around 95%) to limit the growth of organisms at the surface. These three elements are said to be biolimiting. A few other biointermediate elements show partial depletion in surface waters: Ca (1%), C (15%), Ba (75%).

The organic component of plants and animals has the average composition $C_{80}N_{15}P$. It is remarkable that the ratio of N:P in seawater (both surface and deep) is also 15:1; this raises the interesting question of to what extent the ocean and life have co-evolved.

In the deep part of the ocean the elemental ratio corresponds to $C_{800}N_{15}P$, but of course with much larger absolute amounts of these elements. Eventually some of this deeper water returns to the surface where the N and P are quickly taken up by plants. But since plants can only utilize 80 out of every 800 carbon atoms, 90 percent of the carbon will remain in dissolved form, mostly as HCO_3^-.

> *To work out the balance of Ca and Si used in the hard parts of organisms, we add these elements to the average composition of the lower reservior to get $Ca_{3200}Si_{50}C_{800}N_{15}P$. Particulate carbon falls into the deep ocean in the ratio of about two atoms in organic tissue to one atom in the form of calcite. This makes the overall composition of detrital material something like $C_{120}N_{15}P$; i.e., 80 organic C's and 40 in $CaCO_3$. Accompanying these 40 calcite units will be 40 Ca atoms, but this represents a minor depletion of the 3200 Ca atoms that eventually return to the surface, so this element is only slightly depleted in the upper waters. Silicon, being far less abundant, is depleted to a much greater extent.*

The oceanic sediments

The particulate shower.

A continual rain of particulate material from dead organisms falls through the ocean. This shower is comprised of three major kinds of material: calcite ($CaCO_3$), silica (SiO_2), and organic matter. The first two come from the hard parts of both plants and animals (mainly microscopic animals such as foraminifera and radiolarians). The organic matter is derived mainly from the soft tissues of organisms, and from animal fecal material. Some of this solid material dissolves before it reaches the ocean floor, but not usually before it enters the deep ocean where it will remain for about 1600 years.

The remainder of this material settles onto the floor of the sea, where it forms one component of a layer of sediments that provide important information about the evolution of the sea and of the earth. Over a short time scale of months to years, these sediments are in quasi-equilibrium with the seawater. On a scale of millions of years, the sediments are merely way-stations in the geochemical cycling of material between the earth's surface and its interior.

The oceanic sediments have three main origins:

- **Detrital** material is derived largely from particles deposited in the ocean by rivers and also directly by the wind. These materials are mostly aluminosilicates (clays), along with some quartz. These substances accumulate on the deep ocean floor at a rate of about 0.3 g cm^{-2} per 1000 years.
- **Authigenic** materials are formed by precipitation within the ocean or by crystallization within the sediment itself. These constitute only a small fraction of the total sediment.
- **Biogenic** components consist mainly of the calcium carbonate and silica that make up the hard parts of organisms. Scavenging by other organisms is so efficient that only about 0.3 % of the total deep sea sediment consists of actual organic material.

Our main interest lies with the silica and calcium carbonate, since these substances form a crucial part of the biogeological cycle. Also, their distributions in the ocean are not uniform- a fact that must tell us something.

The skeletons of diatoms and radiolarians are the principal sources of silica sediments. Since the ocean is everywhere undersaturated with respect to silica, only the most resistant parts of these skeletons reach the bottom of the deep ocean and get incorporated into sediments. Silica sediments are less common in the Atlantic ocean, owing to the lower content of dissolved silica.

The parts of the ocean where these sediments are increasing most rapidly correspond to regions of upwelling, where deep water that is rich in dissolved silica rises to the surface where the silica is rapidly fixed by organisms. Where upwelling is absent, the growth of the organisms is limited, and little silica is precipitated. Since deep waters tend to flow from the Atlantic into the Pacific ocean where most of the upwelling occurs, Atlantic waters are depleted in silica, and silica sediments are not commonly found in this ocean.

For calcium carbonate, the situation is quite different. In the first place, surface waters are everywhere supersaturated with respect to both calcite and aragonite, the two common crystal forms of $CaCO_3$. Secondly, Ca^{2+} and HCO_3^- are never limiting factors in the growth of the coccoliths (plants) and forams (animals) that precipitate $CaCO_3$; their production depends on the availability of phosphate and nitrogen. Because these elements are efficiently recycled before they fall into the deep ocean, their supply does not depend on upwelling, and so the production of solid is more uniformly distributed over the world's oceans.

More importantly, however, the chances that a piece of carbonate skeleton will end up as sediment will be highly dependent on both the local CO_3^{2-} concentration and the depth of the ocean floor. These factors give rise to small-scale variations in the production of carbonate sediments that can be quite wide-ranging.

Ocean sediments and continental drift

New crust is being generated and moving away from the crests of the mid-ocean ridges at a rate of a few centimetres per year. Although the crests of these ridges are relatively high points, projecting to within about 3000 m of the surface, the continual injection of new material prevents sediments from accumulating in these areas. Farther from the crests, carbonate sediments do build up, eventually reaching a depth of about 500 m, but by this time the elevation has dropped off below the saturation horizon, so from this point on the carbonate sediments are overlaid by red clay.

If we drill a hole down through a part of the ocean floor that is presently below the saturation horizon, the top part of the drill core will consist of clay, followed by $CaCO_3$ at greater depths. The core may also contain regions in which silica predominates. Since silica production is very high in equatorial regions, the appearance of such a layer suggests that this particular region of the oceanic crust has moved across the equator.

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9.5: The hydrosphere and the oceans

> *How inappropriate to call this planet Earth,*
> *when clearly it is Ocean."*
>
> *Arthur C. Clarke*

Water is the most abundant substance at the earth's surface. Almost all of it is in the oceans, which cover 70% of the surface area of the earth. However, the amounts of water present in the atmosphere and on land (as surface runoff, lakes and streams) is great enough to make it a significant agent in transporting substances between the lithosphere and the oceans.

Water interacts with both the atmosphere and the lithosphere, acquiring solutes from each, and thus provides the major chemical link between these two realms. The various transformations undergone by water through the different stages of the hydrologic cycle act to transport both dissolved and particulate substances between different geographic locations.

Table9.5.1: Inventory of water on Earth

Reservoir	Volume / 10^6, km^3	Percent of total
Oceans	1370	97.25
Ice caps and glaciers	39	2.05
Deep groundwater	5.3	0.38
Shallow groundwater	4.3	0.30
Lakes	0.125	0.01
Soil moisture	0.065	0.005
Atmosphere	0.013	0.001
Rivers	0.0017	0.0001
Biosphere	0.0006	0.00004
Total	**1408.7**	**100**

Where did the water come from?

It appears to have been bound up in the silica-based materials such as micas and amphiboles which accreted to form the Earth. The heat released during this process would have been sufficient to drive off this water, which amounted to about 0.01% by mass of the primordial material.

The hydrologic cycle

The *hydrologic cycle* refers to the steady state that exists between evaporation, condensation, percolation, runoff, and circulation of water. The cycle is driven by solar energy, mainly through direct vaporization, but also by convective motion induced by uneven heating.

The major interphase transport process of the hydrologic cycle is evaporation of water from the ocean. However, 90% of this vapor falls directly back into the ocean as rain, while 10% is transported over the land. Of the latter, about two-thirds evaporates again and one third runs off to the ocean.

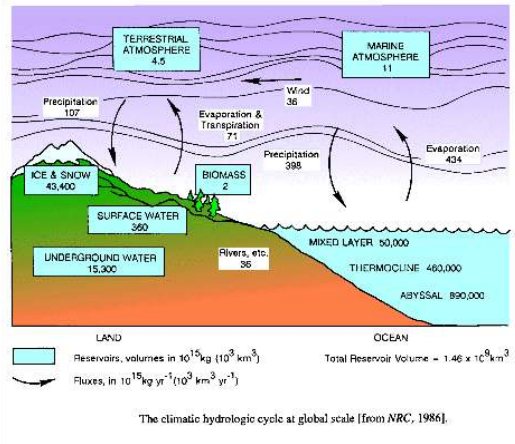


Figure 9.5.1: The climatic hydrological cycle at global scale (Diagram and text from a page at the Web site of the Institute for Global Environment and Society)

The movement of water on the earth's surface and through the atmosphere is known as the hydrologic cycle. Water is taken up by the atmosphere from the earth's surface in vapor form through evaporation. It may then be moved from place to place by the wind until it is condensed back to its liquid phase to form clouds. Water then returns to the

surface of the earth in the form of either liquid (rain) or solid (snow, sleet, etc.) precipitation. Water transport can also take place on or below the earth's surface by flowing glaciers, rivers, and ground water flow.

The amounts of water precipitated onto the land and oceans are in approximate proportion to the relative surface areas, but evaporation from the ocean exceeds that from the land by about 37,400 km^{-3} yr^{-1}. This difference is the amount of water transported to the oceans by river runoff. When water condenses from the atmosphere in the form of rain, it is slightly enriched in H_2O^{18}. During epochs of glacial buildup the fraction of H_2O^{18} in the oceans consequently decreases. Observation of H_2O^{18}/H_2O^{16} ratios in marine sediments is one way of studying the timing and extent of past glaciations. Since the degree of heavy isotope enrichment of condensed water is temperature dependent, this same method can be used to estimate mean world temperatures in the distant past.

The hydrologic cycle also has important effects on the energy budget of the earth. Atmospheric water vapor (along with carbon dioxide and methane) tends to absorb the long-wavelength infrared radiation emitted by the earth's surface, partially trapping the incoming shorter-wavelength energy and thus maintaining the mean surface temperature about 30° higher than would be the case in the absence of water vapor. Of the 51% of the solar radiation incident on the atmosphere that reaches the earth's surface, about half of this (23%) is used to evaporate water. During the ten days that an average molecule resides in the atmosphere, it will travel about 1000 km. The atmospheric transport of water from equatorial to subtropical regions serves as an important mechanism for the transport of thermal energy; at latitudes of about 40°, as much as one-third of the energy input comes from release of latent heat from water vapor formed in equatorial regions.

Oceanic circulation

About 97% of the earth's water is contained in the two reservoirs which comprise the oceans. The upper mixed layer contains about 5% of the total; it is separated from the deeper and colder layer by the thermocline. Mixing between these two stratified layers is very slow; of the total ocean volume of 6.8 $\times$ 10^{18} m^3, only about 0.71 $\times$ 10^{15} m^3, or about 0.01%, moves between the two layers per year. The mean residence time of a water molecule in the deep layer is about 1600 years.

The large-scale motions of ocean water are the primary means by which chemical substances, especially those taken up and excreted by organisms, are transported within the ocean. An understanding of the general patterns of this circulation is essential in order to analyze the observed distribution of many of the chemical elements in different parts of the ocean and in the oceanic sediments.

Atmospheric circulation

The circulation of the surface waters of the ocean is driven by the prevailing winds. The latter arise from uneven heating of the earth's surface, and are arranged in bands that parallel the equator.

Although the motion of the waters at the surface of the ocean are driven by the winds, they do not follow them in a simple manner. The reasons are threefold: the Coriolis effect, the presence of land masses, and uneveness in the sea level due to regional differences in temperature and atmospheric pressure.

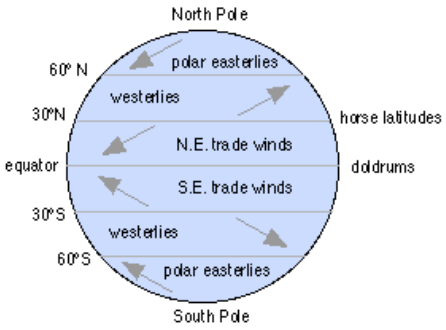


Figure 9.5.2: Atmospheric winds

The most intense heat input into the atmosphere occurs near the equator, where the heated air rises and cools, producing intense local precipitation but little surface wind. After cooling and losing moisture, this air moves north and south and descends at a latitude of about 30°. As it descends, it warms (largely by adiabatic compression) and its relative humidity decreases. The extreme dryness of this air gives rise to the subtropical desert regions between about 15° and 30°. Part of this air flows back toward the equator, giving rise to the northeast and southwest trade winds; the deflection to the east or west is caused by the Coriolis effect. Another part of the descending air travels poleward, producing the prevailing westerlies. Eventually these collide with cold air masses moving away from the polar regions, producing a region of unstable air and storm activity known as a polar front. Some of this polar air picks up enough heat to rise and enter into polar cell circulation patterns.

The flow of air in the prevailing westerlies is subject to considerable turbulence which gives rise to planetary waves. These are moving regions in which warm surface air is lifted to higher levels, producing lines of storms that travel from west to east, and exchanging more air between the polar and temperate regions.

Surface currents of the oceans

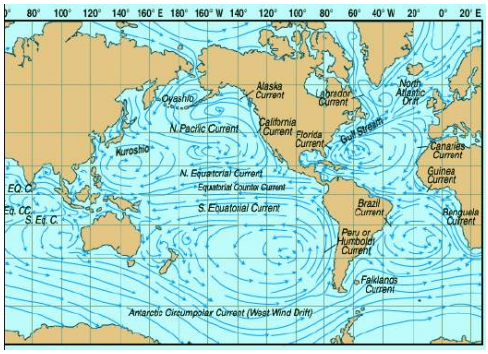


Figure 9.5.3:

In the Northern hemisphere, the Coriolis effect not only deflects south-moving objects to the east but it also causes currents flowing parallel to the equator to veer to the right of the direction of flow, i.e. to the north or south.

In addition, prevailing westerly winds and the eastward rotation of the earth cause water to pile up by a few centimeters at the western edges of the oceans. The resultant downhill flow, interacting with Coriolis forces, produces a *western boundary current* that runs south-to-north in the northern hemisphere. A similar but opposite effect gives rise to a south-flowing *eastern boundary current* on continental east coasts.

Thermohaline circulation

In contrast to the upper levels of the ocean, the deep ocean is *stratified*; the density increases with depth so as to inhibit the vertical transport of water. This stratification divides the deep oceans into several distinct water masses which undergo movement in a more or less horizonal plane, with adjacent masses sometimes moving in opposite directions.

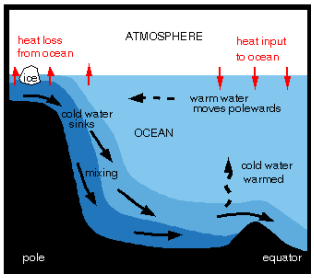


Figure 9.5.4: As the cold water fills up the deepest regions and spills over ridges into other deep basins, it creates huge undersea cascades which rival the greatest terrestrial waterfalls in height and the largest rivers in volume. For more on this, see the Feb. 1989 *Scientific American*

The winds and atmospheric effects outlined above affect only the upper part of the ocean. Below 100 meters or so, oceanic circulation is driven by the *density* of the seawater, which is determined by its temperature and its salinity. Variations in these two quantities give rise to the *thermohaline circulation* of the deep currents of the ocean.

It all starts when seasonal ice begins to form in the polar regions. Because the salts dissolved in seawater cannot be accommodated within the ice structure, they are largely excluded from the new ice and remain in solution. This increases the density of the surrounding unfrozen water, causing it to sink into the bottom ocean.

There are two major locations at which surface waters enter the deep ocean. The northern entry point is in the Norwegian Sea off Greenland; this water forms a mass known as the North Atlantic Deep Water (NADW) which flows southward across the equator.

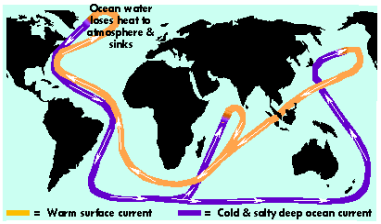


Figure 9.5.5: From Don Reed, Marine Geology 130 at San Jose State U.

Most of the transport into the deep ocean takes place in the Weddell Sea off the coast of Antarctica. The highly saline water flows down the submerged Antarctic Slope to begin a 5000-year trip to the north across the bottom of the ocean. This is the major route by which dissolved CO_2 and O_2 (which are more soluble in this cold water) are transported into the deep ocean where it forms a water mass known as the Antarctic Bottom Water (AABW) which can be traced into all three oceans.

In the south, a flow from the antarctic region forms a water mass known as the Antarctic Bottom Water (AABW) which can be traced into all three oceans.

The Pacific Ocean lacks any major identifiable direct source of cold water, so it is less differentiated and its deep circulation is sluggish and poorly defined.

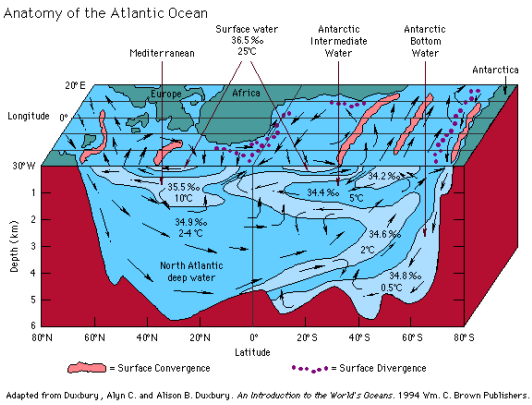


Figure 9.5.6: Temperature and salinity profiles in a north-south subsection of the Atlantic ocean.

As is apparent from the figure above, the vertical profiles of temperature and especially of the salinity are not uniform. To some extent, these two parameters have opposite effects: in equatorial regions, temperatures are higher (leading to lower density) but evaporation rates are also higher (leading to higher density). In polar regions, the formation of sea ice raises the density of the seawater (because only a small proportion of salt is incorporated into the ice).

The nature and extent of the deep ocean currents differ in the Atlantic, Pacific, and Indian oceans. These currents are much slower than the surface currents, and in fact have not been measured directly; their existence is however clearly implied by the chemical composition and temperature of water samples taken from various parts of the ocean. Estimated rates are of the order of kilometers per month, in contrast to the few kilometers per hour of surface waters. The deep currents are the indirect results of processes occuring at the surface in which cold water of high salinity is produced as sea ice forms in the arctic and antarctic regions. This water is so dense that it sinks to the bottom, displacing warmer or less saline water as it moves.

Coastal Upwelling

Recirculation of deep water to the surface occurs to a very small extent in many regions, but it is especially pronounced where water entering the Antarctic Bottom mass displaces other bottom water, and where water piles up at the western edges of continents. This latter water flows downhill (forming the western boundary currents mentioned above) and is replaced by colder water from the deep ocean. The deep ocean contains few organisms to deplete the water of the nutrients it receives from the remains of the dead organisms floating down from above; this upwelled water is therefor exceptionally rich in nutrients, and strongly encourages the growth of new organisms that extend up the food chain to fish. Thus the wind-driven upwelling that occurs off the west coast of South America is responsible for the Peruvian fishing and guano fertilizer industry.

> *About every seven years these prevailing winds disappear for a while, allowing warm equatorial waters to move in. This phenomenon is known as El Niño and it results in massive kills of plankton and fish. Decomposition of the dead organisms reduces the oxygen content of the water, causing the death of still more fish, and allowing reduced compounds such as hydrogen sulfide to accumulate.*

Matthias Tomczak's Introduction to physical oceanography is an excellent source of more information on the topics covered above.

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