CELL BIOLOGY FOR ALLIED HEALTH



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Cell Biology for Allied Health

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1.1: The Science of Biology

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1.1A: Introduction to the Study of Biology

Learning Objectives

- Describe the field of biological science

The Study of Life

Biology is a natural science concerned with the study of life and living organisms. Modern biology is a vast and eclectic field composed of many specialized disciplines that study the structure, function, growth, distribution, evolution, or other features of living organisms. However, despite the broad scope of biology, there are certain general and unifying concepts that govern all study and research:

- the cell is the basic unit of life
- genes (consisting of DNA or RNA) are the basic unit of heredity
- evolution accounts for the unity and diversity seen among living organisms
- all organisms survive by consuming and transforming energy
- all organisms maintain a stable internal environment



Figure 1.1A.1: Biology: The Study of Life: A collection of organisms clockwise from top left: bacteria, koala, fern, toadstool, tree frog, tarantula.

Biological research indicates the first forms of life on Earth were microorganisms that existed for billions of years before the evolution of larger organisms. The mammals, birds, and flowers so familiar to us are all relatively recent, originating within the last 200 million years. Modern-appearing humans, *Homo sapiens*, are a relatively new species, having inhabited this planet for only the last 200,000 years (approximately).



Figure 1.1A.1: Stromatolites: Stromatolites, sedimentary accretions formed by the actions of cyanobacteria, provide fossil evidence of life on Earth about 3.5 billion years ago.

History of Biological Science

Although modern biology is a relatively recent development, sciences related to and included within it have been studied since ancient times. Natural philosophy was studied as early as the ancient civilizations of Mesopotamia, Egypt, the Indian subcontinent, and China. However, the origins of modern biology and its approach to the study of nature are most often traced back to ancient Greece. (Biology is derived from the Greek word “bio” meaning “life” and the suffix “ology” meaning “study of.”)

Advances in microscopy also had a profound impact on biological thinking. In the early 19th century, a number of biologists pointed to the central importance of the cell and in 1838, Schleiden and Schwann began promoting the now universal ideas of the cell theory. Jean-Baptiste Lamarck was the first to present a coherent theory of evolution, although it was the British naturalist Charles Darwin who spread the theory of natural selection throughout the scientific community. In 1953, the discovery of the double helical structure of DNA marked the transition to the era of molecular genetics.



Figure 1.1A.1: Phrenology: Dr. Spurzheim’s divisions of the organs of phrenology marked externally: Phrenology is a pseudoscience that attempted to determine brain function and personality by analyzing an individual’s skull.

Science and Pseudoscience

Science is a process for learning about the natural world. Most scientific investigations involve the testing of potential answers to important research questions. For example, oncologists (cancer doctors) are interested in finding out why some cancers respond well to chemotherapy while others are unaffected. Based on their growing knowledge of molecular biology, some doctors suspect a connection between a patient's genetics and their response to chemotherapy. Many years of research have produced numerous scientific papers documenting the evidence for a connection between cancer, genetics, and treatment response. Once published, scientific information is available for anyone to read, learn from, or even question/dispute. This makes science an iterative, or cumulative, process, where previous research is used as the foundation for new research. Our current understanding of any issue in the sciences is the culmination of all previous work.

Pseudoscience is a belief presented as scientific although it is not a product of scientific investigation. Pseudoscience is often known as fringe or alternative science. It usually lacks the carefully-controlled and thoughtfully-interpreted experiments which provide the foundation of the natural sciences and which contribute to their advancement.

Key Points

- Biology has evolved as a field of science since it was first studied in ancient civilizations, although modern biology is a relatively recent field.
- Science is a process that requires the testing of ideas using evidence gathered from the natural world. Science is iterative in nature and involves critical thinking, careful data collection, rigorous peer review, and the communication of results.
- Science also refers to the body of knowledge produced by scientific investigation.
- Pseudoscience is a belief presented as scientific although it is not a product of scientific investigation.

Key Terms

- **pseudoscience**: Any belief purported to be scientific or supported by science that is not a product of scientific investigation.
- **science**: A process for learning about the natural world that tests ideas using evidence gathered from nature.
- **Biology**: A natural science concerned with the study of life and living organisms.

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1.1B: Scientific Reasoning

Learning Objectives

- Compare and contrast theories and hypotheses

The Process of Science

Science (from the Latin scientia, meaning “knowledge”) can be defined as knowledge that covers general truths or the operation of general laws, especially when acquired and tested by the scientific method. The steps of the scientific method will be examined in detail later, but one of the most important aspects of this method is the testing of hypotheses (testable statements) by means of repeatable experiments. Although using the scientific method is inherent to science, it is inadequate in determining what science is. This is because it is relatively easy to apply the scientific method to disciplines such as physics and chemistry, but when it comes to disciplines like archaeology, paleoanthropology, psychology, and geology, the scientific method becomes less applicable as it becomes more difficult to repeat experiments.

These areas of study are still sciences, however. Consider archaeology: even though one cannot perform repeatable experiments, hypotheses may still be supported. For instance, an archaeologist can hypothesize that an ancient culture existed based on finding a piece of pottery. Further hypotheses could be made about various characteristics of this culture. These hypotheses may be found to be plausible (supported by data) and tentatively accepted, or may be falsified and rejected altogether (due to contradictions from data and other findings). A group of related hypotheses, that have not been disproven, may eventually lead to the development of a verified theory. A theory is a tested and confirmed explanation for observations or phenomena that is supported by a large body of evidence. Science may be better defined as fields of study that attempt to comprehend the nature of the universe.

Scientific Reasoning

One thing is common to all forms of science: an ultimate goal “to know.” Curiosity and inquiry are the driving forces for the development of science. Scientists seek to understand the world and the way it operates. To do this, they use two methods of logical thinking: inductive reasoning and deductive reasoning.

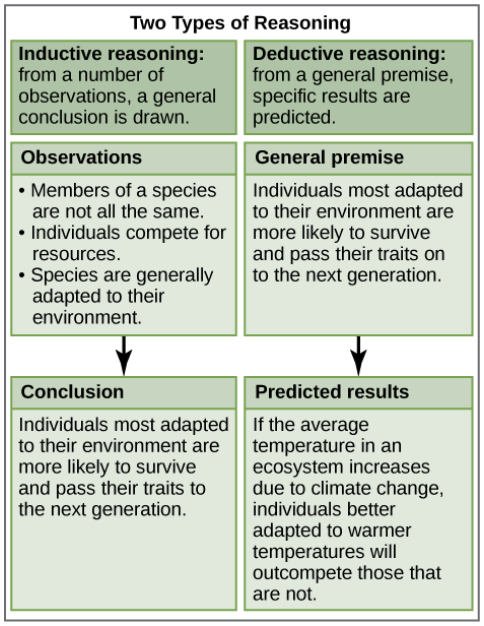


Figure 1.1*B*.1: Scientific Reasoning: Scientists use two types of reasoning, inductive and deductive, to advance scientific knowledge.

Inductive reasoning is a form of logical thinking that uses related observations to arrive at a general conclusion. This type of reasoning is common in descriptive science. A life scientist such as a biologist makes observations and records them. These data can be qualitative or quantitative and the raw data can be supplemented with drawings, pictures, photos, or videos. From many

observations, the scientist can infer conclusions (inductions) based on evidence. Inductive reasoning involves formulating generalizations inferred from careful observation and the analysis of a large amount of data. Brain studies provide an example. In this type of research, many live brains are observed while people are doing a specific activity, such as viewing images of food. The part of the brain that “lights up” during this activity is then predicted to be the part controlling the response to the selected stimulus; in this case, images of food. The “lighting up” of the various areas of the brain is caused by excess absorption of radioactive sugar derivatives by active areas of the brain. The resultant increase in radioactivity is observed by a scanner. Then researchers can stimulate that part of the brain to see if similar responses result.

Deductive reasoning or deduction is the type of logic used in hypothesis-based science. In deductive reason, the pattern of thinking moves in the opposite direction as compared to inductive reasoning. Deductive reasoning is a form of logical thinking that uses a general principle or law to forecast specific results. From those general principles, a scientist can extrapolate and predict the specific results that would be valid as long as the general principles are valid. Studies in climate change can illustrate this type of reasoning. For example, scientists may predict that if the climate becomes warmer in a particular region, then the distribution of plants and animals should change. These predictions have been written and tested, and many such predicted changes have been observed, such as the modification of arable areas for agriculture correlated with changes in the average temperatures.

Both types of logical thinking are related to the two main pathways of scientific study: descriptive science and hypothesis-based science. Descriptive (or discovery) science, which is usually inductive, aims to observe, explore, and discover, while hypothesis-based science, which is usually deductive, begins with a specific question or problem and a potential answer or solution that can be tested. The boundary between these two forms of study is often blurred and most scientific endeavors combine both approaches. The fuzzy boundary becomes apparent when thinking about how easily observation can lead to specific questions. For example, a gentleman in the 1940s observed that the burr seeds that stuck to his clothes and his dog’s fur had a tiny hook structure. Upon closer inspection, he discovered that the burrs’ gripping device was more reliable than a zipper. He eventually developed a company and produced the hook-and-loop fastener popularly known today as Velcro. Descriptive science and hypothesis-based science are in continuous dialogue.



Figure 1.1*B*.1: A Burr: This fruit attaches to animal fur via the hooks on its surface to improve distribution. Velcro is an example of a biomimetic invention which has copied burrs and uses small flexible hooks to reversibly attach to fluffy surfaces.

Key Points

- A hypothesis is a statement/prediction that can be tested by experimentation.
- A theory is an explanation for a set of observations or phenomena that is supported by extensive research and that can be used as the basis for further research.
- Inductive reasoning draws on observations to infer logical conclusions based on the evidence.
- Deductive reasoning is hypothesis-based logical reasoning that deduces conclusions from test results.

Key Terms

- **theory**: a well-substantiated explanation of some aspect of the natural world based on knowledge that has been repeatedly confirmed through observation and experimentation
- **hypothesis**: a tentative conjecture explaining an observation, phenomenon, or scientific problem that can be tested by further observation, investigation, and/or experimentation

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1.1C: The Scientific Method

Learning Objectives

- Discuss hypotheses and the components of a scientific experiment as part of the scientific method

The Scientific Method

Biologists study the living world by posing questions about it and seeking science -based responses. This approach is common to other sciences as well and is often referred to as the scientific method. The scientific method was used even in ancient times, but it was first documented by England's Sir Francis Bacon (1561–1626) who set up inductive methods for scientific inquiry. The scientific method can be applied to almost all fields of study as a logical, rational, problem-solving method.



Figure 1.1*C*.1: Sir Francis Bacon: Sir Francis Bacon (1561–1626) is credited with being the first to define the scientific method.

The scientific process typically starts with an observation (often a problem to be solved) that leads to a question. Let's think about a simple problem that starts with an observation and apply the scientific method to solve the problem. A teenager notices that his friend is really tall and wonders why. So his question might be, "Why is my friend so tall? "

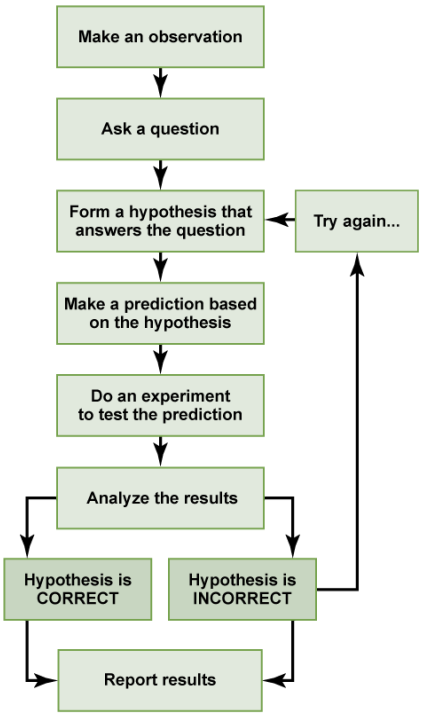


Figure 1.1C.1: The Scientific Method: The scientific method consists of a series of well-defined steps. If a hypothesis is not supported by experimental data, a new hypothesis can be proposed.

Proposing a Hypothesis

Recall that a hypothesis is an educated guess that can be tested. Hypotheses often also include an explanation for the educated guess. To solve one problem, several hypotheses may be proposed. For example, the student might believe that his friend is tall because he drinks a lot of milk. So his hypothesis might be "If a person drinks a lot of milk, then they will grow to be very tall because milk is good for your bones." Generally, hypotheses have the format "If…then…" Keep in mind that there could be other responses to the question; therefore, other hypotheses may be proposed. A second hypothesis might be, "If a person has tall parents, then they will also be tall, because they have the genes to be tall. "

Once a hypothesis has been selected, the student can make a prediction. A prediction is similar to a hypothesis but it is truly a guess. For instance, they might predict that their friend is tall because he drinks a lot of milk.

Testing a Hypothesis

A valid hypothesis must be testable. It should also be falsifiable, meaning that it can be disproven by experimental results. Importantly, science does not claim to "prove" anything because scientific understandings are always subject to modification with further information. This step—openness to disproving ideas—is what distinguishes sciences from non-sciences. The presence of the supernatural, for instance, is neither testable nor falsifiable. To test a hypothesis, a researcher will conduct one or more experiments designed to eliminate one or more of the hypotheses. Each experiment will have one or more variables and one or more controls. A variable is any part of the experiment that can vary or change during the experiment. The control group contains every feature of the experimental group except it is not given the manipulation that is hypothesized. For example, a control group could be a group of varied teenagers that did not drink milk and they could be compared to the experimental group, a group of varied teenagers that did drink milk. Thus, if the results of the experimental group differ from the control group, the difference must be due to the hypothesized manipulation rather than some outside factor. To test the first hypothesis, the student would find out if drinking milk affects height. If drinking milk has no affect on height, then there must be another reason for the height of the friend. To test the second hypothesis, the student could check whether or not his friend has tall parents. Each hypothesis should be tested by carrying out appropriate experiments. Be aware that rejecting one hypothesis does not determine whether or not the other hypotheses can be accepted. It simply eliminates one hypothesis that is not valid. Using the scientific method, the hypotheses that are inconsistent with experimental data are rejected.

While this “tallness” example is based on observational results, other hypotheses and experiments might have clearer controls. For instance, a student might attend class on Monday and realize she had difficulty concentrating on the lecture. One hypothesis to explain this occurrence might be, “If I eat breakfast before class, then I am better able to pay attention.” The student could then design an experiment with a control to test this hypothesis.

The scientific method may seem too rigid and structured. It is important to keep in mind that although scientists often follow this sequence, there is flexibility. Many times, science does not operate in a linear fashion. Instead, scientists continually draw inferences and make generalizations, finding patterns as their research proceeds. Scientific reasoning is more complex than the scientific method alone suggests.

Key Points

- In the scientific method, observations lead to questions that require answers.
- In the scientific method, the hypothesis is a testable statement proposed to answer a question.
- In the scientific method, experiments (often with controls and variables) are devised to test hypotheses.
- In the scientific method, analysis of the results of an experiment will lead to the hypothesis being accepted or rejected.

Key Terms

- **scientific method**: a way of discovering knowledge based on making falsifiable predictions (hypotheses), testing them, and developing theories based on collected data
- **hypothesis**: an educated guess that usually is found in an “if…then…” format
- **control group**: a group that contains every feature of the experimental group except it is not given the manipulation that is hypothesized

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1.1D: Basic and Applied Science

Learning Objectives

- Differentiate between basic and applied science

Two Types of Science: Basic Science and Applied Science

The scientific community has been debating for the last few decades about the value of different types of science. Is it valuable to pursue science for the sake of simply gaining knowledge, or does scientific knowledge only have worth if we can apply it to solving a specific problem or to bettering our lives? This question focuses on the differences between two types of science: basic science and applied science.

Basic science or "pure" science seeks to expand knowledge regardless of the short-term application of that knowledge. It is not focused on developing a product or a service of immediate public or commercial value. The goal of basic science is knowledge for knowledge's sake; though this does not mean that, in the end, it may not result in a practical application.

In contrast, applied science or "technology" aims to use science to solve real-world problems such as improving crop yields, finding a cure for a particular disease, or saving animals threatened by a natural disaster. In applied science, the problem is usually defined for the researcher.



Figure 1.1*D*.1: Example of Applied Science: After Hurricane Ike struck the Gulf Coast in 2008, the U.S. Fish and Wildlife Service rescued this brown pelican. Thanks to applied science, scientists knew how to rehabilitate the bird.

Some individuals may perceive applied science as "useful" and basic science as "useless." A question these people might pose to a scientist advocating knowledge acquisition would be, "What for?" A careful look at the history of science, however, reveals that basic knowledge has resulted in many remarkable applications of great value. Many scientists think that a basic understanding of science is necessary before an application is developed; therefore, applied science relies on the results generated through basic science. Other scientists think that it is time to move on from basic science and instead to find solutions to actual problems. Both approaches are valid. It is true that there are problems that demand immediate attention; however, few solutions would be found without the help of the wide knowledge foundation generated through basic science.

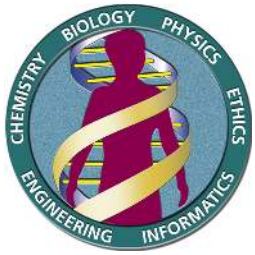


Figure 1.1*D*.2: A Link Between Basic and Applied Science: The Human Genome Project was a 13-year collaborative effort among researchers working in several different fields of science. The project, which sequenced the entire human genome, was completed in 2003.

One example of how basic and applied science can work together to solve practical problems occurred after the discovery of DNA structure led to an understanding of the molecular mechanisms governing DNA replication. Strands of DNA, unique in every human, are found in our cells where they provide the instructions necessary for life. During DNA replication, DNA makes new copies of itself shortly before a cell divides. Understanding the mechanisms of DNA replication enabled scientists to develop laboratory techniques that are now used to identify genetic diseases, pinpoint individuals who were at a crime scene, and determine paternity. Without basic science, it is unlikely that applied science would exist.

Another example of the link between basic and applied research is the Human Genome Project, a study in which each human chromosome was analyzed and mapped to determine the precise sequence of DNA subunits and the exact location of each gene. (The gene is the basic unit of heredity; an individual's complete collection of genes is his or her genome.) Other less complex organisms have also been studied as part of this project in order to gain a better understanding of human chromosomes. The Human Genome Project relied on basic research carried out with simple organisms and, later, with the human genome. An important end goal eventually became using the data for applied research to seek cures and early diagnoses for genetically-related diseases.

While research efforts in both basic science and applied science are usually carefully planned, it is important to note that some discoveries are made by serendipity; that is, by means of a fortunate accident or a lucky surprise. Penicillin was discovered when biologist Alexander Fleming accidentally left a petri dish of *Staphylococcus* bacteria open. An unwanted mold grew on the dish, killing the bacteria. The mold turned out to be Penicillium and a new antibiotic was discovered. Even in the highly organized world of science, luck, when combined with an observant, curious mind, can lead to unexpected breakthroughs.

Key Points

- The only goal of basic science research is to increase the knowledge base of a particular field of study.
- Applied science uses the knowledge base supplied by basic science to devise solutions, often technological, to specific problems.
- The basic science involved in mapping the human genome is leading to applied science techniques that will diagnose and treat genetic diseases.

Key Terms

- **basic science**: research done solely to expand the knowledge base
- **applied science**: The discipline dealing with the art or science of applying scientific knowledge to practical problems.

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1.1E: Publishing Scientific Work

Learning Objectives

- Describe the role played by peer-reviewed scientific articles

Reporting Scientific Work

Scientists must share their findings in order for other researchers to expand and build upon their discoveries. Collaboration with other scientists—when planning, conducting, and analyzing results—are all important for scientific research. For this reason, a major aspect of a scientist's work is communicating with peers and disseminating results to peers. Scientists can share results by presenting them at a scientific meeting or conference, but this approach can reach only the select few who are present. Instead, most scientists present their results in peer-reviewed manuscripts that are published in scientific journals. Peer-reviewed manuscripts are scientific papers that are reviewed by a scientist's colleagues or peers. These colleagues are qualified individuals, often experts in the same research area, who judge whether or not the scientist's work is suitable for publication. The process of peer review helps to ensure that the research described in a scientific paper or grant proposal is original, significant, logical, and thorough. Grant proposals, which are requests for research funding, are also subject to peer review. Scientists publish their work so other scientists can reproduce their experiments under similar or different conditions to expand on the findings. The experimental results must be consistent with the findings of other scientists.



Figure 1.1*E*.1: Scientific Journal: Scientific research is published in peer-reviewed scientific journals.

A scientific paper is very different from creative writing. Although creativity is required to design experiments, there are fixed guidelines when it comes to presenting scientific results. Scientific writing must be brief, concise, and accurate. It needs to be succinct but detailed-enough to allow peers to reproduce the experiments.

The scientific paper consists of several specific sections: introduction, materials and methods, results, and discussion. This structure is sometimes called the "IMRaD" format. There are usually acknowledgment and reference sections, as well as an abstract (a concise summary) at the beginning of the paper. There might be additional sections depending on the type of paper and the journal where it will be published; for example, some review papers require an outline.

The introduction starts with brief, but broad, background information about what is known in the field. A good introduction also gives the rationale and justification for the work. The introduction refers to the published scientific work of others and, therefore, requires citations following the style of the journal. Using the work or ideas of others without proper citation is considered plagiarism.

The materials and methods section includes a complete and accurate description of the substances and the techniques used by the researchers to gather data. The description should be thorough, yet concise, while providing enough information to allow another researcher to repeat the experiment and obtain similar results. This section will also include information on how measurements were made and what types of calculations and statistical analyses were used to examine raw data. Although the materials and methods section gives an accurate description of the experiments, it does not discuss them.

Journals may require separate results and discussion sections, or it may combine them in one section. If the journal does not allow the combination of both sections, the results section simply narrates the findings without any further interpretation. The results are presented by means of tables or graphs, but no duplicate information should be presented. In the discussion section, the researcher will interpret the results, describe how variables may be related, and attempt to explain the observations. It is indispensable to

conduct an extensive literature search to put the results in the context of previously-published scientific research. Therefore, proper citations are included in this section as well.

Finally, the conclusion section summarizes the importance of the experimental findings. While the scientific paper almost certainly answered one or more scientific questions that were stated, any good research should lead to more questions. A well-written scientific paper leaves doors open for the researcher and others to continue and expand on the findings.

Review articles do not follow the IMRAD format because they do not present original scientific findings or primary literature. Instead, they summarize and comment on findings that were published as primary literature. They typically include extensive reference sections.

Key Points

- The body of scientific knowledge is recorded in peer-reviewed science journals which allow other scientists to determine what has been done previously and where their own research fits in the larger field of study.
- A scientific article generally follows the steps of the scientific method: introduction (background, observations, question), materials and methods (hypothesis and experimental plan), results (analysis of collected data), and discussion (conclusions drawn from analysis).
- Peer reviewers are other researchers in that field of study who carefully dissect, analyze, and critique a research article submitted for publication.
- Review articles (summaries and commentaries on prior research in a field of study) also go through the peer-review process.

Key Terms

- **peer review**: The scholarly process whereby manuscripts intended to be published in an academic journal are reviewed by independent researchers to evaluate the contribution, importance, and accuracy of the manuscript's contents.

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1.1F: Branches and Subdisciplines of Biology

Learning Objectives

- Recognize the various subfields of biology; e.g. microbiology, genetics, evolutionary, etc.

Branches of Biological Study

The scope of biology is broad and therefore contains many branches and subdisciplines. Biologists may pursue one of those subdisciplines and work in a more focused field. The biological branches are divided according to the focus of the discipline and can even be divided based on the types of techniques and tools used to study that specific focus. However, with the increasing amount of basic biological information growing due to advances in technology and databases, there is often cross-discipline and collaboration between branches. For instance, molecular biology and biochemistry study biological processes at the molecular and chemical level, respectively, including interactions among molecules such as DNA, RNA, and proteins, as well as the way they are regulated. Microbiology, the study of microorganisms, is the study of the structure and function of single-celled organisms. It is quite a broad branch itself, and depending on the subject of study, there are also microbial physiologists, ecologists, and geneticists, among others.

Biological Disciplines and Careers

Forensic science is the application of science to answer questions related to the law. Biologists as well as chemists and biochemists can be forensic scientists. Forensic scientists provide scientific evidence for use in courts, and their job involves examining trace materials associated with crimes.Their job activities are primarily related to crimes against people such as murder, rape, and assault. Their work involves analyzing samples such as hair, blood, and other body fluids, including the processing of DNA found in many different environments and materials associated with the crime scenes.

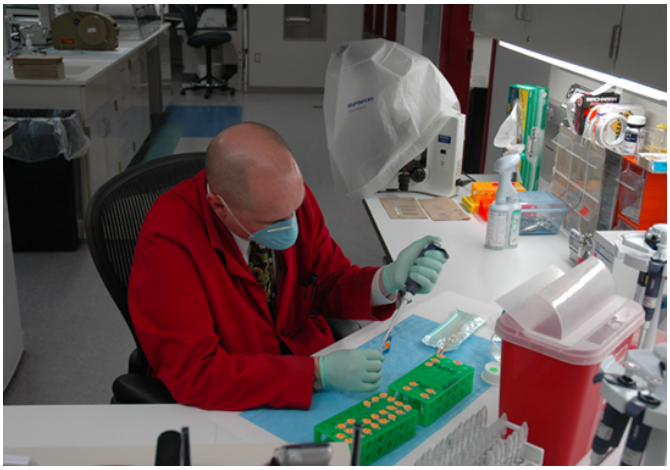


Figure 1.1*F*.1: Forensic Science: This forensic scientist works in a DNA extraction room at the U.S. Army Criminal Investigation Laboratory at Fort Gillem, GA.

Another field of biological study, neurobiology, is the study of the nervous system, and although it is considered a branch of biology, it is also recognized as an interdisciplinary field of study known as neuroscience. Because of its interdisciplinary nature, this subdiscipline focuses on different functions of the nervous system using molecular, cellular, developmental, medical, and computational approaches.

Additional branches of biology include paleontology, which uses fossils to study life's history; zoology, which studies animals; and botany, which studies plants. Biologists can also specialize as biotechnologists, ecologists, or physiologists. This is just a small sample of the many fields that biologists can pursue.



Figure 1.1*F*.1: Paleontology: Researchers work on excavating dinosaur fossils at a site in Castellón, Spain.

Biology is the culmination of the achievements of the natural sciences from their inception to today. Excitingly, it is the cradle of emerging sciences such as the biology of brain activity, genetic engineering of custom organisms, and the biology of evolution that uses the laboratory tools of molecular biology to retrace the earliest stages of life on earth. A scan of news headlines—whether reporting on immunizations, a newly discovered species, sports doping, or a genetically-modified food—demonstrates the way biology is active in and important to our everyday world.

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Key Points

- Biology is broad and focuses on the study of life from various perspectives.
- The branches and subdisciplines of biology, which are highly focused areas, have resulted in the development of careers that are specific to these branches and subdisciplines.
- Branches of biological study include microbiology, physiology, ecology and genetics; subdisciplines within these branches can include: microbial physiology, microbial ecology and microbial genetics.

Key Terms

- **genetic engineering**: the deliberate modification of the genetic structure of an organism
- **forensic**: Relating to the use of science and technology in the investigation and establishment of facts or evidence in a court of law.

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1.2: Themes and Concepts of Biology

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1.2A: Properties of Life

Learning Objectives

- Describe the properties of life

All living organisms share several key characteristics or functions: order, sensitivity or response to the environment, reproduction, growth and development, regulation, homeostasis, and energy processing. When viewed together, these eight characteristics serve to define life.



Figure 1.2A.1: Multicellular Organisms: A toad represents a highly organized structure consisting of cells, tissues, organs, and organ systems.

Order

Organisms are highly organized, coordinated structures that consist of one or more cells. Even very simple, single-celled organisms are remarkably complex: inside each cell, atoms make up molecules; these in turn make up cell organelles and other cellular inclusions. In multicellular organisms, similar cells form tissues. Tissues, in turn, collaborate to create organs (body structures with a distinct function). Organs work together to form organ systems.



Figure 1.2A.2: Response to Stimuli: The leaves of this sensitive plant (Mimosa pudica) will instantly droop and fold when touched. After a few minutes, the plant returns to normal.

Sensitivity or Response to Stimuli

Organisms can respond to diverse stimuli. For example, plants can grow toward a source of light, climb on fences and walls, or respond to touch. Even tiny bacteria can move toward or away from chemicals (a process called chemotaxis) or light (phototaxis). Movement toward a stimulus is considered a positive response, while movement away from a stimulus is considered a negative response.

Reproduction

Single-celled organisms reproduce by first duplicating their DNA. They then divide it equally as the cell prepares to divide to form two new cells. Multicellular organisms often produce specialized reproductive germline cells that will form new individuals. When

reproduction occurs, genes containing DNA are passed along to an organism's offspring. These genes ensure that the offspring will belong to the same species and will have similar characteristics, such as size and shape.



Figure 1.2A.3: Reproduction: Although no two look alike, these kittens have inherited genes from both parents and share many of the same characteristics.

Growth and Development

All organisms grow and develop following specific instructions coded for by their genes. These genes provide instructions that will direct cellular growth and development, ensuring that a species' young will grow up to exhibit many of the same characteristics as its parents.

Regulation

Even the smallest organisms are complex and require multiple regulatory mechanisms to coordinate internal functions, respond to stimuli, and cope with environmental stresses. Two examples of internal functions regulated in an organism are nutrient transport and blood flow. Organs (groups of tissues working together) perform specific functions, such as carrying oxygen throughout the body, removing wastes, delivering nutrients to every cell, and cooling the body.



Figure 1.2A.4: Homeostasis: Polar bears (Ursus maritimus) and other mammals living in ice-covered regions maintain their body temperature by generating heat and reducing heat loss through thick fur and a dense layer of fat under their skin.

Homeostasis

In order to function properly, cells need to have appropriate conditions such as proper temperature, pH, and appropriate concentration of diverse chemicals. These conditions may, however, change from one moment to the next. Organisms are able to maintain internal conditions within a narrow range almost constantly, despite environmental changes, through homeostasis (literally, "steady state")—the ability of an organism to maintain constant internal conditions. For example, an organism needs to regulate body temperature through a process known as thermoregulation. Organisms that live in cold climates, such as the polar bear, have body structures that help them withstand low temperatures and conserve body heat. Structures that aid in this type of insulation include fur, feathers, blubber, and fat. In hot climates, organisms have methods (such as perspiration in humans or panting in dogs) that help them to shed excess body heat.



Figure 1.2A.5: Energy Processing: The California condor (Gymnogyps californianus) uses chemical energy derived from food to power flight.

Energy Processing

All organisms use a source of energy for their metabolic activities. Some organisms capture energy from the sun and convert it into chemical energy in food; others use chemical energy in molecules they take in as food.



Figure 1.2A.6: Adaptation in the flat-tailed horned lizard: This lizard exhibits a flattened body and coloring that helps camouflage it, both of which are adaptive traits that help it avoid predators.

Evolution

As a population of organisms interacts with the environment, individuals with traits that contribute to reproduction and survival in that particular environment will leave more offspring. Over time those advantageous traits (called adaptations) will become more common in the population. This process, change over time, is called evolution, and it is one of the processes that explain the diverse species seen in biology. Adaptations help organisms survive in their ecological niches, and adaptive traits may be structural, behavioral, or physiological; as such, adaptations frequently involve other properties of organisms such as homeostasis, reproduction, and growth and development.

Key Points

- Order can include highly organized structures such as cells, tissues, organs, and organ systems.
- Interaction with the environment is shown by response to stimuli.
- The ability to reproduce, grow and develop are defining features of life.
- The concepts of biological regulation and maintenance of homeostasis are key to survival and define major properties of life.
- Organisms use energy to maintain their metabolic processes.
- Populations of organisms evolve to produce individuals that are adapted to their specific environment.

Key Terms

- **phototaxis**: The movement of an organism either towards or away from a source of light
- **gene**: a unit of heredity; the functional units of chromosomes that determine specific characteristics by coding for specific proteins
- **chemotaxis**: the movement of a cell or an organism in response to a chemical stimulant

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1.2B: Levels of Organization of Living Things

Learning Objectives

- Describe the biological levels of organization from the smallest to highest level

Living things are highly organized and structured, following a hierarchy that can be examined on a scale from small to large. The atom is the smallest and most fundamental unit of matter. It consists of a nucleus surrounded by electrons. Atoms form molecules which are chemical structures consisting of at least two atoms held together by one or more chemical bonds. Many molecules that are biologically important are macromolecules, large molecules that are typically formed by polymerization (a polymer is a large molecule that is made by combining smaller units called monomers, which are simpler than macromolecules). An example of a macromolecule is deoxyribonucleic acid (DNA), which contains the instructions for the structure and functioning of all living organisms.

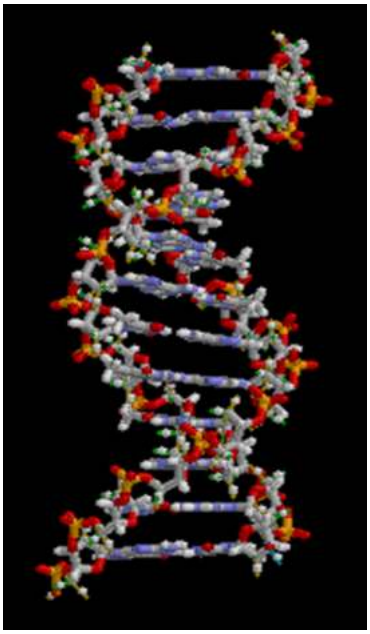


Figure 1.2*B*.1: DNA: All molecules, including this DNA molecule, are composed of atoms.

From Organelles to Biospheres

Macromolecules can form aggregates within a cell that are surrounded by membranes; these are called organelles. Organelles are small structures that exist within cells. Examples of these include: mitochondria and chloroplasts, which carry out indispensable functions. Mitochondria produce energy to power the cell while chloroplasts enable green plants to utilize the energy in sunlight to make sugars. All living things are made of cells, and the cell itself is the smallest fundamental unit of structure and function in living organisms. (This requirement is why viruses are not considered living: they are not made of cells. To make new viruses, they have to invade and hijack the reproductive mechanism of a living cell; only then can they obtain the materials they need to reproduce.) Some organisms consist of a single cell and others are multicellular. Cells are classified as prokaryotic or eukaryotic. Prokaryotes are single-celled or colonial organisms that do not have membrane-bound nuclei; in contrast, the cells of eukaryotes do have membrane-bound organelles and a membrane-bound nucleus.

In larger organisms, cells combine to make tissues, which are groups of similar cells carrying out similar or related functions. Organs are collections of tissues grouped together performing a common function. Organs are present not only in animals but also in plants. An organ system is a higher level of organization that consists of functionally related organs. Mammals have many organ systems. For instance, the circulatory system transports blood through the body and to and from the lungs; it includes organs such as the heart and blood vessels. Furthermore, organisms are individual living entities. For example, each tree in a forest is an

organism. Single-celled prokaryotes and single-celled eukaryotes are also considered organisms and are typically referred to as microorganisms.

All the individuals of a species living within a specific area are collectively called a population. For example, a forest may include many pine trees. All of these pine trees represent the population of pine trees in this forest. Different populations may live in the same specific area. For example, the forest with the pine trees includes populations of flowering plants and also insects and microbial populations. A community is the sum of populations inhabiting a particular area. For instance, all of the trees, flowers, insects, and other populations in a forest form the forest's community. The forest itself is an ecosystem. An ecosystem consists of all the living things in a particular area together with the abiotic, non-living parts of that environment such as nitrogen in the soil or rain water. At the highest level of organization, the biosphere is the collection of all ecosystems, and it represents the zones of life on earth. It includes land, water, and even the atmosphere to a certain extent. Taken together, all of these levels comprise the biological levels of organization, which range from organelles to the biosphere.

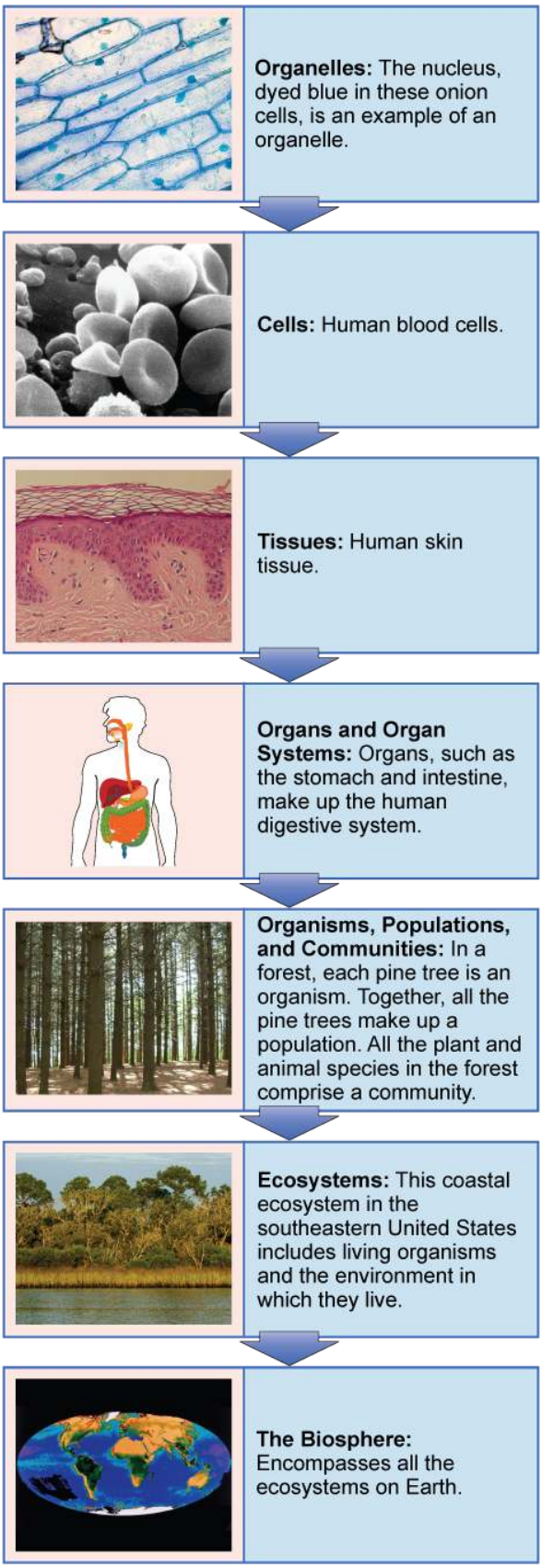


Figure 1.2*B*.1: Biological Levels of Organization: The biological levels of organization of living things follow a hierarchy, such as the one shown. From a single organelle to the entire biosphere, living organisms are part of a highly structured hierarchy.

Key Points

- The atom is the smallest and most fundamental unit of matter. The bonding of at least two atoms or more form molecules.
- The simplest level of organization for living things is a single organelle, which is composed of aggregates of macromolecules.
- The highest level of organization for living things is the biosphere; it encompasses all other levels.
- The biological levels of organization of living things arranged from the simplest to most complex are: organelle, cells, tissues, organs, organ systems, organisms, populations, communities, ecosystem, and biosphere.

Key Terms

- **molecule**: The smallest particle of a specific compound that retains the chemical properties of that compound; two or more atoms held together by chemical bonds.
- **macromolecule**: a very large molecule, especially used in reference to large biological polymers (e.g. nucleic acids and proteins)
- **polymerization**: The chemical process, normally with the aid of a catalyst, to form a polymer by bonding together multiple identical units (monomers).

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1.2C: The Diversity of Life

Learning Objectives

- Recognize the three major domains used for classification

The fact that biology has such a broad scope as a science has to do with the tremendous diversity of life on Earth. The source of this diversity is evolution, the process of gradual change during which new species arise from older species. Evolutionary biologists study the evolution of living things in everything from the microscopic world to ecosystems.

The evolution of various life forms on Earth can be summarized in a phylogenetic tree using phylogeny. A phylogenetic tree is a diagram showing the evolutionary relationships among biological species based on similarities and differences in genetic or physical traits or both. A phylogenetic tree is composed of nodes and branches. The internal nodes represent ancestors and are points in evolution when, based on scientific evidence, an ancestor is thought to have diverged to form two new species. The length of each branch is proportional to the time elapsed since the split.

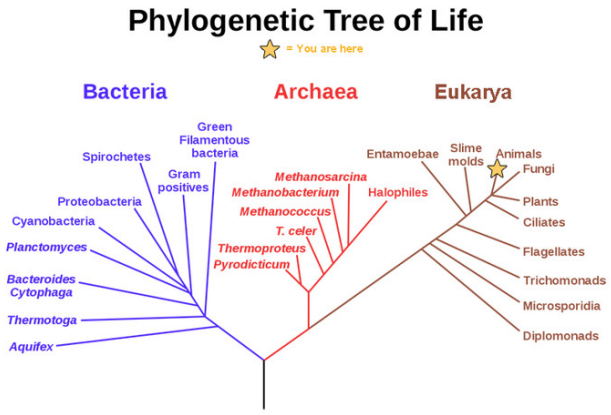


Figure 1.2C.1: Phylogenetic Tree of Life: This phylogenetic tree was constructed by microbiologist Carl Woese using data obtained from sequencing ribosomal RNA genes. The tree shows the separation of living organisms into three domains: Bacteria, Archaea, and Eukarya. Bacteria and Archaea are prokaryotes, single-celled organisms lacking intracellular organelles.

Carl Woese and the Phylogenetic Tree

In the past, biologists grouped living organisms into five kingdoms: animals, plants, fungi, protists, and bacteria. The organizational scheme was based mainly on physical features, as opposed to physiology, biochemistry, or molecular biology, all of which are used by modern systematics. The pioneering work of American microbiologist Carl Woese in the early 1970s has shown, however, that life on Earth has evolved along three lineages, now called domains—Bacteria, Archaea, and Eukarya. The first two are prokaryotic cells with microbes that lack membrane-enclosed nuclei and organelles. The third domain contains the eukaryotes and includes unicellular microorganisms together with the four original kingdoms (excluding bacteria). Woese defined Archaea as a new domain, and this resulted in a new taxonomic tree. Many organisms belonging to the Archaea domain live under extreme conditions and are called extremophiles. To construct his tree, Woese used genetic relationships rather than similarities based on morphology (shape).

Woese's tree was constructed from comparative sequencing of the genes that are universally distributed, present in every organism, and conserved (meaning that these genes have remained essentially unchanged throughout evolution). Woese's approach was revolutionary because comparisons of physical features are insufficient to differentiate between the prokaryotes that appear fairly similar in spite of their tremendous biochemical diversity and genetic variability. The comparison of homologous DNA and RNA sequences provided Woese with a sensitive device that revealed the extensive variability of prokaryotes, and which justified the separation of the prokaryotes into two domains: bacteria and archaea. DNA, the universal genetic material, contains the instructions for the structure and function of all living organisms and can be divided into genes whose expression varies between organisms. The RNA, which is transcribed from DNA, varies between organisms as well based on the expression of specific genes. Thus, to examine differences at this molecular level provides a more accurate depiction of the diversity which exists.

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Key Points

- The three major Domains of Life include: Domain Bacteria, Domain Eukarya and Domain Archaea.
- Domain Bacteria and Domain Archaea include prokaryotic cells that lack membrane-enclosed nuclei and organelles.

- Domain Eukarya include eukaryotes and more complex organisms that contain membrane-bound nuclei and organelles.
- Carl Woese defined Archaea as a new domain and constructed the phylogentic tree of life which shows separation of all living organisms.
- The phylogenetic tree of life was constructed by Carl Woese using sequencing data of ribosomal RNA genes. Therefore, genetics classification surpassed morphological cataloguing, which was the traditional way of organizing living beings.

Key Terms

- **phylogeny**: the evolutionary history of an organism
- **extremophile**: an organism that lives under extreme conditions of temperature, salinity, etc; commercially important as a source of enzymes that operate under similar conditions
- **DNA**: a biopolymer of deoxyribonucleic acids (a type of nucleic acid) that has four different chemical groups, called bases: adenine, guanine, cytosine, and thymine

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CHAPTER OVERVIEW

2: Measurements and Problem-Solving

2.1: Measurements Matter

2.2: Significant Figures

2.3: Scientific Dimensional Analysis

2.4: Percentages

2.5: Measurements and Problem-Solving (Exercises)

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2.1: Measurements Matter

Learning Outcomes

- Demonstrate use of scientific notation.
- Identify base and derived units for measurements.
- Memorize the metric prefixes, abbreviations, and values (Tables 1.1.1 and 1.1.3).
- Convert between temperatures in Celsius and Fahrenheit.

Many aspects of chemistry use quantitative measurements to describe behavior. In this section, we will look at how we deal with very large or very small numbers, units of measure and prefixes used with these units, and how numbers are reported.

Scientific Notation

Scientific notation is a way to express numbers as the product of two numbers: a coefficient and the number 10 raised to a power. It is a very useful tool for working with numbers that are either very large or very small. As an example, the distance from Earth to the Sun is about 150,000,000,000 meters - a very large distance indeed. In scientific notation, the distance is written as $1.5 \times 10^{11}\ \mathrm{m}$. The coefficient is the 1.5 and must be a number greater than or equal to 1 and less than 10. The power of 10, or exponent, is 11 because you would have to multiply 1.5 by 10^{11} to get the correct number. Scientific notation is sometimes referred to as exponential notation.

When working with small numbers, we use a negative exponent. So 0.1 meters is 1×10^{-1} meters, 0.01 is 1×10^{-2} and so forth. A red blood cell has a diameter of 0.000008 meters which is neither convenient to write nor say. It is much easier to report a diameter of $8 \times 10^{-6}\ \mathrm{m}$. Using scientific notation is one way to make writing very large or very small numbers more convenient. Note the use of a **leading zero** (the zero to the left of the decimal point) when writing very small numbers. The leading zero is there to help you see the decimal point more clearly. The figure 0.01 is less likely to be misunderstood that .01 where you may not see the decimal point.

Units

SI Base Units

All measurements depend on the use of units that are all well known and understood. The **English system** of measurement units (inches, feet, ounces, etc.) are not used in science because of the difficulty in converting from one unit to another. The **metric system** is used because all metric units are based on multiples of 10, making conversions very simple. The metric system was originally established in France in 1795. **The International System of Units** is a system of measurement based on the metric system. The acronym **SI** is commonly used to refer to this system and stands for the French term, *Le Système International d'Unités*. The SI was adopted by international agreement in 1960 and is composed of seven base units, five of which are shown in the table below. While some of the base units have a calculation as their standard, the kilogram has a physical standard but there is a movement to change that. Read or listen to more about changes to the standard at http://www.npr.org/templates/story/s...ryId=112003322.

Table 2.1.1: SI Base Units of Measurement

Quantity	SI Base Unit	Symbol
Length	meter	m
Mass	kilogram	kg
Temperature	kelvin	K
Time	second	s
Amount of a Substance	mole	mol

These five units are frequently encountered in chemistry and other units of measurement, such as volume, force, and energy, can be derived from the SI base units.



Figure 2.1.1: *The standard for the unit kilogram is stored in France.*

The map in the figure below shows the adoption of the SI units in countries around the world. The United States has legally adopted the metric system for measurements, but does not use it in everyday practice. Great Britain and much of Canada use a combination of metric and imperial units.



Figure 2.1.2: Countries which use the metric system.

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. These derived units are the standard for these quantities but they are not always the units used in normal practice. For example, the density of a solid or a liquid is often reported as $\mathrm{g/cm^3}$, or $\mathrm{g/mL}$ rather than $\mathrm{kg/m^3}$ (the derived SI unit). Some common examples of derived units are listed in the table below.

Table 2.1.2: Derived SI Units

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

Metric Prefixes

Conversions between metric system units are straightforward because the system is based on powers of ten. For example, meters, centimeters, and millimeters are all metric units of length. There are 10 millimeters in 1 centimeter and 100 centimeters in 1 meter. **Metric prefixes** are used to distinguish between units of different size. These prefixes all derive from either Latin or Greek terms. For example, *mega* comes from the Greek word $\mu\epsilon\gamma\alpha\varsigma$, meaning "great".

The table below lists the most common metric prefixes and their relationship to the base unit that has no prefix. Length is used as an example to demonstrate the relative size of each prefixed unit. However, these prefixes can be used with *any* base unit.

Table 2.1.3: SI Prefixes

Prefix	Unit Abbreviation	Meaning	Example
giga	G	1,000,000,000	1 gigameter $(\mathrm{Gm}) = 10^9\ \mathrm{m}$
mega	M	1,000,000	1 megameter $(\mathrm{Mm}) = 10^6\ \mathrm{m}$
kilo	k	1,000	1 kilometer $(\mathrm{km}) = 1,000\ \mathrm{m}$
		1	**1 meter** (m)
deci	d	1/10	1 decimeter $(\mathrm{dm}) = 0.1\ \mathrm{m}$
centi	c	1/100	1 centimeter $(\mathrm{cm}) = 0.01\ \mathrm{m}$
milli	m	1/1,000	1 millimeter $(\mathrm{mm}) = 0.001\ \mathrm{m}$
micro	μ	1/1,000,000	1 micrometer $(\mu\mathrm{m}) = 10^{-6}\ \mathrm{m}$
nano	n	1/1,000,000,000	1 nanometer $(\mathrm{nm}) = 10^{-9}\ \mathrm{m}$

*Micro is often abbreviated "mc" in healthcare to avoid confusion between the μ and m which often look similar when written by hand.

There are more prefixes, some of them rarely used, that go far beyond what is given here. Have you ever heard of a zeptometer? You can learn more about prefixes at http://www.bipm.org/en/measurement-units/

Since the metric system is not the usual unit system we use, it can be challenging to understand the relative size of each unit. Go to http://learn.genetics.utah.edu/content/cells/scale and use the slider below the image to zoom in and see how the sizes of objects compare.

There are a couple of odd little practices with the use of unit abbreviations. Most abbreviations are lower-case. We use "m" for meter and not "M". However, when it comes to volume, the base unit "liter" is abbreviated as "L" and not "l". So we would write 3.5 milliliters as $3.5\ \mathrm{mL}$.

As a practical matter, whenever possible you should express the units in a small and manageable number. If you are measuring the weight of a material that weighs $6.5\ \mathrm{kg}$, this is easier than saying it weighs $6500\ \mathrm{g}$. Both are correct, bu the kg units in this case make for a small and easily managed number.

Temperature Scales

There are three temperature scales that are commonly used in measurement. Their units are $^{\circ}\mathrm{F}$ (degrees Fahrenheit), $^{\circ}\mathrm{C}$ (degrees Celsius), and K (Kelvin). The **Fahrenheit scale**, which is the most commonly used scale in the United States, defines the normal freezing point and boiling point of water as $32^{\circ}\mathrm{F}$ and $212^{\circ}\mathrm{F}$, respectively. The **Celsius scale** defines the normal freezing point and boiling point of water as $0^{\circ}\mathrm{C}$ and $100^{\circ}\mathrm{C}$, respectively. The Celsius scale is commonly used in most countries across the globe. The **Kelvin scale**, which is also referred to as the absolute temperature scale, defines absolute zero as the lowest theoretically possible temperature, which means that temperatures expressed in Kelvin cannot be negative numbers.

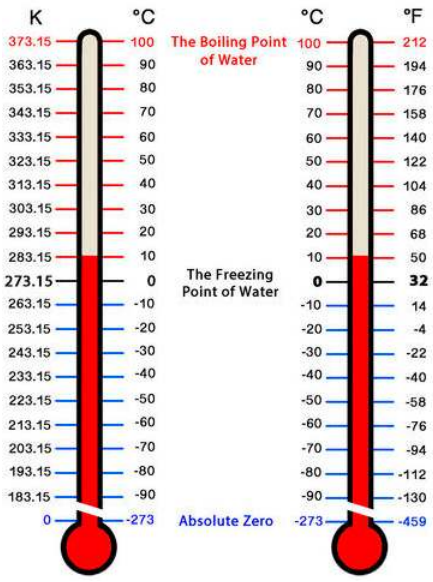


Figure 2.1.3: Comparison of Kelvin, Celsius on a Fahrenheit scale.

Converting Temperature Scales

Regardless of the temperature scale used, it is important to be able to convert from one scale to another. Here are the conversions we use.

°F to °C

$$T_{°\mathrm{C}} = (T_{°\mathrm{F}} - 32) \times \frac{5}{9} \tag{2.1.1}$$

°C to °F

$$T_{°\mathrm{F}} = \frac{9}{5} \times (T_{°\mathrm{C}}) + 32 \tag{2.1.2}$$

°C to K

$$T_{\mathrm{K}} = T_{°\mathrm{C}} + 273.15 \tag{2.1.3}$$

K to °C

$$T_{°\mathrm{C}} = T_{\mathrm{K}} - 273.15 \tag{2.1.4}$$

Example 2.1.1

The melting point of mercury is $-38.84°\mathrm{C}$. Convert this value to degrees Fahrenheit and Kelvin.

Solution

The formulas above can be used to convert among temperature units. First, the given value can be used to convert from °C to °F.

$$T_{°\mathrm{F}} = \frac{9}{5} \times (-38.84°\mathrm{C}) + 32$$
$$T_{°\mathrm{F}} = -37.91°\mathrm{F}$$

Then, the same initial temperature can be used to find the temperature in Kelvin.

$$T_{\mathrm{K}} = -38.84°\mathrm{C} + 273.15$$
$$T_{\mathrm{K}} = 234.75\ \mathrm{K}$$

Supplemental Resources

- Scientific notation practice: http://www.mathisfun.com/numbers/sci...-notation.html
- History of SI Units: http://physics.nist.gov/cuu/Units/history.html

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2.2: Significant Figures

Learning Outcomes

- Distinguish between accuracy and precision.
- Explain the concept of significant figures.
- Report answers to calculations with the correct number of significant figures.

In chemistry, we are looking at measurements and not just numbers. Therefore, it is necessary to be able to count the number of significant figures and report measurements to the correct level of precision. The reported value should be as precise as possible without adding digits to a value that cannot be measured.

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 (see figure below).

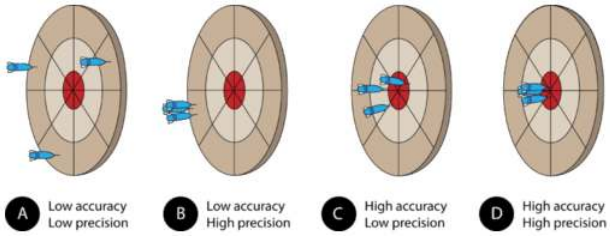


Figure 2.2.3: Distribution of darts on a dartboard to represent precision and accuracy.

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. Pictured above are the 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 they are generally centered around the bulls-eye. This demonstrates poor precision but fairly high accuracy. This situation is not desirable because in a lab situation, we do not know where the "bulls-eye" actually is. Continuing with this analogy, measurements are taken in order to find the bulls-eye. If we could only see the locations of the darts and not the bulls-eye, the large spread would make it difficult to be confident about where the exact center was, even if we knew that the darts were thrown accurately (which would correspond to having equipment that is calibrated and operated correctly).

(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. Turning back to our laboratory situation, where we can see the darts but not the bulls-eye, we have a much narrower range of possibilities for the exact center than in the less precise situation depicted in part C.

Significant Figures in Measurements

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. Pictured below is an object (indicated by the blue arrow) whose length is being measured by two different rulers.

With either ruler, it is clear that the length of the object is between 2 and 3 centimeters. The bottom ruler contains no millimeter markings, so the tenths digit can only be estimated, and the length may be reported by one observer 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). Now, 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.

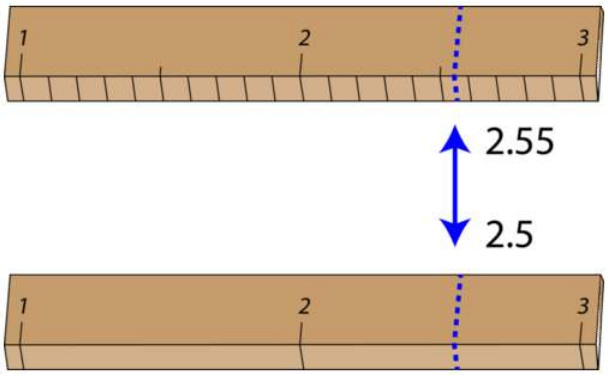


Figure $2.2.4$: Measurements can be more or less precise depending on the markings on the ruler.

Again, another measurer may report the length to be 2.54 cm or 2.66 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.

The **significant figures** in a measurement consist of all the certain digits in that measurement plus one uncertain (estimated) digit. In a correctly reported measurement, the final digit is significant but not certain. Insignificant digits are not reported.

Rules for Determination of Significant Figures

1. All nonzero digits are significant.

- 237 has three significant figures
- 1.897 has four significant figures

2. Zeroes between significant figures are significant.

- 39004 has five significant figures
- 2.03 has three significant figures

3. Zeroes that appear to the left of all of the nonzero digits are called placeholder zeroes and are not significant.

- 0.008 has one significant figure
- 0.0000416 has three significant figures

4. Zeroes that appear after the last nonzero digit may be significant.

a. If the number is greater than 1 and the zero(es) are not followed by a decimal point, then the number of significant figures is ambiguous.

- 140 is ambiguous

b. If the zero is followed by a decimal point, then the zero is significant.

- 140. has three significant figures (note the decimal point after the zero)

c. If the zero is after a decimal point, then the zero is significant.

- 141.0 has four significant figures

It needs to be emphasized that just because a certain digit is not significant does not mean that it is not important or that it 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 or as 1.40×10^3, with three significant figures. A number less than one, such as 0.000416, can be written in scientific notation as 4.16×10^{-4}, which has 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 15,000,00 with four significant figures, it would need to be written as 1.500×10^7.

Exact Quantities

When numbers are known exactly, the significant figure rules do not apply. This occurs when objects are counted rather than measured. For example, a carton of eggs has 12 eggs. The actual value cannot be 11.8 eggs, since we count eggs in whole number quantities. So the 12 is an exact quantity. Exact quantities are considered to have an infinite number of significant figures; the importance of this concept will be seen later when we begin looking at how significant figures are dealt with during calculations. Numbers in many conversion factors, especially for simple unit conversions, are also exact quantities and have infinite significant figures. There are exactly 100 centimeters in 1 meter and exactly 60 seconds in 1 minute. Those values are definitions and are not the result of a measurement.

Calculations

Adding and Subtracting Significant Figures

The sum or difference is determined by the smallest number of digits to the right of the decimal point in any of the original numbers.

Example 2.2.1

What is the result of $89.332 + 1.1$ when answered to the correct number of significant figures?

Solution

The mathematical result is $89.332 + 1.1 = 90.432$. However, we need to round the answer to the correct number of significant figures. For addition and subtraction, the answer should have the same number of decimal places as the starting value with the *least* number of decimal places. Since 1.1 only has one digit after the decimal place, the answer will be rounded to one decimal place. The first digit to be dropped is less than five so we round down.

The correct answer is 90.4.

Multiplying and Dividing Significant Figures

The number of significant figures in the final product or quotient is equal to the number of significant figures in the starting value that has the fewest significant figures.

Example 2.2.2

What is the product of 2.8 and 4.5039 reported to the correct number of significant figures?

Solution

First, we find the mathematical answer to the calculation which is $2.8 \times 4.5039 = 12.61092$. Next, we need to round the answer to the correct number of significant figures. For multiplication and division, the answer should be rounded to that it has the same number of significant figures as the starting value with the least number of significant figures. The value 2.8 has two significant figures while 4.5039 has five. Therefore, the answer should have two significant figures so we should round the answer to 13 because the first digit to be dropped is greater than 5, so we need to round up.

Example 2.2.3

A bag of chocolate candies has a mass of 8.25 ounces. The candies were to be divided among 4 people. How many ounces should each person get? Report your answer to the correct number of significant figures.

Solution

First, we'll find the mathematical answer to this calculation: $8.25 \div 4 = 2.0625$. Now, we need to round to the correct number of significant figures so we look back at the starting values. There are three significant figures in 8.25 but 4 is an exact number so it is not considered when determining the number of significant figures in the answer. Therefore, the answer should be rounded to three significant figures or 2.06 ounces.

Supplemental Resources

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2.3: Scientific Dimensional Analysis

Learning Outcomes

- Convert values among units.
- Use dimensional analysis to solve problems.

Dimensional analysis (also called factor label method or unit analysis) is used to convert from one set of units to another. This method is used for both simple (feet to inches) and complex ($\mathrm{g/cm^3}$ to kg/gallon) conversions and uses relationships or conversion factors between different sets of units. While the terms are frequently used interchangeably, conversion factors and relationships are different. Conversion factors are quantities that are equal to one another, such as $100\ \mathrm{cm} = 1\ \mathrm{m}$, in which both values describe a length. Relationships are between two values that are not necessarily a measure of the same quantity. For example, the density of water is $1.00\ \mathrm{g/mL}$. Grams are a measure of mass while milliliters measure volume so this is considered a relationship rather than a conversion factor. Either way, we depend on units to help set up and solve the calculation. We will see additional examples of relationships as we explore other details about chemical substance.

Importance of using Correct Conversions

In healthcare professions, a calculation error can quite literally have a life or death consequence. Read the short article, Med-Math Errors and the Nursing Student at http://www.alysion.org/dimensional/matherrors.htm, to better understand the importance of units and correct calculations.

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. $4\ \mathrm{cups} = 2\ \mathrm{pints} = 1\ \mathrm{quart} = 0.25\ \mathrm{gallon}$. Notice that the numerical component of each quantity is different, while the actual amount of material that it represents is the same. That is because the units are different. We can establish the same set of equalities for the metric system: $1\ \mathrm{meter} = 10\ \mathrm{decimeters} = 100\ \mathrm{centimeters} = 1000\ \mathrm{millimeters}$. The metric system's use of powers of 10 for all conversions makes this quite simple. We can write conversion factors between any pair of equivalent quantities. In each conversion factor, the numerator and denominator represent equal quantities so they are all valid conversion factors. Additionally, these conversion factors can be inverted or used in combination with other conversion factors in a dimensional analysis problem.

$$\frac{4\ \mathrm{cups}}{2\ \mathrm{pints}} = \frac{1\ \mathrm{quart}}{4\ \mathrm{cups}} = \frac{0.25\ \mathrm{gallen}}{1\ \mathrm{quarter}} = 1$$

$$\frac{1\ \mathrm{meter}}{10\ \mathrm{decimeters}} = \frac{100\ \mathrm{centimeters}}{1000\ \mathrm{milimeters}} = \frac{1000\ \mathrm{milimeters}}{1\ \mathrm{meter}} = 1$$

Example 2.3.1

How many centimeters are in $3.4\ \mathrm{m}$?

Solution

This problem requires the conversion from one unit to another so we can use dimensional analysis to solve the problem. We need to identify the units that are given (m), the units for the answer (cm), and any relationships that relate the units of the known and unknown values. In this case, we will use the relationship of $1\ \mathrm{m} = 100\ \mathrm{cm}$. Start with the known value and its unit.

$$3.4\ \mathrm{m} \times \frac{?}{?}$$

Then, we look at the units of our relationship to see which value goes in the numerator and which value goes in the denominator. Remember, we are trying to find the value in centimeters. Since our known value is in units of meters, we need meters to be in the denominator so that it will cancel. As a result, centimeters will be in the numerator.

$$3.4\ \mathrm{m} \times \frac{100\ \mathrm{cm}}{1\ \mathrm{m}}$$

Note that the numbers stay with the appropriate unit (100 with centimeters and 1 with meters). Now, the meters will cancel out and we are left with units of centimeters. Always check that your problem is set up completely and that your units cancel correctly before you do the actual calculation.

$$3.4 \cancel{\text{ m}} \times \frac{100 \text{ cm}}{1 \cancel{\text{ m}}} = 340 \text{ cm}$$

$$= 3.4 \times 10^2 \text{ cm}$$

We find the answer to be 340 cm or $3.4 \times 10^2 \text{ cm}$.

Derived Units

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 or cubed. Two convenient volume units are the liter, which is equal to a cubic decimeter, and the milliliters, which is equal to a cubic centimeter. There are thus 1000 cm^3 in 1 dm^3, which is the same thing as saying there are 1000 mL in 1 L. *The conversion factor of* $1 \text{ cm}^3 = 1 \text{ mL}$ *is a very useful conversion.*

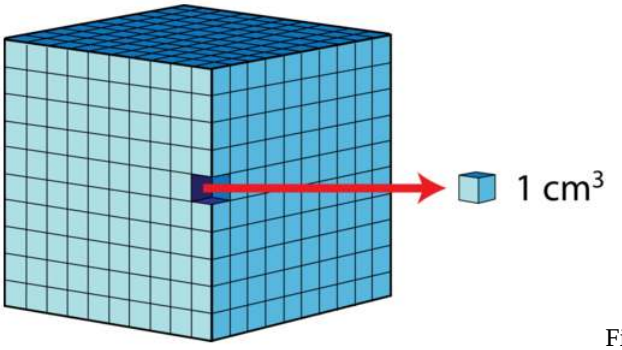


Figure 2.3.1: One centimeter cubed is the volume occupied by a cube with an edge length of 1 cm.

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.

Example 2.3.2

Convert 3.6 mm^3 to mL.

Solution

Determine the units of the known value (mm^3) and the units of the unknown value (mL). The starting and ending units will help guide the setup of the problem. Next, list any known conversion factors that might be helpful.

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

Now, we can set up the problem to find the value in units of mL. Once we know the starting units, we can then use the conversion factors to find the answer.

$$3.6 \text{ mm}^3 \times \left(\frac{?}{?}\right)$$

Continue to use the conversion factors between the units to set up the rest of the problem. Note that all of the units cancel except mL, which are the requested units for the answer. Since the values in these conversion factors are exact numbers, they will not affect the number of significant figures in the answer. Only the original value (3.6) will be considered in determining significant figures.

$$3.6 \text{ mm}^3 \times \left(\frac{1 \text{ m}}{1000 \text{ mm}}\right)^3 \times \left(\frac{?}{?}\right)$$

Once you have solved the problem, always ask if the answer seems reasonable. Remember, a millimeter is very small and a cubic millimeter is also very small. Therefore, we would expect a small volume which means $0.0036\ \mathrm{mL}$ is reasonable.

If you find that you forgot to cube numbers as well as units, you can setup the problem in an expanded form which is the equivalent to the previous method to cube the numerical values.

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2.4: Percentages

Learning Outcomes

- Calculate percentages and use in calculations.

In chemistry and healthcare, values are reported with a variety of units. Percentages are often used in the concentration of IV solutions and medications. There are multiple ways to report percentages so it is important to understand the basic meaning of a percent, which will be the focus here, as well as the type of percentage, such as mass or volume percent.

Percent

Percents are used to report many different values, such as a grade on an assignment as 85%, the shoes are 20% off their original price, or the concentration of the IV solution is 5.5% NaCl by mass. While all of these numbers use percent very differently, the values are all found the same way. For now, we will focus on some basic calculations using percents. Percents are all calculated with the same basic formula using the amount of the "part" and the amount of the "whole". Note that the percent will always be less than or equal to 100% because the "part" must be less than or equal to the "whole". The basic percent equation is shown here.

$$\% = \frac{\text{part}}{\text{whole}} \times 100 \tag{2.4.1}$$

Example 2.4.1

What percent of 70 is 14?

Solution

Since this is a percent problem, first look at the equation for percent and see which values are given in the problem. In this case, we know the part (14) and the whole (70). With this information and the formula, we can solve for the percent by inserting the known values into the equation and solving for the unknown.

$$\% = \frac{\text{part}}{\text{whole}} \times 100$$
$$\% = \frac{14}{70} \times 100$$
$$\% = 0.20 \times 100$$
$$\% = 20$$

Therefore, 14 is 20% of 70.

Example 2.4.2

What is 35% of 80?

Solution

This problem also involves percent so we will use the same equation as the previous example. However, in this example, we know the percentage (35) and the whole (80) and we are trying to find the value of the part. As before, we will insert the known values into the equation and solve for our unknown.

$$\% = \frac{\text{part}}{\text{whole}} \times 100$$
$$35 = \frac{\text{part}}{80} \times 100$$
$$0.35 = \frac{\text{part}}{80}$$
$$\text{part} = 28$$

So 28 is 35% of 80.

If you need to review how to rearrange equations and solve for an unknown, check out the worked examples and practice problems at https://www.mathisfun.com/algebra/in...-multiply.html.

Example 2.4.3

A patient has a fasting blood sugar level of $150\ \mathrm{mg/dL}$. The doctor has recommended some dietary changes and is hoping to see at least a 20% reduction in the patient's blood sugar level at their next appointment. If the patient meets this goal, what will their blood sugar level be?

Solution

We can start this problem like we do other percent problems. The problem gives use the percent (20) and the whole (150) and we need to calculate the part which will be the amount of decrease in the patient's blood sugar.

$$\begin{aligned} \% &= \frac{\text{part}}{\text{whole}} \times 100 \\ 20 &= \frac{\text{part}}{150} \times 100 \\ 0.20 &= \frac{\text{part}}{150} \\ \text{part} &= 30 \end{aligned}$$

The part that was calculated is the *decrease* that should be seen in the patient's blood sugar level. However, it's not the actual blood sugar level that the doctor wants to see at the next visit. To find that, we need to subtract from the original value.

$$\text{original} - \text{loss} = \text{final} \tag{2.4.2}$$

$$150\ \frac{\text{mg}}{\text{dL}} - 30\ \frac{\text{mg}}{\text{dL}} = 120\ \frac{\text{mg}}{\text{dL}} \tag{2.4.3}$$

At the next visit, the patient's blood sugar level should be $120\ \mathrm{mg/dL}$ (or less!) if they are making sufficient progress towards improving their health and reducing their risk of diabetes.

Supplemental Resources

- Percents: http://www.mathisfun.com/percentage.html

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2.5: Measurements and Problem-Solving (Exercises)

These are homework exercises to accompany Chapter 1 of the University of Kentucky's LibreText for CHE 103 - Chemistry for Allied Health. Solutions are available below the questions.

Questions

1.1: Measurements Matter

(click here for solutions)

Q1.1.1

Express the following values in scientific notation.

a. 150,000,000
b. 0.000043
c. 332000
d. 0.0293
e. 932
f. 0.1873
g. 78,000
h. 0.0001
i. 4500
j. 0.00290
k. 6281
l. 0.00700

Q1.1.2

Express the following values in decimal notation.

a. 3.8×10^{-3}
b. 9.21×10^{5}
c. 7.91×10^{-2}
d. 2.5×10^{6}
e. 3.42×10^{-8}
f. 5.4×10^{5}
g. 3×10^{-3}
h. 7.34×10^{2}
i. 9.8×10^{-4}
j. 6×10^{7}
k. 4.20×10^{-6}
l. 4.20×10^{6}

Q1.1.3

What SI base unit would be appropriate for each measurement?

a. the length of a room
b. the amount of carbon in a diamond
c. the mass of NaCl in a bottle

Q1.1.4

List the meaning of each abbreviation of the base units.

a. m
b. K

c. kg
d. s
e. mol

Q1.1.5

What is the the derived unit from the SI base units for the relationship of each pair of quantities?

a. mass and volume
b. distance and time
c. amount of substance and volume
d. area

Q1.1.6

Give the meaning and name of each metrix prefix abbreviation.

a. M
b. m
c. n
d. d

Q1.1.7

Give the abbreviation and meaning of each metrix prefix.

a. kilo
b. centi
c. micro
d. giga

Q1.1.8

Name the prefix with the following numerical meaning.

a. 1/10
b. 1,000,000
c. 1/1,000,000
d. 1/100
e. 1

Q1.1.9

Convert each temperature to the missing one between Celsius and Fahrenheit.

a. 77°F
b. 212°F
c. 37°C
d. 22°C
e. 95°F
f. 15°C
g. 0°F
h. 0°C
i. –10°C
j. –10°F

1.2 Significant Figures

(click here for solutions)

Q1.2.1

Explain the similarities and differences between accuracy and precision.

Q1.2.2

The density of a copper sample was determined by three different students (shown below). Each performed the measurement three times and is reported below (all values in units of g/cm^3). The accepted value for the density of copper is 8.92 g/cm^3.

a. Determine if each student's data is accurate, precise, neither or both.
b. What is the average density based on Justin's data?
c. What is the average density based on Jane's data?

- Jane: 8.94, 8.89, 8.91
- Justin: 8.32, 8.31, 8.34
- Julia: 8.64, 9.71, and 9.10

Q1.2.3

Determine the number of significant figures in each of the following values.

a. 406
b. 3.00
c. 3.20
d. 0.25
e. 0.0689
f. 0.002910
g. 3941
h. 46.250
i. 30.21
j. 0.10300

Q1.2.4

Write each value with three significant figures, use scientific notation if necessary.

a. 34500
b. 24
c. 0.0345
d. 0.012
e. 612.8
f. 98.22
g. 0.14928
h. 300

Q1.2.5

Give three examples of exact numbers.

Q1.2.6

Find the result of each of the following calculations and report the value with the correct number of significant figures.

a. 0.23 + 12.2 =
b. 13 - 1.03 =
c. 0.839 + 0.28925 =
d. 28 + 34.4 =
e. 0.8 + 2.3 =
f. 34.9 - 0.583 =

g. 21 - 0.132 =
h. 0.840 + 0.9334

Q1.2.7

Find the result of each of the following calculations and report the value with the correct number of significant figures.

a. 34 x 0.12 =
b. 68.2 / 0.78 =
c. $3.29 \times 10^4 \times 16.2$ =
d. 0.8449 x 29.7 =
e. $5.92 \times 10^3 / 0.628$ =
f. 3.00 x 2.6 =
g. 2.50 x 9.331 =
h. 3.20 / 12.75 =

1.3 Scientific Dimensional Analysis

(click here for solutions)

Q1.3.1

What is a conversion factor?

Q1.3.2

What is the conversion factor between each pair of units?

a. feet and inches
b. mL and cm^3
c. kg and g
d. cm and m
e. mm and cm
f. inches and centimeters
g. grams and pounds
h. g and µg (mcg)

Q1.3.3

Complete each of the following conversions.

a. 34 cm to m
b. 3.7 ft to in
c. 345 mg to Mg
d. 5.3 km to mm
e. 4.0 L to mL
f. 3.45×10^3 mm to km
g. 78 cm^3 to mL
h. 0.85 kg to dg
i. 13 pints to gallon
j. 0.35 L to cm^3

Q1.3.4

Complete each of the following conversions.

a. 342 cm^3 to dm^3
b. 2.70 g/cm^3 to kg/L
c. 34 mi/hr to km/min
d. 0.00722 km^2 to m^2

e. 4.9 x 10^5 mcm^3 to mm^3
f. 80. km/hr to mi/hr

1.4 Percentages

(click here for solutions)

Q1.4.1

Solve each of the following.

a. What percent of 35 is 8.2?
b. What percent of 56 is 12?
c. What percent of 923 is 38?
d. What percent of 342 is 118?

Q1.4.2

Solve each of the following?

a. What is 42% of 94?
b. What is 83% of 239?
c. What is 16% of 45?
d. What is 38% of 872?

Q1.4.3

Solve each of the following?

a. 42 is 34% of what number?
b. 73 is 82% of what number?
c. 13 is 57% of what number?
d. 75 is 25% of what number?
e. 25 is 15% of what number?
f. 98 is 76% of what number?

Q1.4.4

A patient originally weighs 182 pounds and loses 15.0% of their body weight. What is their final weight?

Q1.4.5

A patient's original weight was 135 pounds and they lose 12 pounds. What percent of their body weight did they lose?

Q1.4.6

A patient needs to increase their calcium supplement by 25% a week. If they are currently taking a 300. mg supplement, how much more will they need to take?

Q1.4.7

An infant's birth weight is 7 pounds, 1 ounce. Her discharge weight is 6 pounds, 13 ounces. What percent of her birth weight did she lose?

Q1.4.8

A patient needs a 20.% decrease in their medication dosage from 125 mg. What will his dosage be after the decrease?

Answers

1.1: Measurements Matter

Q1.1.1

a. 1.5×10^8

b. 4.3×10^{-5}
c. 3.32×10^{5}
d. 2.93×10^{-2}
e. 9.32×10^{2}
f. 1.873×10^{-1}
g. 7.8×10^{4}
h. 1×10^{-4}
i. 4.5×10^{3}
j. 2.9×10^{-3}
k. 6.281×10^{3}
l. 7×10^{-3}

Q1.1.2

a. 0.0038
b. 921000
c. 0.0791
d. 2500000
e. 0.0000000342
f. 540000
g. 0.003
h. 734
i. 0.00098
j. 60000000
k. 0.00000420
l. 4200000

Q1.1.3

a. meter
b. mole
c. kilogram

Q1.1.4

a. meter
b. Kelvin
c. kilogram
d. second
e. mole

Q1.1.5

a. kg/m^3
b. m/s
c. mol/m^3 is based on SI base units, but mol/L is also acceptable
d. m^2

Q1.1.6

a. Mega, 10^6
b. milli, 10^{-3}
c. nano, 10^{-9}
d. deci, 10^{-1}

Q1.1.7

a. k, 10^3
b. c, 10^{-2}
c. μ (or mc), 10^{-6}
d. G, 10^9

Q1.1.8

a. deci
b. mega
c. micro
d. centi
e. none (base unit)

Q1.1.9

a. 77°F = 25°C
b. 212°F = 100°C
c. 37°C = 98.6°F
d. 22°C = 72°F
e. 95°F = 35°C
f. 15°C = 59°F
g. 0°F = –18°C
h. 0°C = 32°F
i. –10°C = 14°F
j. –10°F = –23°C

1.2 Significant Figures

Q1.2.1

Accuracy is a measure of how close the values are close to the correct value while precision is a measure of how close values are to each other.

Q1.2.2

a.

- Jane: 8.94, 8.89, 8.91 - accurate and precise
- Justin: 8.32, 8.31, 8.34 - precise
- Julia: 8.64, 9.71, and 9.10 - neither accurate nor precise

a. 8.32 g/cm^3
b. 8.91 g/cm^3

Q1.2.3

a. 3
b. 3
c. 3
d. 2
e. 3
f. 4
g. 4
h. 5
i. 4
j. 5

Q1.2.4

a. 3.45×10^{4}
b. 2.40×10^{1}
c. 3.45×10^{-2}
d. 1.20×10^{-2}
e. 613 or 6.13×10^{2}
f. 9.82×10^{1}
g. 0.149 or 1.49×10^{-1}
h. 300. or 3.00×10^{2}

Q1.2.5

Answers will vary. 12 eggs, 100 cm = 1 m, 1 inch = 2.54 cm, 4 people

Q1.2.6

a. 0.23 + 12.2 = 12.43 = **12.4**
b. 13 - 1.03 = 11.97 = **12**
c. 0.839 + 0.28925 = 1.12825 = **1.128**
d. 28 + 34.4 = 62.4 = **62**
e. 0.8 + 2.3 = **3.1**
f. 34.9 - 0.583 = 34.317 = **34.3**
g. 21 - 0.132 = 20.868 = **21**
h. 0.840 + 0.9334 = 1.7734 = **1.773**

Q1.2.7

a. 34 x 0.12 = 4.08 = **4.1**
b. 68.2 / 0.78 = 87.4358974 = **87**
c. $3.29 \text{ x } 10^{4} \text{ x } 16.2 = 5.32980 \times 10^{5} = 5.33 \times 10^{5}$
d. 0.8449 x 29.7 = 25.09353 = **25.1**
e. $5.92 \text{ x } 10^{3} / 0.628 = 9.4267515 \times 10^{3} =$ **9.43×10^{3}**
f. 3.00 x 2.6 = **7.8**
g. 2.50 x 9.331 = 23.3275 = **23.3**
h. 3.20 / 12.75 = 0.25098 = **0.251**

1.3 Scientific Dimensional Analysis

Q1.3.1

A conversion factor is a relationship between two units. The value in the numerator has some equivalence to the value in the denominator.

Q1.3.2

a. 1 foot = 12 inches
b. 1 mL = 1 cm^3
c. 1 kg = 1000 g or 1×10^{-3} kg = 1 g
d. 100 cm = 1 m or 1 cm = 1×10^{-2} m
e. 10 mm = 1 cm
f. 1 inch = 2.54 cm
g. 454 grams = 1 pound
h. 1 g = 1×10^{6} µg (mcg) or 1×10^{-6} g = 1 µg (mcg)

Q1.3.3

a. $34\ cm \times \frac{1\ m}{100\ cm} = 0.34\ m$
b. $3.7\ ft \times \frac{12\ in}{1\ ft} = 44.4\ in = 44\ in$
c. $345\ mg \times \frac{1\ g}{1000\ mg} \times \frac{1\ Mg}{1 \times 10^{6}\ g} = 3.45 \times 10^{-7}\ Mg$

d. $5.3\ km \times \frac{1000\ m}{1\ km} \times \frac{1000\ mm}{1\ m} = 5.3 \times 10^6\ mm$

e. $4.0\ L \times \frac{1000\ mL}{1\ L} = 4.0 \times 10^3\ mL$

f. $3.45 \times 10^3\ mm \times \frac{1\ m}{1000\ mm} \times \frac{1\ km}{1000\ m} = 3.45 \times 10^{-3}\ km$

g. $78\ cm^3 \times \frac{1\ mL}{cm^3} = 78\ mL$

h. $0.85\ kg \times \frac{1000\ g}{1\ kg} \times \frac{10\ dg}{1\ g} = 8.5 \times 10^3\ dg$

i. $13\ pints \times \frac{1\ quart}{2\ pints} \times \frac{1\ gallon}{4\ quarts} = 1.6\ gallons$

j. $0.35\ L \times \frac{1000\ mL}{1\ L} \times \frac{1\ mL}{1\ cm^3} = 3.5 \times 10^2\ cm^3$

Q1.3.4

a. $342\ cm^3 \times \frac{1\ dm}{10\ cm} \times \frac{1\ dm}{10\ cm} \times \frac{1\ dm}{10\ cm} = 0.342\ dm^3$ **or** $342\ cm^3 \times \left(\frac{1\ dm}{10\ cm}\right)^3 = 342\ cm^3 \times \frac{1^3\ dm^3}{10^3\ cm^3} = 0.342\ dm^3$

b. $\frac{2.70\ g}{cm^3} \times \frac{1\ kg}{1000\ g} \times \frac{1\ cm^3}{1\ mL} \times \frac{1000\ mL}{1\ L} = \frac{2.70\ kg}{L}$

c. $\frac{34\ mi}{hr} \times \frac{5280\ ft}{1\ mi} \times \frac{12\ in}{1\ ft} \times \frac{2.54\ cm}{1\ in} \times \frac{1\ m}{100\ cm} \times \frac{1\ km}{1000\ m} \times \frac{1\ hr}{60\ min} = \frac{0.91\ km}{min}$

d. $0.00722\ km^2 \times \frac{1000\ m}{1\ km} \times \frac{1000\ m}{1\ km} = 7.22 \times 10^3\ m^2$

e. $4.95 \times 10^5\ mcm^3 \times \frac{1\ mm}{1000\ mcm} \times \frac{1\ mm}{1000\ mcm} \times \frac{1\ mm}{1000\ mcm} = 4.95 \times 10^{-4}\ mm^3$

f. $\frac{80.\ km}{hr} \times \frac{1000\ m}{1\ km} \times \frac{100\ cm}{1\ m} \times \frac{1\ in}{2.54\ cm} \times \frac{1\ ft}{12\ in} \times \frac{1\ mi}{5280\ ft} = \frac{50.\ mi}{hr}$

1.4 Percentages

Q1.4.1

a. $\% = \frac{part}{whole} \times 100 = \frac{8.2}{35} \times 100 = 23\%$

b. $\% = \frac{part}{whole} \times 100 = \frac{12}{56} \times 100 = 21\%$

c. $\% = \frac{part}{whole} \times 100 = \frac{38}{923} \times 100 = 4.1\%$

d. $\% = \frac{part}{whole} \times 100 = \frac{118}{342} \times 100 = 34.5\%$

Q1.4.2

a.
$$\% = \frac{part}{whole} \times 100$$
$$42\% = \frac{part}{94} \times 100$$
$$part = 39$$

b.
$$\% = \frac{part}{whole} \times 100$$
$$83\% = \frac{part}{239} \times 100$$
$$part = 198 = 2.0 \times 10^2$$

c.
$$\% = \frac{part}{whole} \times 100$$
$$16\% = \frac{part}{45} \times 100$$
$$part = 7.2$$

d.
$$\% = \frac{part}{whole} \times 100$$
$$38\% = \frac{part}{872} \times 100$$
$$part = 3.3 \times 10^2$$

Q1.4.3

a.
$$\% = \frac{part}{whole} \times 100$$
$$34\% = \frac{42}{whole} \times 100$$
$$whole = 1.2 \times 10^2$$

b.
$$\% = \frac{part}{whole} \times 100$$
$$82\% = \frac{73}{whole} \times 100$$
$$whole = 89$$

c.
$$\% = \frac{part}{whole} \times 100$$
$$57\% = \frac{13}{whole} \times 100$$
$$whole = 23$$

d.
$$\% = \frac{part}{whole} \times 100$$
$$25\% = \frac{75}{whole} \times 100$$
$$whole = 3.0 \times 10^2$$

e.
$$\% = \frac{part}{whole} \times 100$$
$$15\% = \frac{25}{whole} \times 100$$
$$whole = 1.7 \times 10^2$$

f.
$$\% = \frac{part}{whole} \times 100$$
$$76\% = \frac{98}{whole} \times 100$$
$$whole = 129$$

Q1.4.4

$$\% = \frac{part}{whole} \times 100$$
$$15.0\% = \frac{part}{182\ pounds} \times 100$$
$$part = 27.3\ pounds\ lost$$

$$182\ pounds - 27.3\ pounds = 154.7\ pounds = 155\ pounds$$

Q1.4.5

$$\% = \frac{part}{whole} \times 100$$
$$\% = \frac{12\ pounds}{135\ pounds} \times 100$$
$$\% = 8.9\%\ lost$$

Q1.4.6

$$\% = \frac{part}{whole} \times 100$$
$$25\% = \frac{part}{300.\ mg} \times 100$$
$$part = 75\ mg\ more$$

Q1.4.7

Convert both weights to ounces, find the ounces lost, and then find the percent lost.

Birth weight: $(7\ pounds \times 16) + 1\ ounce = 113\ ounces$

Discharge weight: $(6\ pounds \times 16) + 13\ ounces = 109\ ounces$

Weight lost: $113\ ounces - 109\ ounces = 4\ ounces$

Percent lost from original brith weight.

$$\% = \frac{part}{whole} \times 100$$
$$\% = \frac{4\ ounces}{113\ ounces} \times 100$$
$$\% = 3.5\% = 4\%$$

Q1.4.8

$$\% = \frac{part}{whole} \times 100$$
$$20\% = \frac{part}{125\ mg} \times 100$$
$$part = 25\ mg\ lost$$

$$125\ mg - 25\ mg = 100.\ mg$$

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CHAPTER OVERVIEW

3: The Chemical Foundation of Life

Elements in various combinations comprise all matter, including living things. Some of the most abundant elements in living organisms include carbon, hydrogen, nitrogen, oxygen, sulfur, and phosphorus. These form the nucleic acids, proteins, carbohydrates, and lipids that are the fundamental components of living matter. Biologists must understand these important building blocks and the unique structures of the atoms that make up molecules, allowing for the formation of cells, tissues, organ systems, and entire organisms.

3.1: Prelude to The Chemical Foundation of Life

3.2: The Classification of Matter

3.3: Atoms, Isotopes, Ions, and Molecules - The Building Blocks

3.4: Lewis Electron Dot Structures

3.5: Representing Structures

3.E: The Chemical Foundation of Life (Exercises)

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3.1: Prelude to The Chemical Foundation of Life

Elements in various combinations comprise all matter, including living things. Some of the most abundant elements in living organisms include carbon, hydrogen, nitrogen, oxygen, sulfur, and phosphorus. These form the nucleic acids, proteins, carbohydrates, and lipids that are the fundamental components of living matter. Biologists must understand these important building blocks and the unique structures of the atoms that make up molecules, allowing for the formation of cells, tissues, organ systems, and entire organisms.

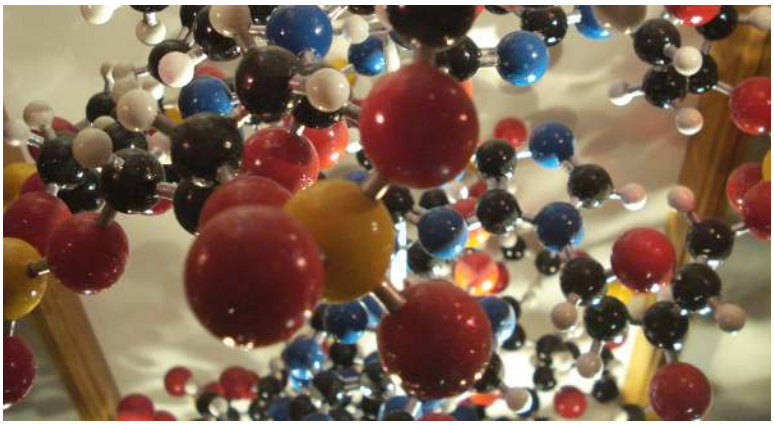


Figure 3.1.1: Atoms are the building blocks of molecules found in the universe—air, soil, water, rocks ... and also the cells of all living organisms. In this model of an organic molecule, the atoms of carbon (black), hydrogen (white), nitrogen (blue), oxygen (red), and sulfur (yellow) are shown in proportional atomic size. The silver rods indicate chemical bonds. (credit: modification of work by Christian Guthier)

All biological processes follow the laws of physics and chemistry, so in order to understand how biological systems work, it is important to understand the underlying physics and chemistry. For example, the flow of blood within the circulatory system follows the laws of physics that regulate the modes of fluid flow. The breakdown of the large, complex molecules of food into smaller molecules—and the conversion of these to release energy to be stored in adenosine triphosphate (ATP)—is a series of chemical reactions that follow chemical laws. The properties of water and the formation of hydrogen bonds are key to understanding living processes. Recognizing the properties of acids and bases is important, for example, to our understanding of the digestive process. Therefore, the fundamentals of physics and chemistry are important for gaining insight into biological processes.

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3.2: The Classification of Matter

Learning Objectives

- Use physical and chemical properties, including phase, to describe matter.
- Identify a sample of matter as an element, a compound, or a mixture.

Part of understanding matter is being able to describe it. One way chemists describe matter is to assign different kinds of properties to different categories.

Physical and Chemical Properties

The properties that chemists use to describe matter fall into two general categories. **Physical properties** are characteristics that describe matter. They include characteristics such as size, shape, color, and mass. These characteristics can be observed or measured without changing the *identity* of the matter in question. **Chemical properties** are characteristics that describe how matter changes its chemical structure or composition. An example of a chemical property is flammability—a material's ability to burn—because burning (also known as combustion) changes the chemical composition of a material. The observation of chemical properties involves a *chemical change* of the matter in question, resulting in matter with a different *identity* and different physical and chemical properties.



Figure 3.2.1: (left) Ice Melting is a physical change. When liquid water (H_2O) freezes into a solid state (ice), it appears changed; However, this change is only physical as the the composition of the constituent molecules is the same: 11.19% hydrogen and 88.81% oxygen by mass. (right) Burning of wax to generate water and carbon dioxide is a chemical reaction. (CC-SA-BY-3.0; Andrikkos)

Elements and Compounds

Any sample of matter that has the *same physical and chemical properties throughout* the sample is called a **substance**. There are two types of substances. A substance that cannot be broken down into chemically simpler components is called an **element**. Aluminum, which is used in soda cans and is represented by the symbol Al, is an element. A substance that can be broken down into chemically simpler components (because it consists of more than one element) is called a **compound**. Water is a compound composed of the elements hydrogen and oxygen and is described by the chemical formula, H_2O. Today, there are about 118 elements in the known universe. In contrast, scientists have identified tens of millions of different compounds to date.

> Sometimes the word *pure* is used to describe a substance, but this is not absolutely necessary. By definition, any single substance, element or compound is *pure*.

The smallest part of an element that maintains the identity of that element is called an **atom**. Atoms are extremely tiny; to make a line of iron atoms that is 1 inch long, you would need approximately 217 million iron atoms. The smallest part of a compound that maintains the identity of that compound is called a **molecule**. Molecules are composed of two or more atoms that are attached

together and behave as a unit. Scientists usually work with millions and millions of atoms and molecules at a time. When a scientist is working with large numbers of atoms or molecules at a time, the scientist is studying the *macroscopic viewpoint* of the universe. However, scientists can also describe chemical events on the level of individual atoms or molecules, which is referred to as the *microscopic viewpoint*. We will see examples of both macroscopic and microscopic viewpoints throughout this book (Figure 3.2.2).

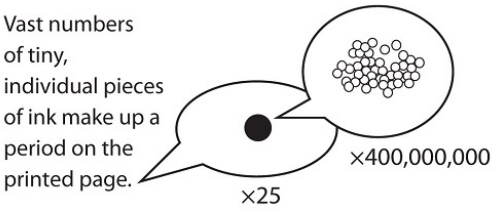


Figure 3.2.2: How Many Particles Are Needed for a Period in a Sentence? Although we do not notice it from a macroscopic perspective, matter is composed of microscopic particles so tiny that billions of them are needed to make a speck we can see with the naked eye. The ×25 and ×400,000,000 indicate the number of times the image is magnified.

Mixtures

A material composed of two or more substances is a **mixture**. In a mixture, the individual substances maintain their chemical identities. Many mixtures are obvious combinations of two or more substances, such as a mixture of sand and water. Such mixtures are called **heterogeneous mixtures**. In some mixtures, the components are so intimately combined that they act like a single substance (even though they are not). Mixtures with a consistent or uniform composition throughout are called **homogeneous mixtures** (or solutions). For example, when sugar is dissolved in water to form a liquid solution, the individual properties of the components cannot be distinguished. Other examples or homogenous mixtures include solid solutions, like the metal alloy steel, and gaseous solutions, like air which is a mixture of mainly nitrogen and oxygen.

✔ Example 3.2.1

How would a chemist categorize each example of matter?

a. saltwater
b. soil
c. water
d. oxygen

Answer a

Saltwater acts as if it were a single substance even though it contains two substances—salt and water. Saltwater is a *homogeneous mixture*, or a solution.

Answer b

Soil is composed of small pieces of a variety of materials, so it is a ***h**eterogeneous mixture*.

Answer c

Water is a *substance*; more specifically, because water is composed of hydrogen and oxygen, it is a *compound*.

Answer d

Oxygen, a *substance*, is an *element*.

? Exercise 3.2.2

How would a chemist categorize each example of matter?

a. breakfast coffee
b. hydrogen
c. an egg

Answer a

homogeneous mixture or solution

Answer b

element

Answer c

heterogeneous mixture

Phases or Physical States of Matter

All matter can be further classified by one of three physical **states** or **phases**, solid, liquid or gas. These three descriptions each imply that the matter has certain physical properties when in these states. A solid has a definite shape and a definite volume. Liquids ordinarily have a definite volume but not a definite shape; they take the shape of their containers. Gases have neither a definite shape nor a definite volume, and they expand to fill their containers.

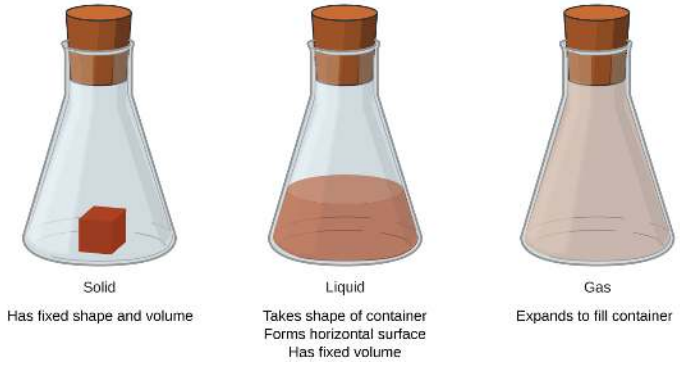


Figure 3.2.3: The three most common states or phases of matter are solid, liquid, and gas. (CC BY-4.0; OpenStax) A beaker labeled solid contains a cube of red matter and says has fixed shape and volume. A beaker labeled liquid contains a brownish-red colored liquid. This beaker says takes shape of container, forms horizontal surfaces, has fixed volume. The beaker labeled gas is filled with a light brown gas. This beaker says expands to fill container.

We encounter matter in each phase every day; in fact, we regularly encounter water in all three phases: ice (solid), water (liquid), and steam (gas) (Figure 3.2.2).



Figure 3.2.5: Boiling Water. When liquid water boils to make gaseous water, it undergoes a phase change. (CC BY-SA 3.0 Unported; Markus Schweiss via Wikipedia)

We know from our experience with water that substances can change from one phase to another if the conditions are right. Typically, varying the temperature of a substance (and, less commonly, the pressure exerted on it) can cause a **phase change**, a physical process in which a substance changes from one phase to another (Figure 3.2.5). Phase changes are identified by particular names depending on what phases are involved, as summarized in Table 3.2.1.

Table 3.2.1: Phase Changes

Change	Name
solid to liquid	melting, fusion
solid to gas	sublimation
liquid to gas	boiling, evaporation
liquid to solid	solidification, freezing
gas to liquid	condensation
gas to solid	deposition

Figure 3.2.3 illustrates the relationships between the different ways matter can be classified.

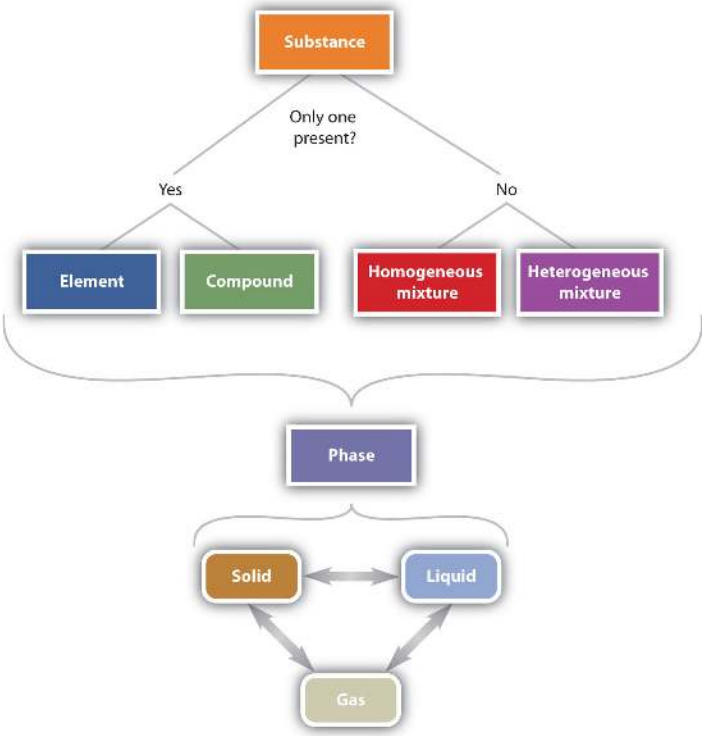


Figure 3.2.6: The Classification of Matter. Matter can be classified in a variety of ways, depending on its properties. This table starts with a substance. If there is only one present, it can either be an element or a compound. If there is more than one present, it can either be a homogeneous mixture or a heterogeneous mixture. From these choices, the substance can be in a certain phase. It can either be solid, liquid, or gas, and each phase can go from one to another.

Concept Review Exercises

1. Explain the differences between the physical properties of matter and the chemical properties of matter.
2. What is the difference between a heterogeneous mixture and a homogeneous mixture? Give an example of each.
3. Give at least two examples of a phase change and state the phases involved in each.

Answers

1. Physical properties describe the existence of matter, and chemical properties describe how substances change into other substances.
2. A heterogeneous mixture is obviously a mixture, such as dirt; a homogeneous mixture behaves like a single substance, such as saltwater.
3. solid to liquid (melting) and liquid to gas (boiling) (answers will vary)

Key Takeaways

- Matter can be described with both physical properties and chemical properties.
- Matter can be identified as an element, a compound, or a mixture

Exercise 3.2.3

Does each statement refer to a chemical property or a physical property?

1. Balsa is a very light wood.
2. If held in a flame, magnesium metal burns in air.
3. Mercury has a density of 13.6 g/mL.
4. Human blood is red.

Answer

1. physical property
2. chemical property
3. physical property
4. physical property

Exercise 3.2.4

Does each statement refer to a chemical property or a physical property?

1. The elements sodium and chlorine can combine to make table salt.
2. The metal tungsten does not melt until its temperature exceeds 3,000°C.
3. The ingestion of ethyl alcohol can lead to disorientation and confusion.
4. The boiling point of isopropyl alcohol, which is used to sterilize cuts and scrapes, is lower than the boiling point of water

Answer

1. chemical property
2. physical property
3. chemical property
4. physical property

Exercise 3.2.5

Define *element*. How does it differ from a compound?

Answer

An element is a substance that cannot be broken down into chemically simpler components. Compounds can be broken down into simpler substances.

Exercise 3.2.6

Define *compound*. How does it differ from an element?

Answer

A compound is composed of two or more elements combined in a fixed ratio. An element is the simplest chemical substance.

Exercise 3.2.7

Give two examples of a heterogeneous mixture.

Answer

a salt and pepper mix and a bowl of cereal (answers will vary)

Exercise 3.2.8

Give two examples of a homogeneous mixture.

Answer

vinegar and rubbing alcohol (answers will vary)

Exercise 3.2.9

Identify each substance as an element, a compound, a heterogeneous mixture, or a solution.

1. xenon, a substance that cannot be broken down into chemically simpler components
2. blood, a substance composed of several types of cells suspended in a salty solution called plasma
3. water, a substance composed of hydrogen and oxygen

Answer

1. element
2. heterogeneous mixture
3. compound

Exercise 3.2.10

Identify each substance as an element, a compound, a heterogeneous mixture, or a solution.

1. sugar, a substance composed of carbon, hydrogen, and oxygen
2. hydrogen, the simplest chemical substance
3. dirt, a combination of rocks and decaying plant matter

Answer

1. compound
2. element
3. heterogeneous mixture

Exercise 3.2.11

Identify each substance as an element, a compound, a heterogeneous mixture, or a solution.

1. air, primarily a mixture of nitrogen and oxygen
2. ringer's lactate, a standard fluid used in medicine that contains salt, potassium, and lactate compounds all dissolved in sterile water
3. tartaric acid, a substance composed of carbon, hydrogen, and oxygen

Answer

1. heterogeneous mixture
2. solution
3. compound

Exercise 3.2.12

What word describes each phase change?

1. solid to liquid
2. liquid to gas
3. solid to gas

Answer

1. melting or fusion
2. boiling or evaporation
3. sublimation

Exercise 3.2.13

1. What word describes each phase change?
    1. liquid to solid
    2. gas to liquid
    3. gas to solid

Answer

1. freezing
2. condensation
3. deposition

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3.3: Atoms, Isotopes, Ions, and Molecules - The Building Blocks

Skills to Develop

- Define matter and elements
- Describe the interrelationship between protons, neutrons, and electrons
- Compare the ways in which electrons can be donated or shared between atoms
- Explain the ways in which naturally occurring elements combine to create molecules, cells, tissues, organ systems, and organisms

At its most fundamental level, life is made up of matter. Matter is any substance that occupies space and has mass. Elements are unique forms of matter with specific chemical and physical properties that cannot be broken down into smaller substances by ordinary chemical reactions. There are 118 elements, but only 92 occur naturally. The remaining elements are synthesized in laboratories and are unstable.

Each element is designated by its chemical symbol, which is a single capital letter or, when the first letter is already "taken" by another element, a combination of two letters. Some elements follow the English term for the element, such as C for carbon and Ca for calcium. Other elements' chemical symbols derive from their Latin names; for example, the symbol for sodium is Na, referring to *natrium*, the Latin word for sodium.

The four elements common to all living organisms are oxygen (O), carbon (C), hydrogen (H), and nitrogen (N). In the non-living world, elements are found in different proportions, and some elements common to living organisms are relatively rare on the earth as a whole, as shown in Table 3.3.1. For example, the atmosphere is rich in nitrogen and oxygen but contains little carbon and hydrogen, while the earth's crust, although it contains oxygen and a small amount of hydrogen, has little nitrogen and carbon. In spite of their differences in abundance, all elements and the chemical reactions between them obey the same chemical and physical laws regardless of whether they are a part of the living or non-living world.

Table 3.3.1: Approximate Percentage of Elements in Living Organisms (Humans) Compared to the Non-living World

Element	Life (Humans)	Atmosphere	Earth's Crust
Oxygen (O)	65%	21%	46%
Carbon (C)	18%	trace	trace
Hydrogen (H)	10%	trace	0.1%
Nitrogen (N)	3%	78%	trace

The Structure of the Atom

To understand how elements come together, we must first discuss the smallest component or building block of an element, the atom. An atom is the smallest unit of matter that retains all of the chemical properties of an element. For example, one gold atom has all of the properties of gold in that it is a solid metal at room temperature. A gold coin is simply a very large number of gold atoms molded into the shape of a coin and containing small amounts of other elements known as impurities. Gold atoms cannot be broken down into anything smaller while still retaining the properties of gold.

An atom is composed of two regions: the nucleus, which is in the center of the atom and contains protons and neutrons, and the outermost region of the atom which holds its electrons in orbit around the nucleus, as illustrated in Figure 3.3.1. Atoms contain protons, electrons, and neutrons, among other subatomic particles. The only exception is hydrogen (H), which is made of one proton and one electron with no neutrons.

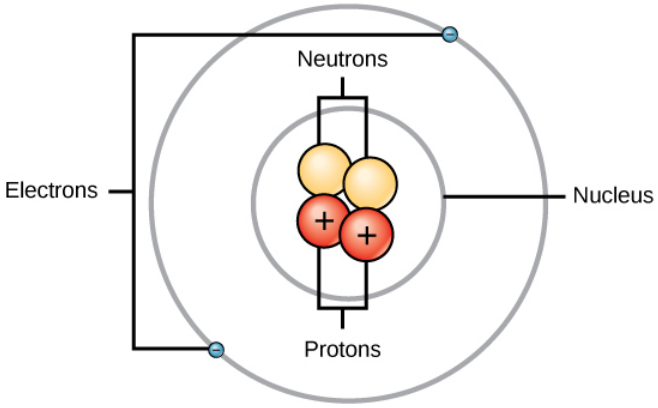


Figure 3.3.1: Elements, such as helium, depicted here, are made up of atoms. Atoms are made up of protons and neutrons located within the nucleus, with electrons in orbitals surrounding the nucleus.

Protons and neutrons have approximately the same mass, about 1.67×10^{-24} grams. Scientists arbitrarily define this amount of mass as one atomic mass unit (amu) or one Dalton, as shown in Table 3.3.2. Although similar in mass, protons and neutrons differ in their electric charge. A proton is positively charged whereas a neutron is uncharged. Therefore, the number of neutrons in an atom contributes significantly to its mass, but not to its charge. Electrons are much smaller in mass than protons, weighing only 9.11×10^{-28} grams, or about 1/1800 of an atomic mass unit. Hence, they do not contribute much to an element's overall atomic mass. Therefore, when considering atomic mass, it is customary to ignore the mass of any electrons and calculate the atom's mass based on the number of protons and neutrons alone. Although not significant contributors to mass, electrons do contribute greatly to the atom's charge, as each electron has a negative charge equal to the positive charge of a proton. In uncharged, neutral atoms, the number of electrons orbiting the nucleus is equal to the number of protons inside the nucleus. In these atoms, the positive and negative charges cancel each other out, leading to an atom with no net charge.

Accounting for the sizes of protons, neutrons, and electrons, most of the volume of an atom—greater than 99 percent—is, in fact, empty space. With all this empty space, one might ask why so-called solid objects do not just pass through one another. The reason they do not is that the electrons that surround all atoms are negatively charged and negative charges repel each other.

Table 3.3.2: Protons, Neutrons, and Electrons

	Charge	Mass (amu)	Location
Proton	+1	1	nucleus
Neutron	0	1	nucleus
Electron	–1	0	orbitals

Atomic Number and Mass

Atoms of each element contain a characteristic number of protons and electrons. The number of protons determines an element's atomic number and is used to distinguish one element from another. The number of neutrons is variable, resulting in isotopes, which are different forms of the same atom that vary only in the number of neutrons they possess. Together, the number of protons and the number of neutrons determine an element's mass number, as illustrated in Figure 3.3.2. Note that the small contribution of mass from electrons is disregarded in calculating the mass number. This approximation of mass can be used to easily calculate how many neutrons an element has by simply subtracting the number of protons from the mass number. Since an element's isotopes will have slightly different mass numbers, scientists also determine the atomic mass, which is the calculated mean of the mass number for its naturally occurring isotopes. Often, the resulting number contains a fraction. For example, the atomic mass of chlorine (Cl) is 35.45 because chlorine is composed of several isotopes, some (the majority) with atomic mass 35 (17 protons and 18 neutrons) and some with atomic mass 37 (17 protons and 20 neutrons).

Art Connection

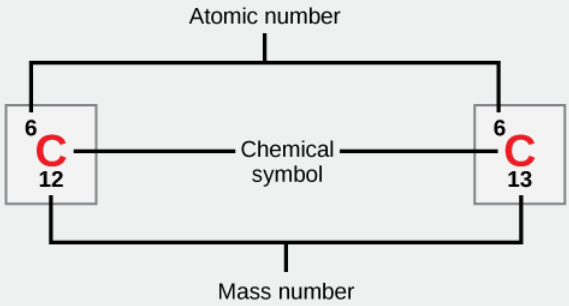


Figure 3.3.2: Carbon has an atomic number of six, and two stable isotopes with mass numbers of twelve and thirteen, respectively. Its atomic mass is 12.11.

How many neutrons do carbon-12 and carbon-13 have, respectively?

Isotopes

Isotopes are different forms of an element that have the same number of protons but a different number of neutrons. Some elements—such as carbon, potassium, and uranium—have naturally occurring isotopes. Carbon-12 contains six protons, six neutrons, and six electrons; therefore, it has a mass number of 12 (six protons and six neutrons). Carbon-14 contains six protons, eight neutrons, and six electrons; its atomic mass is 14 (six protons and eight neutrons). These two alternate forms of carbon are isotopes. Some isotopes may emit neutrons, protons, and electrons, and attain a more stable atomic configuration (lower level of potential energy); these are radioactive isotopes, or radioisotopes. Radioactive decay (carbon-14 losing neutrons to eventually become carbon-12) describes the energy loss that occurs when an unstable atom's nucleus releases radiation.

Evolution Connection: Carbon Dating

Carbon is normally present in the atmosphere in the form of gaseous compounds like carbon dioxide and methane. Carbon-14 (C^{14}) is a naturally occurring radioisotope that is created in the atmosphere from atmospheric N^{14} (nitrogen) by the addition of a neutron and the loss of a proton because of cosmic rays. This is a continuous process, so more C^{14} is always being created. As a living organism incorporates C^{14} initially as carbon dioxide fixed in the process of photosynthesis, the relative amount of C^{14} in its body is equal to the concentration of C^{14} in the atmosphere. When an organism dies, it is no longer ingesting C^{14}, so the ratio between C^{14} and C^{12} will decline as C^{14} decays gradually to N^{14} by a process called beta decay—the emission of electrons or positrons. This decay gives off energy in a slow process.

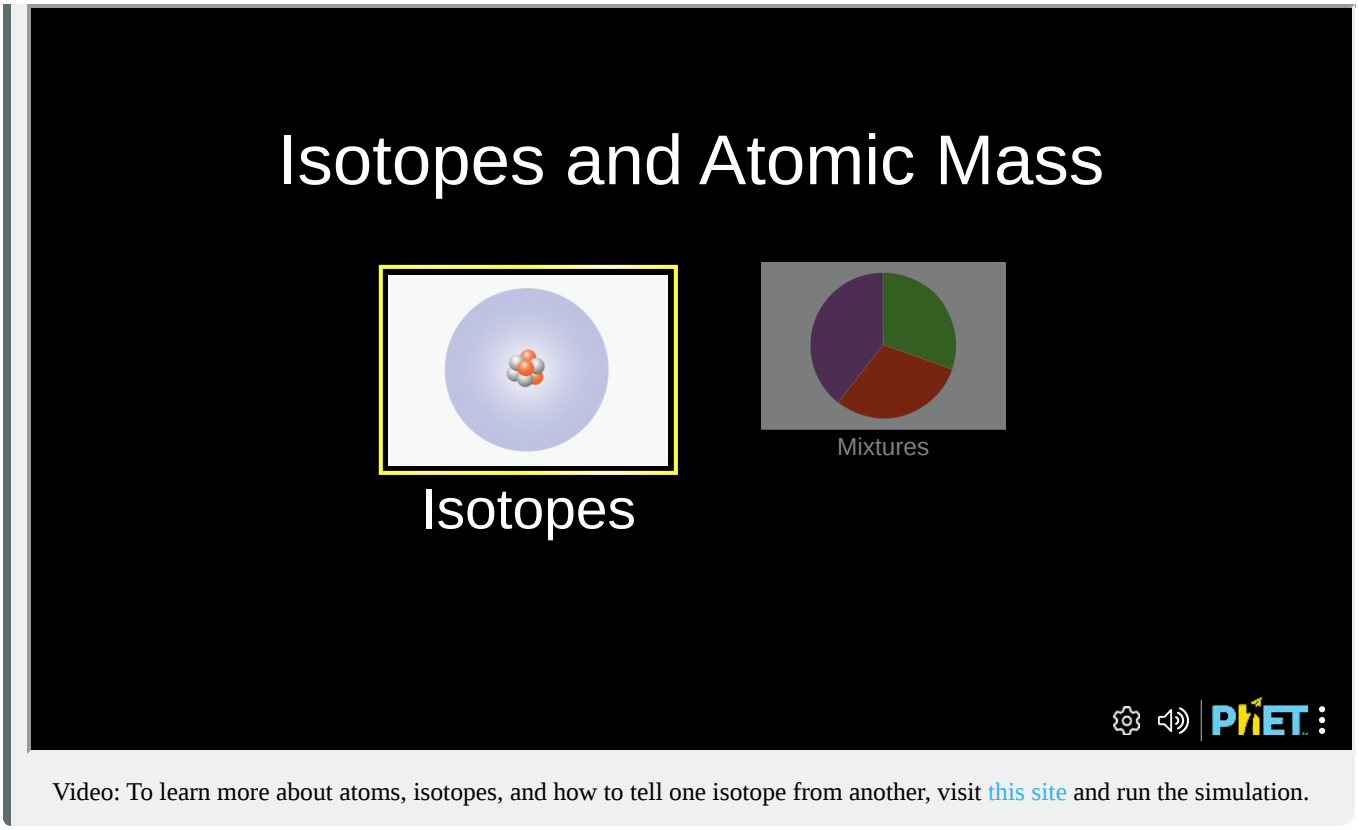
After approximately 5,730 years, half of the starting concentration of C^{14} will have been converted back to N^{14}. The time it takes for half of the original concentration of an isotope to decay back to its more stable form is called its half-life. Because the half-life of C^{14} is long, it is used to date formerly living objects such as old bones or wood. Comparing the ratio of the C^{14} concentration found in an object to the amount of C^{14} detected in the atmosphere, the amount of the isotope that has not yet decayed can be determined. On the basis of this amount, the age of the material, such as the pygmy mammoth shown in Figure 3.3.3, can be calculated with accuracy if it is not much older than about 50,000 years. Other elements have isotopes with different half lives. For example, K^{40} (potassium-40) has a half-life of 1.25 billion years, and U^{235} (Uranium 235) has a half-life of about 700 million years. Through the use of radiometric dating, scientists can study the age of fossils or other remains of extinct organisms to understand how organisms have evolved from earlier species.



Figure 3.3.3: The age of carbon-containing remains less than about 50,000 years old, such as this pygmy mammoth, can be determined using carbon dating. (credit: Bill Faulkner, NPS)

Link to Learning

https://bio.libretexts.org/@go/page/74092



Video: To learn more about atoms, isotopes, and how to tell one isotope from another, visit this site and run the simulation.

The Periodic Table

The different elements are organized and displayed in the periodic table. Devised by Russian chemist Dmitri Mendeleev (1834–1907) in 1869, the table groups elements that, although unique, share certain chemical properties with other elements. The properties of elements are responsible for their physical state at room temperature: they may be gases, solids, or liquids. Elements also have specific chemical reactivity, the ability to combine and to chemically bond with each other.

In the periodic table, shown in Figure 3.3.4, the elements are organized and displayed according to their atomic number and are arranged in a series of rows and columns based on shared chemical and physical properties. In addition to providing the atomic number for each element, the periodic table also displays the element's atomic mass. Looking at carbon, for example, its symbol (C) and name appear, as well as its atomic number of six (in the upper left-hand corner) and its atomic mass of 12.11.

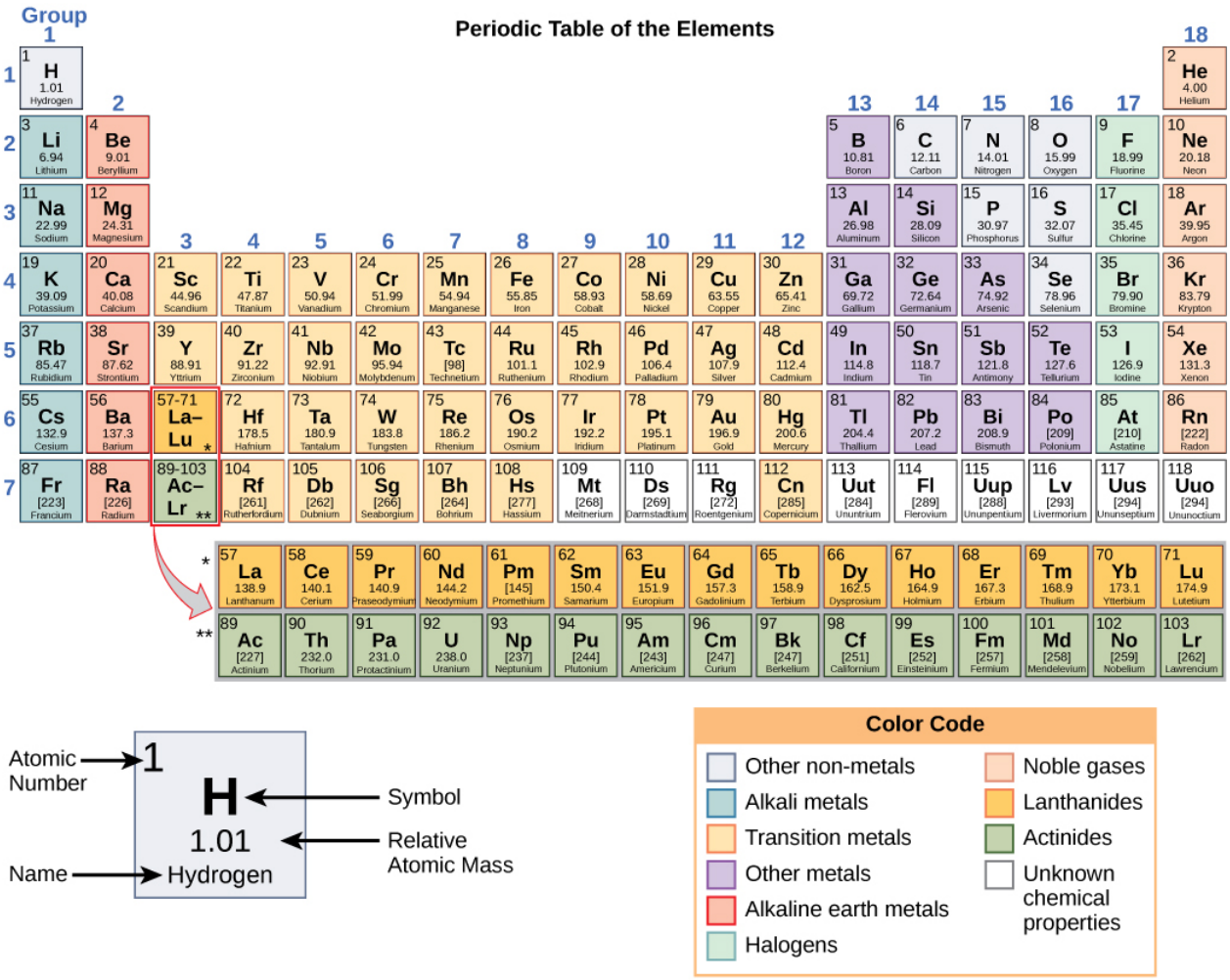


Figure 3.3.4: The periodic table shows the atomic mass and atomic number of each element. The atomic number appears above the symbol for the element and the approximate atomic mass appears below it.

The periodic table groups elements according to chemical properties. The differences in chemical reactivity between the elements are based on the number and spatial distribution of an atom's electrons. Atoms that chemically react and bond to each other form molecules. Molecules are simply two or more atoms chemically bonded together. Logically, when two atoms chemically bond to form a molecule, their electrons, which form the outermost region of each atom, come together first as the atoms form a chemical bond.

Electron Shells and the Bohr Model

It should be stressed that there is a connection between the number of protons in an element, the atomic number that distinguishes one element from another, and the number of electrons it has. In all electrically neutral atoms, the number of electrons is the same as the number of protons. Thus, each element, at least when electrically neutral, has a characteristic number of electrons equal to its atomic number.

An early model of the atom was developed in 1913 by Danish scientist Niels Bohr (1885–1962). The Bohr model shows the atom as a central nucleus containing protons and neutrons, with the electrons in circular orbitals at specific distances from the nucleus, as illustrated in Figure 3.3.5. These orbits form electron shells or energy levels, which are a way of visualizing the number of electrons in the outermost shells. These energy levels are designated by a number and the symbol "n." For example, 1n represents the first energy level located closest to the nucleus.

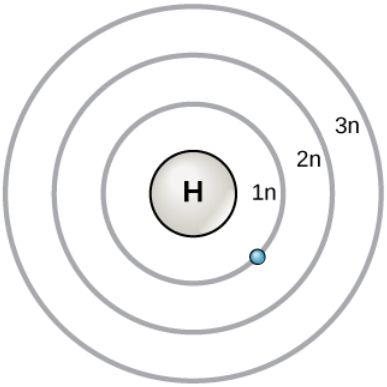


Figure 3.3.5: The Bohr model was developed by Niels Bohrs in 1913. In this model, electrons exist within principal shells. An electron normally exists in the lowest energy shell available, which is the one closest to the nucleus. Energy from a photon of light can bump it up to a higher energy shell, but this situation is unstable, and the electron quickly decays back to the ground state. In the process, a photon of light is released

Electrons fill orbitals in a consistent order: they first fill the orbitals closest to the nucleus, then they continue to fill orbitals of increasing energy further from the nucleus. If there are multiple orbitals of equal energy, they will be filled with one electron in each energy level before a second electron is added. The electrons of the outermost energy level determine the energetic stability of the atom and its tendency to form chemical bonds with other atoms to form molecules.

Under standard conditions, atoms fill the inner shells first, often resulting in a variable number of electrons in the outermost shell. The innermost shell has a maximum of two electrons but the next two electron shells can each have a maximum of eight electrons. This is known as the octet rule, which states, with the exception of the innermost shell, that atoms are more stable energetically when they have eight electrons in their valence shell, the outermost electron shell. Examples of some neutral atoms and their electron configurations are shown in Figure 3.3.6. Notice that in this figure, helium has a complete outer electron shell, with two electrons filling its first and only shell. Similarly, neon has a complete outer 2n shell containing eight electrons. In contrast, chlorine and sodium have seven and one in their outer shells, respectively, but theoretically they would be more energetically stable if they followed the octet rule and had eight.

Art Connection

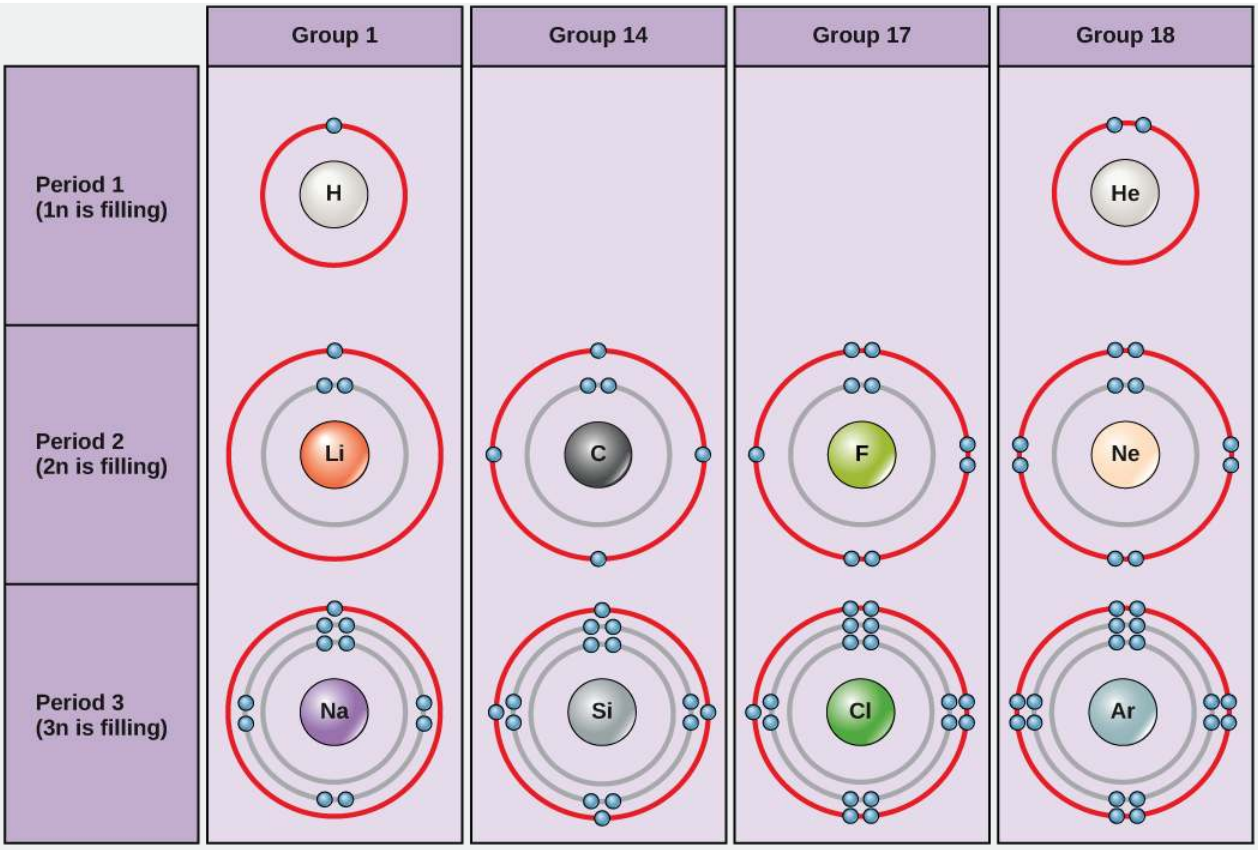


Figure 3.3.6: Bohr diagrams indicate how many electrons fill each principal shell. Group 18 elements (helium, neon, and argon are shown) have a full outer, or valence, shell. A full valence shell is the most stable electron configuration. Elements in other groups have partially filled valence shells and gain or lose electrons to achieve a stable electron configuration.

An atom may give, take, or share electrons with another atom to achieve a full valence shell, the most stable electron configuration. Looking at this figure, how many electrons do elements in group 1 need to lose in order to achieve a stable electron configuration? How many electrons do elements in groups 14 and 17 need to gain to achieve a stable configuration?

Understanding that the organization of the periodic table is based on the total number of protons (and electrons) helps us know how electrons are distributed among the outer shell. The periodic table is arranged in columns and rows based on the number of electrons and where these electrons are located. Take a closer look at the some of the elements in the table's far right column in Figure 3.3.6. The group 18 atoms helium (He), neon (Ne), and argon (Ar) all have filled outer electron shells, making it unnecessary for them to share electrons with other atoms to attain stability; they are highly stable as single atoms. Their non-reactivity has resulted in their being named the inert gases (or noble gases). Compare this to the group 1 elements in the left-hand column. These elements, including hydrogen (H), lithium (Li), and sodium (Na), all have one electron in their outermost shells. That means that they can achieve a stable configuration and a filled outer shell by donating or sharing one electron with another atom or a molecule such as water. Hydrogen will donate or share its electron to achieve this configuration, while lithium and sodium will donate their electron to become stable. As a result of losing a negatively charged electron, they become positively charged ions. Group 17 elements, including fluorine and chlorine, have seven electrons in their outmost shells, so they tend to fill this shell with an electron from other atoms or molecules, making them negatively charged ions. Group 14 elements, of which carbon is the most important to living systems, have four electrons in their outer shell allowing them to make several covalent bonds (discussed below) with other atoms. Thus, the columns of the periodic table represent the potential shared state of these elements' outer electron shells that is responsible for their similar chemical characteristics.

Electron Orbitals

Although useful to explain the reactivity and chemical bonding of certain elements, the Bohr model of the atom does not accurately reflect how electrons are spatially distributed surrounding the nucleus. They do not circle the nucleus like the earth orbits the sun,

but are found in electron orbitals. These relatively complex shapes result from the fact that electrons behave not just like particles, but also like waves. Mathematical equations from quantum mechanics known as wave functions can predict within a certain level of probability where an electron might be at any given time. The area where an electron is most likely to be found is called its orbital.

Recall that the Bohr model depicts an atom's electron shell configuration. Within each electron shell are subshells, and each subshell has a specified number of orbitals containing electrons. While it is impossible to calculate exactly where an electron is located, scientists know that it is most probably located within its orbital path. Subshells are designated by the letter s, *p*, *d*, and *f*. The *s* subshell is spherical in shape and has one orbital. Principal shell 1n has only a single *s* orbital, which can hold two electrons. Principal shell 2n has one *s* and one *p* subshell, and can hold a total of eight electrons. The *p* subshell has three dumbbell-shaped orbitals, as illustrated in Figure 3.3.7. Subshells *d* and *f* have more complex shapes and contain five and seven orbitals, respectively. These are not shown in the illustration. Principal shell 3n has *s*, *p*, and *d* subshells and can hold 18 electrons. Principal shell 4n has *s*, *p*, *d* and *f* orbitals and can hold 32 electrons. Moving away from the nucleus, the number of electrons and orbitals found in the energy levels increases. Progressing from one atom to the next in the periodic table, the electron structure can be worked out by fitting an extra electron into the next available orbital.

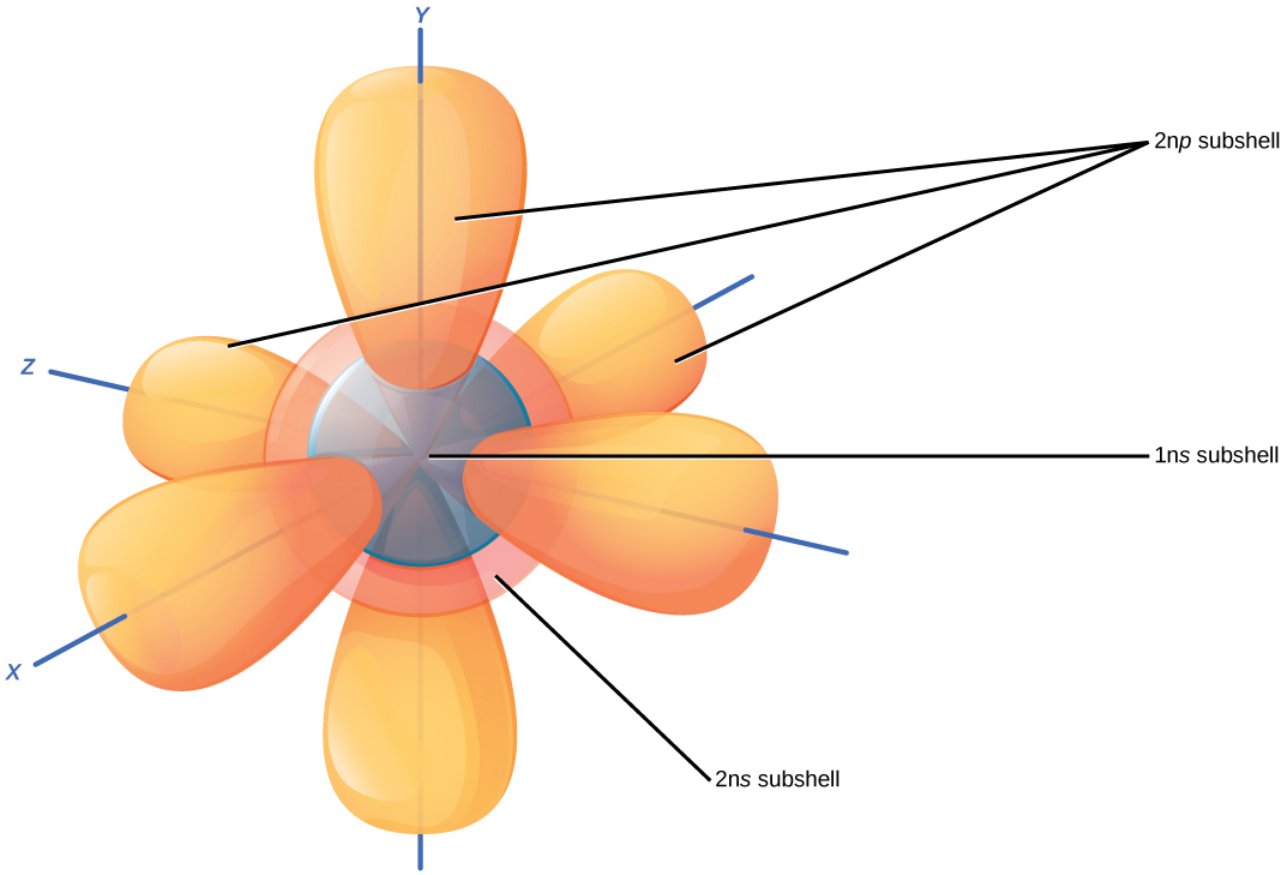


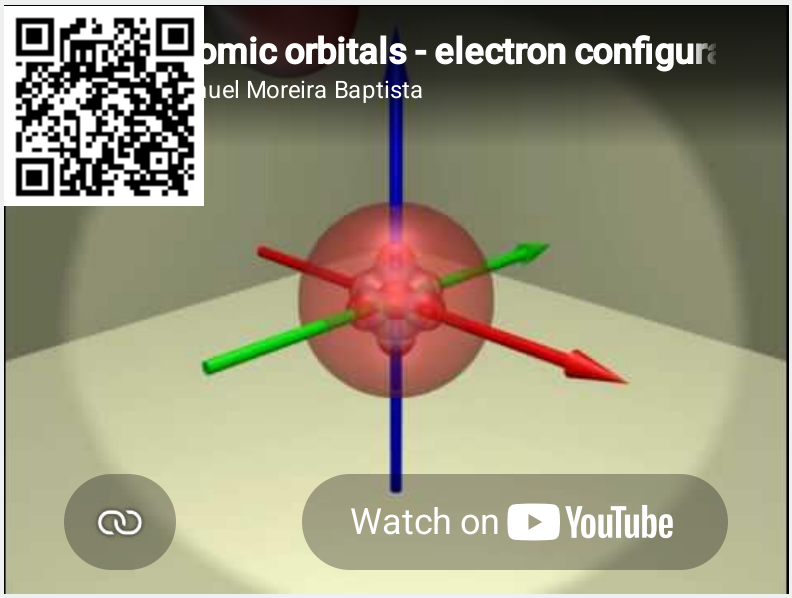
Figure 3.3.7: The *s* subshells are shaped like spheres. Both the 1n and 2n principal shells have an *s* orbital, but the size of the sphere is larger in the 2n orbital. Each sphere is a single orbital. *p* subshells are made up of three dumbbell-shaped orbitals. Principal shell 2n has a *p* subshell, but shell 1 does not.

The closest orbital to the nucleus, called the 1s orbital, can hold up to two electrons. This orbital is equivalent to the innermost electron shell of the Bohr model of the atom. It is called the 1*s* orbital because it is spherical around the nucleus. The 1*s* orbital is the closest orbital to the nucleus, and it is always filled first, before any other orbital can be filled. Hydrogen has one electron; therefore, it has only one spot within the 1*s* orbital occupied. This is designated as $1s^1$, where the superscripted 1 refers to the one electron within the 1*s* orbital. Helium has two electrons; therefore, it can completely fill the 1*s* orbital with its two electrons. This is designated as $1s^2$, referring to the two electrons of helium in the 1*s* orbital. On the periodic table Figure 3.3.4, hydrogen and helium

are the only two elements in the first row (period); this is because they only have electrons in their first shell, the 1*s* orbital. Hydrogen and helium are the only two elements that have the 1*s* and no other electron orbitals in the electrically neutral state.

The second electron shell may contain eight electrons. This shell contains another spherical *s* orbital and three "dumbbell" shaped *p* orbitals, each of which can hold two electrons, as shown in Figure 3.3.7. After the 1*s* orbital is filled, the second electron shell is filled, first filling its 2*s* orbital and then its three *p* orbitals. When filling the *p* orbitals, each takes a single electron; once each *p* orbital has an electron, a second may be added. Lithium (Li) contains three electrons that occupy the first and second shells. Two electrons fill the 1*s* orbital, and the third electron then fills the 2*s* orbital. Its electron configuration is $1s^2 2s^1$. Neon (Ne), on the other hand, has a total of ten electrons: two are in its innermost 1*s* orbital and eight fill its second shell (two each in the 2*s* and three *p* orbitals); thus, it is an inert gas and energetically stable as a single atom that will rarely form a chemical bond with other atoms. Larger elements have additional orbitals, making up the third electron shell. While the concepts of electron shells and orbitals are closely related, orbitals provide a more accurate depiction of the electron configuration of an atom because the orbital model specifies the different shapes and special orientations of all the places that electrons may occupy.

Link to Learning



Video: Watch this visual animation to see the spatial arrangement of the *p* and *s* orbitals.

Chemical Reactions and Molecules

All elements are most stable when their outermost shell is filled with electrons according to the octet rule. This is because it is energetically favorable for atoms to be in that configuration and it makes them stable. However, since not all elements have enough electrons to fill their outermost shells, atoms form chemical bonds with other atoms thereby obtaining the electrons they need to attain a stable electron configuration. When two or more atoms chemically bond with each other, the resultant chemical structure is a molecule. The familiar water molecule, H_2O, consists of two hydrogen atoms and one oxygen atom; these bond together to form water, as illustrated in Figure 3.3.8. Atoms can form molecules by donating, accepting, or sharing electrons to fill their outer shells.

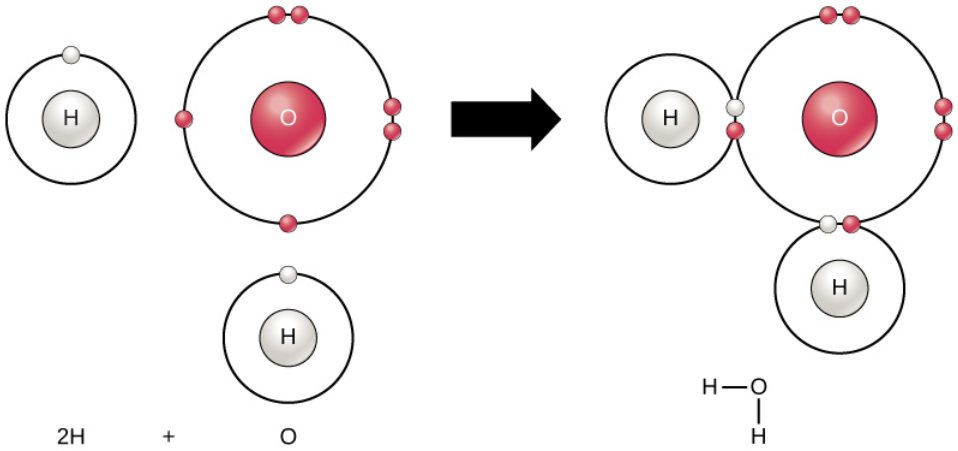


Figure 3.3.8: Two or more atoms may bond with each other to form a molecule. When two hydrogens and an oxygen share electrons via covalent bonds, a water molecule is formed.

Chemical reactions occur when two or more atoms bond together to form molecules or when bonded atoms are broken apart. The substances used in the beginning of a chemical reaction are called the reactants (usually found on the left side of a chemical equation), and the substances found at the end of the reaction are known as the products (usually found on the right side of a chemical equation). An arrow is typically drawn between the reactants and products to indicate the direction of the chemical reaction; this direction is not always a "one-way street." For the creation of the water molecule shown above, the chemical equation would be:

$$2\,H + O \rightarrow H_2O$$

An example of a simple chemical reaction is the breaking down of hydrogen peroxide molecules, each of which consists of two hydrogen atoms bonded to two oxygen atoms (H_2O_2). The reactant hydrogen peroxide is broken down into water, containing one oxygen atom bound to two hydrogen atoms (H_2O), and oxygen, which consists of two bonded oxygen atoms (O_2). In the equation below, the reaction includes two hydrogen peroxide molecules and two water molecules. This is an example of a balanced chemical equation, wherein the number of atoms of each element is the same on each side of the equation. According to the law of conservation of matter, the number of atoms before and after a chemical reaction should be equal, such that no atoms are, under normal circumstances, created or destroyed.

$$2\,H_2O_2\ \text{(hydrogen peroxide)} \rightarrow 2\,H_2O\ \text{(water)} + O_2\ \text{(oxygen)}$$

Even though all of the reactants and products of this reaction are molecules (each atom remains bonded to at least one other atom), in this reaction only hydrogen peroxide and water are representatives of compounds: they contain atoms of more than one type of element. Molecular oxygen, on the other hand, as shown in Figure 3.3.9, consists of two doubly bonded oxygen atoms and is not classified as a compound but as a mononuclear molecule.

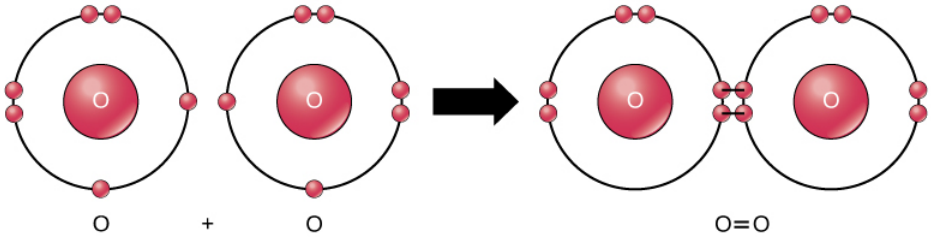


Figure 3.3.9: The oxygen atoms in an O_2 molecule are joined by a double bond.

Some chemical reactions, such as the one shown above, can proceed in one direction until the reactants are all used up. The equations that describe these reactions contain a unidirectional arrow and are irreversible. Reversible reactions are those that can go in either direction. In reversible reactions, reactants are turned into products, but when the concentration of product goes beyond a certain threshold (characteristic of the particular reaction), some of these products will be converted back into reactants; at this point, the designations of products and reactants are reversed. This back and forth continues until a certain relative balance between

reactants and products occurs—a state called equilibrium. These situations of reversible reactions are often denoted by a chemical equation with a double headed arrow pointing towards both the reactants and products.

For example, in human blood, excess hydrogen ions (H^+) bind to bicarbonate ions (HCO_3^-) forming an equilibrium state with carbonic acid (H_2CO_3). If carbonic acid were added to this system, some of it would be converted to bicarbonate and hydrogen ions.

$$HCO_3^- + H^+ \leftrightarrow H_2CO_3$$

In biological reactions, however, equilibrium is rarely obtained because the concentrations of the reactants or products or both are constantly changing, often with a product of one reaction being a reactant for another. To return to the example of excess hydrogen ions in the blood, the formation of carbonic acid will be the major direction of the reaction. However, the carbonic acid can also leave the body as carbon dioxide gas (via exhalation) instead of being converted back to bicarbonate ion, thus driving the reaction to the right by the chemical law known as law of mass action. These reactions are important for maintaining the homeostasis of our blood.

$$HCO_3^- + H^+ \leftrightarrow H_2CO_3 \leftrightarrow CO_2 + H_2O$$

Ions and Ionic Bonds

Some atoms are more stable when they gain or lose an electron (or possibly two) and form ions. This fills their outermost electron shell and makes them energetically more stable. Because the number of electrons does not equal the number of protons, each ion has a net charge. Cations are positive ions that are formed by losing electrons. Negative ions are formed by gaining electrons and are called anions. Anions are designated by their elemental name being altered to end in "-ide": the anion of chlorine is called chloride, and the anion of sulfur is called sulfide, for example.

This movement of electrons from one element to another is referred to as electron transfer. As Figure 3.3.10 illustrates, sodium (Na) only has one electron in its outer electron shell. It takes less energy for sodium to donate that one electron than it does to accept seven more electrons to fill the outer shell. If sodium loses an electron, it now has 11 protons, 11 neutrons, and only 10 electrons, leaving it with an overall charge of +1. It is now referred to as a sodium ion. Chlorine (Cl) in its lowest energy state (called the ground state) has seven electrons in its outer shell. Again, it is more energy-efficient for chlorine to gain one electron than to lose seven. Therefore, it tends to gain an electron to create an ion with 17 protons, 17 neutrons, and 18 electrons, giving it a net negative (–1) charge. It is now referred to as a chloride ion. In this example, sodium will donate its one electron to empty its shell, and chlorine will accept that electron to fill its shell. Both ions now satisfy the octet rule and have complete outermost shells. Because the number of electrons is no longer equal to the number of protons, each is now an ion and has a +1 (sodium cation) or –1 (chloride anion) charge. Note that these transactions can normally only take place simultaneously: in order for a sodium atom to lose an electron, it must be in the presence of a suitable recipient like a chlorine atom.

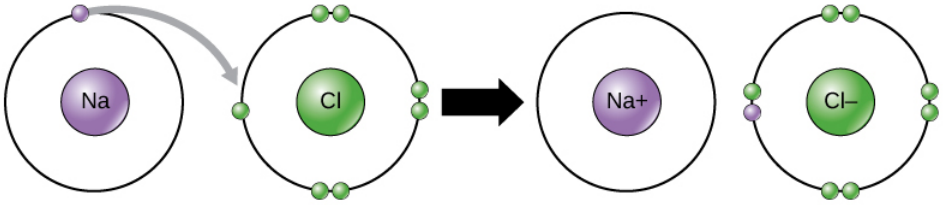


Figure 3.3.10: In the formation of an ionic compound, metals lose electrons and nonmetals gain electrons to achieve an octet.

Ionic bonds are formed between ions with opposite charges. For instance, positively charged sodium ions and negatively charged chloride ions bond together to make crystals of sodium chloride, or table salt, creating a crystalline molecule with zero net charge.

Certain salts are referred to in physiology as electrolytes (including sodium, potassium, and calcium), ions necessary for nerve impulse conduction, muscle contractions and water balance. Many sports drinks and dietary supplements provide these ions to replace those lost from the body via sweating during exercise.

Covalent Bonds and Other Bonds and Interactions

Another way the octet rule can be satisfied is by the sharing of electrons between atoms to form covalent bonds. These bonds are stronger and much more common than ionic bonds in the molecules of living organisms. Covalent bonds are commonly found in

carbon-based organic molecules, such as our DNA and proteins. Covalent bonds are also found in inorganic molecules like H_2O, CO_2, and O_2. One, two, or three pairs of electrons may be shared, making single, double, and triple bonds, respectively. The more covalent bonds between two atoms, the stronger their connection. Thus, triple bonds are the strongest.

The strength of different levels of covalent bonding is one of the main reasons living organisms have a difficult time in acquiring nitrogen for use in constructing their molecules, even though molecular nitrogen, N_2, is the most abundant gas in the atmosphere. Molecular nitrogen consists of two nitrogen atoms triple bonded to each other and, as with all molecules, the sharing of these three pairs of electrons between the two nitrogen atoms allows for the filling of their outer electron shells, making the molecule more stable than the individual nitrogen atoms. This strong triple bond makes it difficult for living systems to break apart this nitrogen in order to use it as constituents of proteins and DNA.

The formation of water molecules provides an example of covalent bonding. The hydrogen and oxygen atoms that combine to form water molecules are bound together by covalent bonds, as shown in Figure 3.3.8. The electron from the hydrogen splits its time between the incomplete outer shell of the hydrogen atoms and the incomplete outer shell of the oxygen atoms. To completely fill the outer shell of oxygen, which has six electrons in its outer shell but which would be more stable with eight, two electrons (one from each hydrogen atom) are needed: hence the well-known formula H_2O. The electrons are shared between the two elements to fill the outer shell of each, making both elements more stable.

Link to Learning



Video: View this short video to see an animation of ionic and covalent bonding.

Polar Covalent Bonds

There are two types of covalent bonds: polar and nonpolar. In a polar covalent bond, shown in Figure 3.3.11, the electrons are unequally shared by the atoms and are attracted more to one nucleus than the other. Because of the unequal distribution of electrons between the atoms of different elements, a slightly positive (δ+) or slightly negative (δ–) charge develops. This partial charge is an important property of water and accounts for many of its characteristics.

Water is a polar molecule, with the hydrogen atoms acquiring a partial positive charge and the oxygen a partial negative charge. This occurs because the nucleus of the oxygen atom is more attractive to the electrons of the hydrogen atoms than the hydrogen nucleus is to the oxygen's electrons. Thus oxygen has a higher electronegativity than hydrogen and the shared electrons spend more time in the vicinity of the oxygen nucleus than they do near the nucleus of the hydrogen atoms, giving the atoms of oxygen and hydrogen slightly negative and positive charges, respectively. Another way of stating this is that the probability of finding a shared electron near an oxygen nucleus is more likely than finding it near a hydrogen nucleus. Either way, the atom's relative electronegativity contributes to the development of partial charges whenever one element is significantly more electronegative than the other, and the charges generated by these polar bonds may then be used for the formation of hydrogen bonds based on the

attraction of opposite partial charges. (Hydrogen bonds, which are discussed in detail below, are weak bonds between slightly positively charged hydrogen atoms to slightly negatively charged atoms in other molecules.) Since macromolecules often have atoms within them that differ in electronegativity, polar bonds are often present in organic molecules.

Nonpolar Covalent Bonds

Nonpolar covalent bonds form between two atoms of the same element or between different elements that share electrons equally. For example, molecular oxygen (O_2) is nonpolar because the electrons will be equally distributed between the two oxygen atoms.

Another example of a nonpolar covalent bond is methane (CH_4), also shown in Figure 3.3.11. Carbon has four electrons in its outermost shell and needs four more to fill it. It gets these four from four hydrogen atoms, each atom providing one, making a stable outer shell of eight electrons. Carbon and hydrogen do not have the same electronegativity but are similar; thus, nonpolar bonds form. The hydrogen atoms each need one electron for their outermost shell, which is filled when it contains two electrons. These elements share the electrons equally among the carbons and the hydrogen atoms, creating a nonpolar covalent molecule.

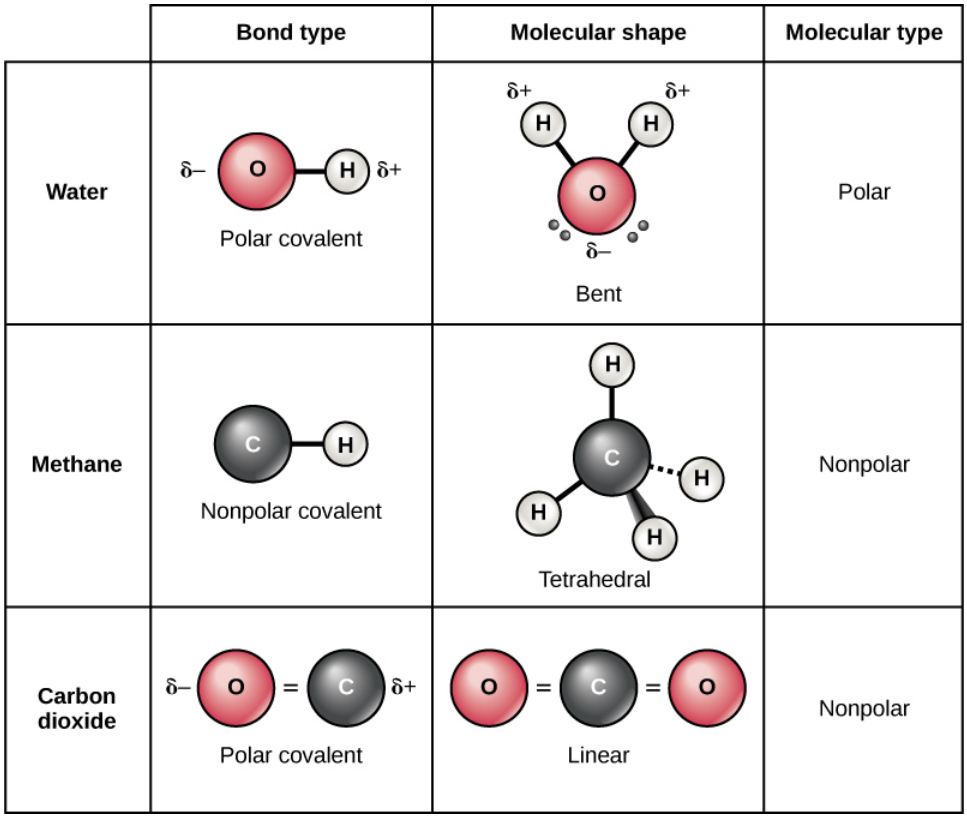


Figure 3.3.11: Whether a molecule is polar or nonpolar depends both on bond type and molecular shape. Both water and carbon dioxide have polar covalent bonds, but carbon dioxide is linear, so the partial charges on the molecule cancel each other out.

Hydrogen Bonds and Van Der Waals Interactions

Ionic and covalent bonds between elements require energy to break. Ionic bonds are not as strong as covalent, which determines their behavior in biological systems. However, not all bonds are ionic or covalent bonds. Weaker bonds can also form between molecules. Two weak bonds that occur frequently are hydrogen bonds and van der Waals interactions. Without these two types of bonds, life as we know it would not exist. Hydrogen bonds provide many of the critical, life-sustaining properties of water and also stabilize the structures of proteins and DNA, the building block of cells.

When polar covalent bonds containing hydrogen form, the hydrogen in that bond has a slightly positive charge because hydrogen's electron is pulled more strongly toward the other element and away from the hydrogen. Because the hydrogen is slightly positive, it will be attracted to neighboring negative charges. When this happens, a weak interaction occurs between the $\delta^+$of the hydrogen from one molecule and the δ– charge on the more electronegative atoms of another molecule, usually oxygen or nitrogen, or within the same molecule. This interaction is called a hydrogen bond. This type of bond is common and occurs regularly between water

molecules. Individual hydrogen bonds are weak and easily broken; however, they occur in very large numbers in water and in organic polymers, creating a major force in combination. Hydrogen bonds are also responsible for zipping together the DNA double helix.

Like hydrogen bonds, van der Waals interactions are weak attractions or interactions between molecules. Van der Waals attractions can occur between any two or more molecules and are dependent on slight fluctuations of the electron densities, which are not always symmetrical around an atom. For these attractions to happen, the molecules need to be very close to one another. These bonds—along with ionic, covalent, and hydrogen bonds—contribute to the three-dimensional structure of the proteins in our cells that is necessary for their proper function.

Career Connection: Pharmaceutical Chemist

Pharmaceutical chemists are responsible for the development of new drugs and trying to determine the mode of action of both old and new drugs. They are involved in every step of the drug development process. Drugs can be found in the natural environment or can be synthesized in the laboratory. In many cases, potential drugs found in nature are changed chemically in the laboratory to make them safer and more effective, and sometimes synthetic versions of drugs substitute for the version found in nature.

After the initial discovery or synthesis of a drug, the chemist then develops the drug, perhaps chemically altering it, testing it to see if the drug is toxic, and then designing methods for efficient large-scale production. Then, the process of getting the drug approved for human use begins. In the United States, drug approval is handled by the Food and Drug Administration (FDA) and involves a series of large-scale experiments using human subjects to make sure the drug is not harmful and effectively treats the condition it aims to treat. This process often takes several years and requires the participation of physicians and scientists, in addition to chemists, to complete testing and gain approval.

An example of a drug that was originally discovered in a living organism is Paclitaxel (Taxol), an anti-cancer drug used to treat breast cancer. This drug was discovered in the bark of the pacific yew tree. Another example is aspirin, originally isolated from willow tree bark. Finding drugs often means testing hundreds of samples of plants, fungi, and other forms of life to see if any biologically active compounds are found within them. Sometimes, traditional medicine can give modern medicine clues to where an active compound can be found. For example, the use of willow bark to make medicine has been known for thousands of years, dating back to ancient Egypt. It was not until the late 1800s, however, that the aspirin molecule, known as acetylsalicylic acid, was purified and marketed for human use.

Occasionally, drugs developed for one use are found to have unforeseen effects that allow these drugs to be used in other, unrelated ways. For example, the drug minoxidil (Rogaine) was originally developed to treat high blood pressure. When tested on humans, it was noticed that individuals taking the drug would grow new hair. Eventually the drug was marketed to men and women with baldness to restore lost hair.

The career of the pharmaceutical chemist may involve detective work, experimentation, and drug development, all with the goal of making human beings healthier.

Summary

Matter is anything that occupies space and has mass. It is made up of elements. All of the 92 elements that occur naturally have unique qualities that allow them to combine in various ways to create molecules, which in turn combine to form cells, tissues, organ systems, and organisms. Atoms, which consist of protons, neutrons, and electrons, are the smallest units of an element that retain all of the properties of that element. Electrons can be transferred, shared, or cause charge disparities between atoms to create bonds, including ionic, covalent, and hydrogen bonds, as well as van der Waals interactions.

Art Connections

Figure 3.3.2: How many neutrons do carbon-12 and carbon-13 have, respectively?

Answer

Carbon-12 has six neutrons. Carbon-13 has seven neutrons.

Figure 3.3.6: An atom may give, take, or share electrons with another atom to achieve a full valence shell, the most stable electron configuration. Looking at this figure, how many electrons do elements in group 1 need to lose in order to achieve a stable electron configuration? How many electrons do elements in groups 14 and 17 need to gain to achieve a stable configuration?

Answer

Elements in group 1 need to lose one electron to achieve a stable electron configuration. Elements in groups 14 and 17 need to gain four and one electrons, respectively, to achieve a stable configuration.

Glossary

anion
negative ion that is formed by an atom gaining one or more electrons

atom
the smallest unit of matter that retains all of the chemical properties of an element

atomic mass
calculated mean of the mass number for an element's isotopes

atomic number
total number of protons in an atom

balanced chemical equation
statement of a chemical reaction with the number of each type of atom equalized for both the products and reactants

cation
positive ion that is formed by an atom losing one or more electrons

chemical bond
interaction between two or more of the same or different atoms that results in the formation of molecules

chemical reaction
process leading to the rearrangement of atoms in molecules

chemical reactivity
the ability to combine and to chemically bond with each other

compound
substance composed of molecules consisting of atoms of at least two different elements

covalent bond
type of strong bond formed between two of the same or different elements; forms when electrons are shared between atoms

electrolyte
ion necessary for nerve impulse conduction, muscle contractions and water balance

electron
negatively charged subatomic particle that resides outside of the nucleus in the electron orbital; lacks functional mass and has a negative charge of –1 unit

electron configuration
arrangement of electrons in an atom's electron shell (for example, $1s^2 2s^2 2p^6$)

electron orbital
how electrons are spatially distributed surrounding the nucleus; the area where an electron is most likely to be found

electron transfer
movement of electrons from one element to another; important in creation of ionic bonds

electronegativity
ability of some elements to attract electrons (often of hydrogen atoms), acquiring partial negative charges in molecules and creating partial positive charges on the hydrogen atoms

element
one of 118 unique substances that cannot be broken down into smaller substances; each element has unique properties and a specified number of protons

equilibrium
steady state of relative reactant and product concentration in reversible chemical reactions in a closed system

hydrogen bond
weak bond between slightly positively charged hydrogen atoms to slightly negatively charged atoms in other molecules

inert gas
(also, noble gas) element with filled outer electron shell that is unreactive with other atoms

ion
atom or chemical group that does not contain equal numbers of protons and electrons

ionic bond
chemical bond that forms between ions with opposite charges (cations and anions)

irreversible chemical reaction
chemical reaction where reactants proceed uni-directionally to form products

isotope
one or more forms of an element that have different numbers of neutrons

law of mass action
chemical law stating that the rate of a reaction is proportional to the concentration of the reacting substances

mass number
total number of protons and neutrons in an atom

matter
anything that has mass and occupies space

molecule
two or more atoms chemically bonded together

neutron
uncharged particle that resides in the nucleus of an atom; has a mass of one amu

noble gas

see inert gas

nonpolar covalent bond
type of covalent bond that forms between atoms when electrons are shared equally between them

nucleus
core of an atom; contains protons and neutrons

octet rule
rule that atoms are most stable when they hold eight electrons in their outermost shells

orbital
region surrounding the nucleus; contains electrons

periodic table
organizational chart of elements indicating the atomic number and atomic mass of each element; provides key information about the properties of the elements

polar covalent bond
type of covalent bond that forms as a result of unequal sharing of electrons, resulting in the creation of slightly positive and slightly negative charged regions of the molecule

product
molecule found on the right side of a chemical equation

proton
positively charged particle that resides in the nucleus of an atom; has a mass of one amu and a charge of +1

radioisotope
isotope that emits radiation composed of subatomic particles to form more stable elements

reactant
molecule found on the left side of a chemical equation

reversible chemical reaction
chemical reaction that functions bi-directionally, where products may turn into reactants if their concentration is great enough

valence shell
outermost shell of an atom

van der Waals interaction
very weak interaction between molecules due to temporary charges attracting atoms that are very close together

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3.4: Lewis Electron Dot Structures

Learning Outcomes

- Determine Lewis structure of a compound.

Ionic substances are completely held together by ionic bonds. The full charges of the ions (for example, Na^+ and Cl^- in sodium chloride) cause electrostatic interactions that result in a stable crystal lattice. Ionic compounds exist as extended, orderly arrangements of ions. This is quite different from the structure of molecular substances, which take the form of collections of individual molecules.

The electrons that form a covalent bond are not fully possessed by a single atom (as the electrons in an ion would be) but are shared between the two atoms involved in the bond. The concept of the covalent bond was first proposed in 1916 by the American chemist G. N. Lewis (1875 - 1946), who suggested that sharing electrons was one way that atoms could attain a complete octet of valence electrons. This idea was expanded upon by Linus Pauling (1901 - 1994), who eventually won the Nobel Prize in Chemistry in 1954 for his work on chemical bonding.

Single Covalent Bonds

The simplest covalent bond is formed between two hydrogen atoms. Each hydrogen atom has a single electron, and each needs two electrons for a full outer shell. The hydrogen molecule, H_2, consists of two hydrogen atoms sharing their two valence electrons. Hydrogen can also form covalent bonds with other atoms. For example, hydrogen and chlorine each need one more electron to achieve a noble gas configuration. By sharing valence electrons (each atom donates one), the stable HCl molecule is formed.

We will use a simplified representation of covalent bonds known as **Lewis structures**. These drawings are also know by various other names, including Lewis dot structures or electron dot structures. Each dot in the structure represents one valence electron in the compound. For example, H_2 could be drawn as $H:H$. Each dot represents one valence electron, and the fact that they are placed between the two atoms means that they are being shared bas a covalent bond. For larger molecules, it can become cumbersome to draw out all of the valence electrons, so a bonding pair of electrons can also be drawn as a straight line. Thus, H_2 can also be represented as $H–H$.

If we wanted to show the Lewis structure of HCl, we would draw the following:



We can see that the covalent bond consists of two electrons between the H and the Cl. The H has a full outer shell of two electrons and the chlorine has a full outer shell of eight electrons. Covalent bonds with other halogens can be written the same way.

Similar types of Lewis structures can be written for other molecules that form covalent bonds. Many compounds that contain O, N, C, S, and P are held together by covalent bonds. The number of covalent bonds an atom will form can generally be predicted by the number of electrons an atom requires to fill its valence shell. For example, oxygen has 6 electrons in its outer shell and needs two more to fill this shell, so it will only form two covalent bonds with other atoms. If we look at the water molecule (H_2O) (see figure below), we see that the oxygen atom makes two total bonds (one with each hydrogen atom).

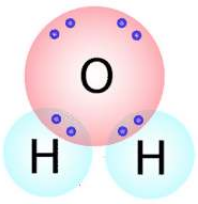
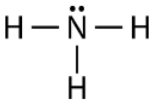


Figure 3.4.1: Electron sharing in a water molecule.

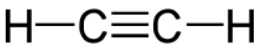
As you can see, there are two pairs of electrons not involved in covalent bonding. These unbonded pairs of electrons are known as **lone pairs** and contribute to the overall shape of the molecule. Similarly, nitrogen needs three electrons to complete its valence shell, so it tends to make three covalent bonds, with one lone pair of non-bonding electrons left over.



Again, each of the lines stands for a *pair* of bonding electrons (a single bond), and the lone pair of nitrogen is drawn as two dots.

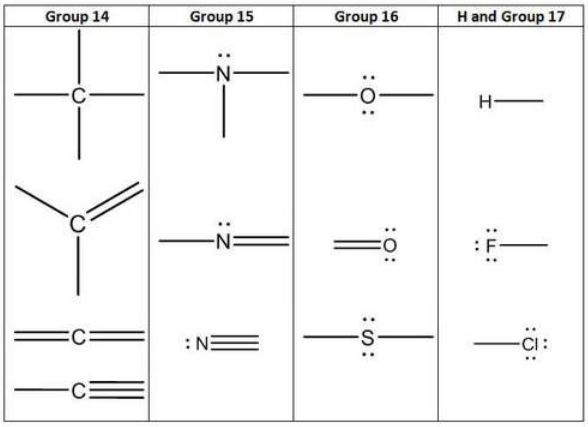
Double and Triple Bonds

So far we have considered only single bonds, formed by the sharing of one electron from each atom. Many molecules contain **double bonds**, in which each atom shares two electrons, or **triple bonds**, in which each atom shares three electrons. These are represented by drawing two or three lines between the bonded atoms. For example, a carbon-carbon double bond can be written as C :: C or C=C. A carbon-carbon triple bond is shown as C ::: C or with three lines between the two carbon atoms, as seen in the structure of an organic molecule called acetylene (shown in the figure below). Just as N wants to form 3 bonds, other elements tend to form the same number of bonds in different compounds.

 Figure 3.4.2: Acetylene molecule.

We will build Lewis structures that satisfy the octet rule to determine how atoms are attached to one another using the components shown in the table below to create structures that follow the octet rule.

Table 3.4.1***:*** *Components to Build Lewis Structures*



Supplemental Resources

Practice drawing Lewis Dot Structures of Covalent Compounds: http://www.wisc-online.com/objects/V...spx?ID=GCH6404

Contributors and Attributions

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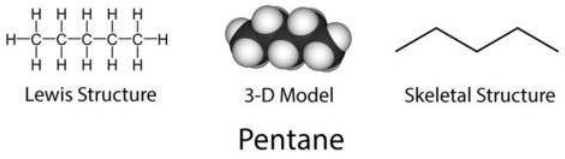
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3.5: Representing Structures

Learning Outcomes

- Use condensed structural formulas to represent molecules.
- Use skeletal structures to represent molecules.

Lewis structures are great for small molecules but can be complicated when dealing with large molecules. There are a variety of ways that we can represent molecules that provide use with enough information without creating a complicated figure. The structures in the figure below all represent the molecules pentane, which is a straight-chain alkane with five carbon atoms.



Lewis Structures

The Lewis structure shows bonds to represent the sharing of electrons and include all atoms in the molecule so we have information about connectivity of atoms but not the molecular shape or geometry.

Space-Filling Model

A 3-D space-filling model shows connectivity of atoms and the shape of the molecule. These work well for smaller molecules, but can be a challenge to interpret since atoms are so close together. This is the most accurate representation of what a molecule looks like.

Skeletal Structure

These are the simplest way to represent the structure of a molecule. Hydrogen atoms are omitted (except when attached to O or S) and carbon atoms are at the intersection of each pair of lines and at the terminal end of each line. Each of the circles in the figure below indicate where a carbon is located.

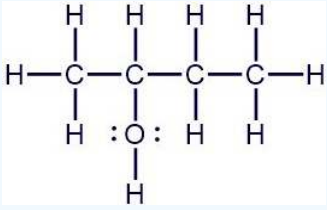

Figure $3.5.1$: Pentane molecule with circles indicating locations of carbon atoms.

Condensed Structures

These provide more information than a chemical formula (like $\mathrm{C_5H_{12}}$ for pentane) but are condensed as given by their name, so they can be written out rather than in a drawing. The best way to write a condensed structure is to "read" a Lewis structure and see how atoms are connected.

Example $3.5.1$

Draw the skeletal and condensed structure of 2-butanol based on the given Lewis structure.

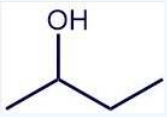


Skeletal Structure

Count the number of carbon atoms and draw the carbon chain with the correct number of carbon atoms. This represents a chain of four carbon atoms.



Now look for any atoms other than hydrogen that are attached to the carbon chain. The second carbon has an $-\mathrm{OH}$ group. Add that to the second carbon in the chain.



The skeletal structure is complete and all of the remaining hydrogen atoms are implied because every carbon must have four bonds.

Condensed Structure

For the condensed structure, we "read" the Lewis structure from left to right.

The first carbon has three hydrogen atoms attached so we start with

$$\mathrm{CH_3} \tag{3.5.1}$$

The second carbon has one hydrogen attached and one $-\mathrm{OH}$ group. Since the $-\mathrm{OH}$ group is to the side, we put it in parentheses

$$\mathrm{CH_3CH(OH)} \tag{3.5.2}$$

The third carbon has two hydrogen atoms attached so we add $\mathrm{CH_2}$

$$\mathrm{CH_3CH(OH)CH_2} \tag{3.5.3}$$

The fourth, and last, carbon has three hydrogen atoms attached, so we add $\mathrm{CH_3}$

$$\mathrm{CH_3CH(OH)CH_2CH_3} \tag{3.5.4}$$

The result is the condensed structure of 2-butanol.

Contributors and Attributions

- Allison Soult, Ph.D. (Department of Chemistry, University of Kentucky)

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3.E: The Chemical Foundation of Life (Exercises)

2.1: Atoms, Isotopes, Ions, and Molecules - The Building Blocks

Review Questions

If xenon has an atomic number of 54 and a mass number of 108, how many neutrons does it have?

A. 54
B. 27
C. 100
D. 108

Answer

A

Atoms that vary in the number of neutrons found in their nuclei are called _____.

A. ions
B. neutrons
C. neutral atoms
D. isotopes

Answer

D

Potassium has an atomic number of 19. What is its electron configuration?

A. shells 1 and 2 are full, and shell 3 has nine electrons
B. shells 1, 2 and 3 are full and shell 4 has three electrons
C. shells 1, 2 and 3 are full and shell 4 has one electron
D. shells 1, 2 and 3 are full and no other electrons are present

Answer

C

Which type of bond represents a weak chemical bond?

A. hydrogen bond
B. atomic bond
C. covalent bond
D. nonpolar covalent bond

Answer

A

Free Response

What makes ionic bonds different from covalent bonds?

Answer

https://bio.libretexts.org/@go/page/74095

Ionic bonds are created between ions. The electrons are not shared between the atoms, but rather are associated more with one ion than the other. Ionic bonds are strong bonds, but are weaker than covalent bonds, meaning it takes less energy to break an ionic bond compared with a covalent one.

Why are hydrogen bonds and van der Waals interactions necessary for cells?

Answer

Hydrogen bonds and van der Waals interactions form weak associations between different molecules or within different regions of the same molecule. They provide the structure and shape necessary for proteins and DNA within cells so that they function properly.

2.2: Water

Review Questions

Which of the following statements is not true?

A. Water is polar.
B. Water stabilizes temperature.
C. Water is essential for life.
D. Water is the most abundant molecule in the Earth's atmosphere.

Answer

D

When acids are added to a solution, the pH should _____.

A. decrease
B. increase
C. stay the same
D. cannot tell without testing

Answer

A

A molecule that binds up excess hydrogen ions in a solution is called a(n) _____.

A. acid
B. isotope
C. base
D. donator

Answer

C

Which of the following statements is true?

A. Acids and bases cannot mix together.
B. Acids and bases will neutralize each other.
C. Acids, but not bases, can change the pH of a solution.
D. Acids donate hydroxide ions (OH^-); bases donate hydrogen ions (H^+).

Answer

B

Free Response

Discuss how buffers help prevent drastic swings in pH.

Answer

Buffers absorb the free hydrogen ions and hydroxide ions that result from chemical reactions. Because they can bond these ions, they prevent increases or decreases in pH. An example of a buffer system is the bicarbonate system in the human body. This system is able to absorb hydrogen and hydroxide ions to prevent changes in pH and keep cells functioning properly.

Why can some insects walk on water?

Answer

Some insects can walk on water, although they are heavier (denser) than water, because of the surface tension of water. Surface tension results from cohesion, or the attraction between water molecules at the surface of the body of water (the liquid-air/gas interface).

2.3: Carbon

Review Questions

Each carbon molecule can bond with as many as_____ other atom(s) or molecule(s).

A. one
B. two
C. six
D. four

Answer

D

Which of the following is not a functional group that can bond with carbon?

A. sodium
B. hydroxyl
C. phosphate
D. carbonyl

Answer

A

Free Response

What property of carbon makes it essential for organic life?

Answer

Carbon is unique and found in all living things because it can form up to four covalent bonds between atoms or molecules. These can be nonpolar or polar covalent bonds, and they allow for the formation of long chains of carbon molecules that combine to form proteins and DNA.

Compare and contrast saturated and unsaturated triglycerides.

Answer

Saturated triglycerides contain no double bonds between carbon atoms; they are usually solid at room temperature. Unsaturated triglycerides contain at least one double bond between carbon atoms and are usually liquid at room temperature.

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CHAPTER OVERVIEW

4: Chemical Bonds and Organic Molecules

4.1: The Periodic Table

4.2: Covalent Bonds

4.3: Polarity and Intermolecular Forces

4.4: Carbon

4.5: Functional Groups

4.E: Covalent Bonding and Simple Molecular Compounds (Exercises)

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4.1: The Periodic Table

Learning Objectives

- Explain how elements are organized into the periodic table.
- Describe how some characteristics of elements relate to their positions on the periodic table.

In the 19th century, many previously unknown elements were discovered, and scientists noted that certain sets of elements had similar chemical properties. For example, chlorine, bromine, and iodine react with other elements (such as sodium) to make similar compounds. Likewise, lithium, sodium, and potassium react with other elements (such as oxygen) to make similar compounds. Why is this so?

In 1864, Julius Lothar Meyer, a German chemist, organized the elements by atomic mass and grouped them according to their chemical properties. Later that decade, Dmitri Mendeleev, a Russian chemist, organized all the known elements according to similar properties. He left gaps in his table for what he thought were undiscovered elements, and he made some bold predictions regarding the properties of those undiscovered elements. When elements were later discovered whose properties closely matched Mendeleev's predictions, his version of the table gained favor in the scientific community. Because certain properties of the elements repeat on a regular basis throughout the table (that is, they are periodic), it became known as the periodic table.

> *Mendeleev had to list some elements out of the order of their atomic masses to group them with other elements that had similar properties.*

The periodic table is one of the cornerstones of chemistry because it organizes all the known elements on the basis of their chemical properties. A modern version is shown in Figure 4.1.1. Most periodic tables provide additional data (such as atomic mass) in a box that contains each element's symbol. The elements are listed in order of atomic number.

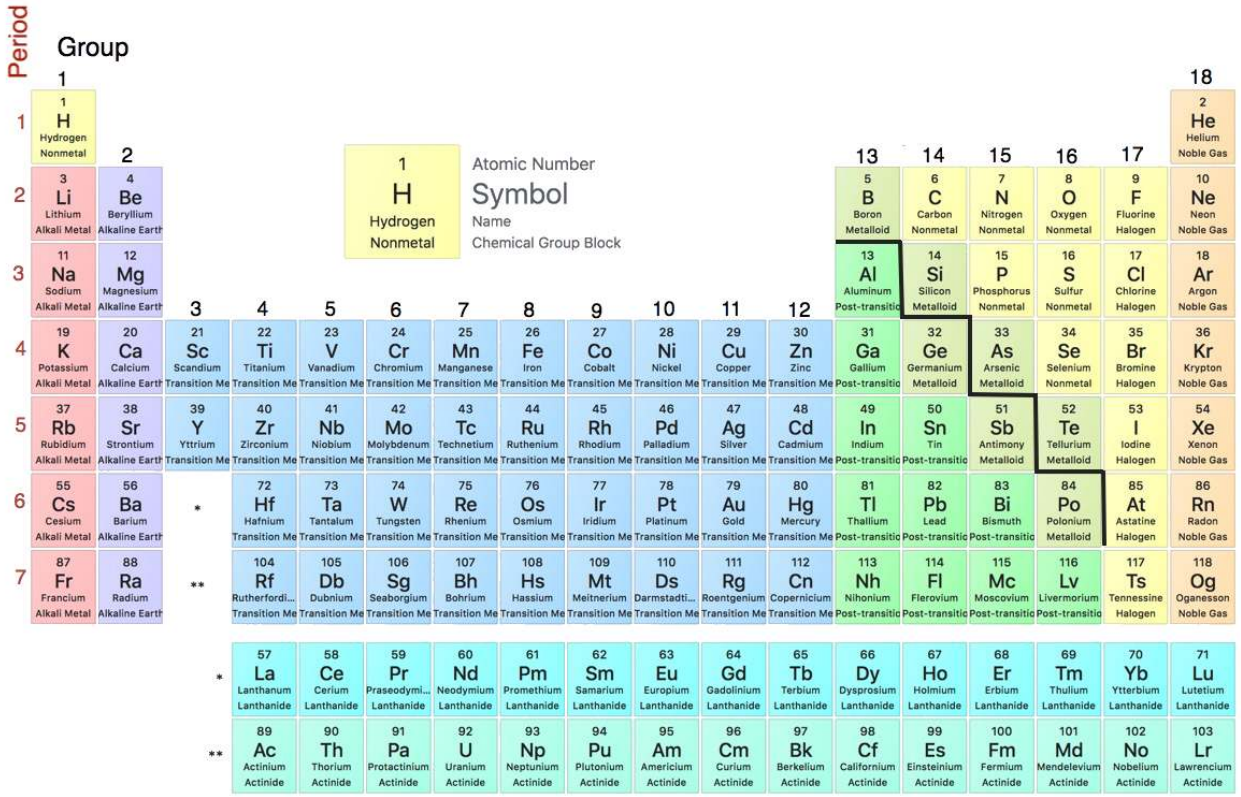


Figure 4.1.1: Modern Periodic Table. (Public Domain; PubChem modified Leticia Colmenares).

Features of the Periodic Table

Elements that have similar chemical properties are grouped in columns called **groups** (or families). As well as being numbered, some of these groups have names—for example, *alkali metals* (the first column of elements), *alkaline earth metals* (the second column of elements), *halogens* (the next-to-last column of elements), and *noble gases* (the last column of elements).

Each row of elements on the periodic table is called a **period**. Periods have different lengths; the first period has only 2 elements (hydrogen and helium), while the second and third periods have 8 elements each. The fourth and fifth periods have 18 elements each, and later periods are so long that a segment from each is removed and placed beneath the main body of the table.

Metals, Nonmetals and Metalloids

Certain elemental properties become apparent in a survey of the periodic table as a whole. Every element can be classified as either a metal, a nonmetal, or a semimetal, as shown in Figure 4.1.2. A metal is a substance that is shiny, typically (but not always) silvery in color, and an excellent conductor of electricity and heat. Metals are also malleable (they can be beaten into thin sheets) and ductile (they can be drawn into thin wires). A nonmetal is typically dull and a poor conductor of electricity and heat. Solid nonmetals are also very brittle. As shown in Figure 4.1.2, **metals** occupy the left three-fourths of the periodic table, while **nonmetals** (except for hydrogen) are clustered in the upper right-hand corner of the periodic table. The elements with properties intermediate between those of metals and nonmetals are called **semimetals** (or **metalloids**). Elements adjacent to the **bold zigzag** line in the right-hand portion of the periodic table have semimetal properties.

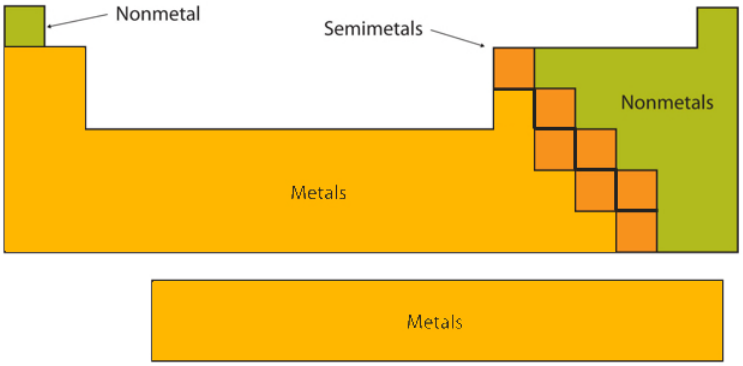


Figure 4.1.2: Types of Elements. Elements are either metals, nonmetals, or semimetals. Each group is located in a different part of the periodic table.

Example 4.1.1

Based on its position in the periodic table, do you expect selenium (Se) to be a metal, a nonmetal, or a semimetal?

Solution

The atomic number of selenium is 34, which places it in period 4 and group 16. In Figure 2.7.1, selenium lies above and to the right of the diagonal line marking the boundary between metals and nonmetals, so it should be a nonmetal. Note, however, that because selenium is close to the metal-nonmetal dividing line, it would not be surprising if selenium were similar to a semimetal in some of its properties.

4.1.1 Exercise

Based on its location in the periodic table, do you expect indium (In) to be a nonmetal, a metal, or a semimetal?

Answer

metal

Representative, Transition and Inner-transition

Another way to categorize the elements of the periodic table is shown in Figure 4.1.3. The first two columns on the left and the last six columns on the right are called the **main group** or **representative** elements. The ten-column block between these columns

contains the **transition metals**. The two rows beneath the main body of the periodic table contain the inner transition metals. The elements in these two rows are also referred to as, respectively, the **lanthanide metals** and the **actinide metals**.

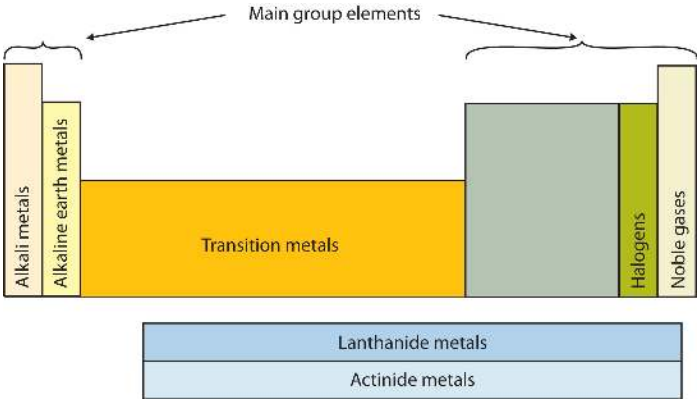


Figure 4.1.3: Special Names for Sections of the Periodic Table. Some sections of the periodic table have special names. The elements lithium, sodium, potassium, rubidium, cesium, and francium are collectively known as alkali metals. Alkali metals are the first column. Alkaline earth metals are the second. Halogens are the second to last column. Noble gases are the last column.

To Your Health: Transition Metals in the Body

Most of the elemental composition of the human body consists of main group elements. The first element appearing on the list that is not a main group element is iron, at 0.006 percentage by mass. Because iron has relatively massive atoms, it would appear even lower on a list organized in terms of percent by *atoms* rather than percent by mass.

Iron is a transition metal. Transition metals have interesting chemical properties, partially because some of their electrons are in *d* subshells. The chemistry of iron makes it a key component in the proper functioning of red blood cells.

Red blood cells are cells that transport oxygen from the lungs to cells of the body and then transport carbon dioxide from the cells to the lungs. Without red blood cells, animal respiration as we know it would not exist. The critical part of the red blood cell is a protein called *hemoglobin*. Hemoglobin combines with oxygen and carbon dioxide, transporting these gases from one location to another in the body. Hemoglobin is a relatively large molecule, with a mass of about 65,000 u.

The crucial atom in the hemoglobin protein is iron. Each hemoglobin molecule has four iron atoms, which act as binding sites for oxygen. It is the presence of this particular transition metal in your red blood cells that allows you to use the oxygen you inhale.

Other transition metals have important functions in the body, despite being present in low amounts. Zinc is needed for the body's immune system to function properly, as well as for protein synthesis and tissue and cell growth. Copper is also needed for several proteins to function properly in the body. Manganese is needed for the body to metabolize oxygen properly. Cobalt is a necessary component of vitamin B-12, a vital nutrient. These last three metals are not listed explicitly in Table 2.1.2, so they are present in the body in very small quantities. However, even these small quantities are required for the body to function properly.

As previously noted, the periodic table is arranged so that elements with similar chemical behaviors are in the same group. Chemists often make general statements about the properties of the elements in a group using descriptive names with historical origins. For example, the elements of Group 1 are known as the alkali metals, Group 2 are the alkaline earth metals, Group 17 are the halogens, and Group 18 are the noble gases.

Group 1: The Alkali Metals

The alkali metals are lithium, sodium, potassium, rubidium, cesium, and francium. Hydrogen is unique in that it is generally placed in Group 1, but it is not a metal. The compounds of the alkali metals are common in nature and daily life. One example is table salt (sodium chloride); lithium compounds are used in greases, in batteries, and as drugs to treat patients who exhibit manic-depressive, or bipolar, behavior. Although lithium, rubidium, and cesium are relatively rare in nature, and francium is so unstable and highly

radioactive that it exists in only trace amounts, sodium and potassium are the seventh and eighth most abundant elements in Earth's crust, respectively.

Group 2: The Alkaline Earth Metals

The alkaline earth metals are beryllium, magnesium, calcium, strontium, barium, and radium. Beryllium, strontium, and barium are rare, and radium is unstable and highly radioactive. In contrast, calcium and magnesium are the fifth and sixth most abundant elements on Earth, respectively; they are found in huge deposits of limestone and other minerals.

Group 17: The Halogens

The halogens are fluorine, chlorine, bromine, iodine, and astatine. The name halogen is derived from the Greek words for "salt forming," which reflects that all the halogens react readily with metals to form compounds, such as sodium chloride and calcium chloride (used in some areas as road salt).

Compounds that contain the fluoride ion are added to toothpaste and the water supply to prevent dental cavities. Fluorine is also found in Teflon coatings on kitchen utensils. Although chlorofluorocarbon propellants and refrigerants are believed to lead to the depletion of Earth's ozone layer and contain both fluorine and chlorine, the latter is responsible for the adverse effect on the ozone layer. Bromine and iodine are less abundant than chlorine, and astatine is so radioactive that it exists in only negligible amounts in nature.

Group 18: The Noble Gases

The noble gases are helium, neon, argon, krypton, xenon, and radon. Because the noble gases are composed of only single atoms, they are called monatomic. At room temperature and pressure, they are **unreactive gases**. Because of their lack of reactivity, for many years they were called **inert gases** or rare gases. However, the first chemical compounds containing the noble gases were prepared in 1962. Although the noble gases are relatively minor constituents of the atmosphere, natural gas contains substantial amounts of helium. Because of its low reactivity, argon is often used as an unreactive (inert) atmosphere for welding and in light bulbs. The red light emitted by neon in a gas discharge tube is used in neon lights.

To Your Health: Radon

Radon is an invisible, odorless noble gas that is slowly released from the ground, particularly from rocks and soils whose uranium content is high. Because it is a noble gas, radon is not chemically reactive. Unfortunately, it is radioactive, and increased exposure to it has been correlated with an increased lung cancer risk.

Because radon comes from the ground, we cannot avoid it entirely. Moreover, because it is denser than air, radon tends to accumulate in basements, which if improperly ventilated can be hazardous to a building's inhabitants. Fortunately, specialized ventilation minimizes the amount of radon that might collect. Special fan-and-vent systems are available that draw air from below the basement floor, before it can enter the living space, and vent it above the roof of a house.

After smoking, radon is thought to be the second-biggest *preventable* cause of lung cancer in the United States. The American Cancer Society estimates that 10% of all lung cancers are related to radon exposure. There is uncertainty regarding what levels of exposure cause cancer, as well as what the exact causal agent might be (either radon or one of its breakdown products, many of which are also radioactive and, unlike radon, not gases). The US Environmental Protection Agency recommends testing every floor below the third floor for radon levels to guard against long-term health effects.

Why do elements in a given group have similar properties?

The periodic table is organized on the basis of similarities in elemental properties, but what explains these similarities? It turns out that the shape of the periodic table reflects the filling of subshells with electrons, as shown in Figure 4.1.4. Starting with the first period and going from left to right, the table reproduces the order of filling of the electron subshells in atoms. Furthermore, elements in the same *group* share the same valence shell electron configuration. For example, all elements in the first column have a single *s* electron in their valence shells, so their electron configurations can be described as ns^1 (where *n* represents the shell number). This last observation is crucial. Chemistry is largely the result of interactions between the valence electrons of different atoms. Thus, atoms that have **the same valence shell electron configuration** will have **similar chemistry.**

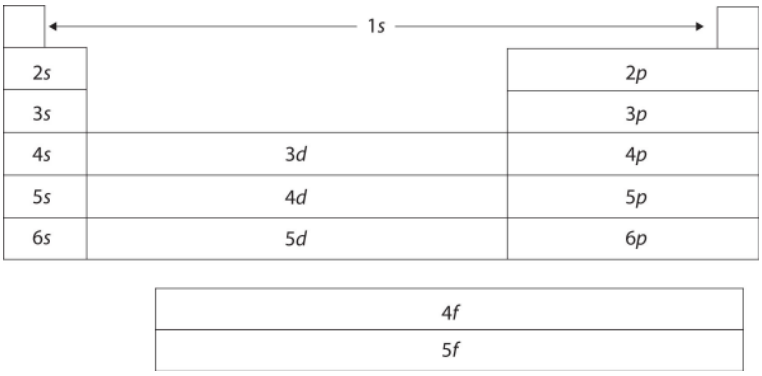


Figure 4.1.4 The Shape of the Periodic Table. The shape of the periodic table reflects the order in which electron shells and subshells fill with electrons.

Example 4.1.1

Using the variable *n* to represent the number of the valence electron shell, write the valence shell electron configuration for each group.

a. the alkaline earth metals
b. the column of elements headed by carbon

Answer a

The alkaline earth metals are in the second column of the periodic table. This column corresponds to the *s* subshell being filled with 2 electrons. Therefore, the valence shell electron configuration is ns^2.

Answer b

The electron configuration of carbon is $1s^2 2s^2 2p^2$. Its valence shell electron configuration is $2s^2 2p^2$. Every element in the same column should have a similar valence shell electron configuration, which we can represent as $ns^2 np^2$.

Exercise 4.1.1

Using the variable *n* to represent the number of the valence electron shell, write the valence shell electron configuration for each group.

a. the halogens
b. the column of elements headed by oxygen

Answer a

The halogens are in the 17th column (or Group 7A) of the periodic table. This column corresponds to the *p* subshell being filled with 5 electrons. Therefore, the valence shell electron configuration is $ns^2 np^5$.

Answer b

The column headed by O is the 16th column (or Group 6A). This column corresponds to the *p* subshell being filled with 4 electrons. Therefore, the valence shell electron configuration is $ns^2 np^4$.

Valence Electrons and Group Number

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

Table 4.1.1. The Group number and the number of valence electrons.

Periodic table group	Valence electrons
Group 1 (I) (alkali metals)	1
Group 2 (II) (alkaline earth metals)	2
Groups 3-12 (transition metals)	2*
Group 13 (III) (boron group)	3
Group 14 (IV) (carbon group)	4
Group 15 (V) (pnictogens)	5
Group 16 (VI) (chalcogens)	6
Group 17 (VII) (halogens)	7
Group 18 (VIII or 0) (noble gases)	8**

** The general method for counting valence electrons is generally not useful for transition metals.*

*** Except for helium, which has only two valence electrons.*

Atomic Radius

The periodic table is useful for understanding atomic properties that show periodic trends. One such property is the atomic radius (Figure 4.1.5). The atomic radius is defined as one-half the distance between the nuclei of identical atoms that are bonded together. 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 $74\ \text{pm}$. Therefore, the atomic radius of a hydrogen atom is $\frac{74}{2} = 37\ \text{pm}$.

As mentioned earlier, the higher the shell number, the farther from the nucleus the electrons in that shell are likely to be. In other words, the size of an atom is generally determined by the number of the valence electron shell. Therefore, as we go down a column on the periodic table, the atomic radius increases. As we go *across* a period on the periodic table, however, electrons are being added to the *same* valence shell; meanwhile, more protons are being added to the nucleus, so the positive charge of the nucleus is increasing. The increasing positive charge attracts the electrons more strongly, pulling them closer to the nucleus. Consequently, as we go across a period, from left to right, the atomic radius decreases. These trends are seen clearly in Figure 4.1.5

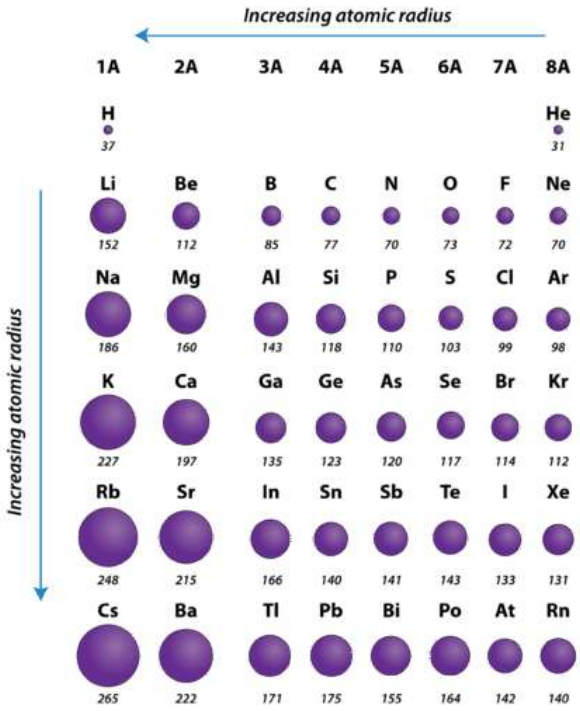


Figure 4.1.5 Trends on the Periodic Table. Atomic radii of the representative elements measured in picometers. The relative sizes of the atoms show several trends with regard to the structure of the periodic table. Atoms become larger going down a group and going from right to left across a period.

Example 4.1.2

Using the periodic table (rather than Figure 4.1.5), which atom is larger?

a. N or Bi
b. Mg or Cl

Answer a

Bi is below N in Group 5A in the periodic table and has electrons in higher-numbered shells, hence we expect that Bi atoms are larger than N atoms.

Answer b

Both Mg and Cl are in period 3 of the periodic table, but Cl lies farther to the right. Therefore we expect Mg atoms to be larger than Cl atoms.

Exercise 4.1.2

Using the periodic table (rather than Figure 4.1.5), which atom is larger?

a. Li or F
b. Na or K

Answer a

Li and F are on the same period, but F lies farther to the right. Therefore, we expect Li to be larger than F atoms.

Answer b

K lies below Na in Group 1A, hence has more electron shells, making it larger than Na.

Career Focus: Clinical Chemist

Clinical chemistry is the area of chemistry concerned with the analysis of body fluids to determine the health status of the human body. Clinical chemists measure a variety of substances, ranging from simple elements such as sodium and potassium to complex molecules such as proteins and enzymes, in blood, urine, and other body fluids. The absence or presence, or abnormally low or high amounts, of a substance can be a sign of some disease or an indication of health. Many clinical chemists use sophisticated equipment and complex chemical reactions in their work, so they not only need to understand basic chemistry, but also be familiar with special instrumentation and how to interpret test results.

Concept Review Exercises

1. How are the elements organized into the periodic table?
2. Looking at the periodic table, where do the following elements appear?
    a. the metals
    b. the nonmetals
    c. the halogens
    d. the transition metals
    e. the noble gases
3. Describe the trends in atomic radii as related to an element's position on the periodic table.

Answers

1. Elements are organized in order of increasing atomic number.
2. a. the left three-quarters of the periodic table (to the left of the zigzag band)
    b. the right quarter of the periodic table (to the right of the zigzag band)
    c. the next-to-last column of the periodic table
    d. the middle section of the periodic table
    e. the last column of the periodic table
3. As you go across the periodic table, atomic radii decrease; as you go down the periodic table, atomic radii increase.

Key Takeaways

- The chemical elements are arranged in a chart called the periodic table.
- Some characteristics of the elements are related to their position on the periodic table.
- The number of valence electrons of an element can be determined by the group (vertical column) number in the Periodic Table. Elements with the same number of valence electrons have similar chemical properties.

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4.2: Covalent Bonds

Learning Objectives

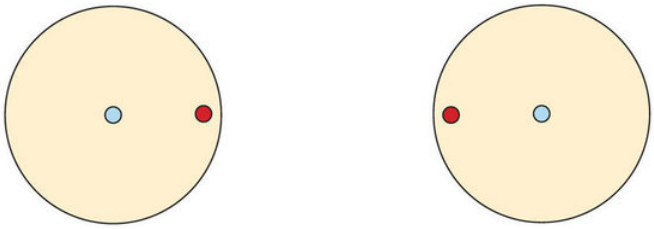
- To describe how a covalent bond forms.
- To apply the octet rule to covalent compounds

You have already seen examples of substances that contain covalent bonds. One substance mentioned previously was water (H_2O). You can tell from its formula that it is not an ionic compound; it is not composed of a metal and a nonmetal. Consequently, its properties are different from those of ionic compounds.

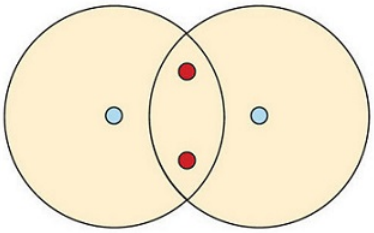
Electron Sharing

Previously, we discussed ionic bonding where electrons can be transferred from one atom to another so that both atoms have an energy-stable outer electron shell. Because most filled electron shells have eight electrons in them, chemists called this tendency the octet rule. However, there is another way an atom can achieve a full valence shell: atoms can *share* electrons.

This concept can be illustrated by using two hydrogen atoms, each of which has a single electron in its valence shell. (For small atoms such as hydrogen atoms, the valence shell will be the first shell, which holds only two electrons.) We can represent the two individual hydrogen atoms as follows:



In contrast, when two hydrogen atoms get close enough together to share their electrons, they can be represented as follows:



By sharing their valence electrons, both hydrogen atoms now have two electrons in their respective valence shells. Because each valence shell is now filled, this arrangement is more stable than when the two atoms are separate. The sharing of electrons between atoms is called a covalent bond, and the two electrons that join atoms in a covalent bond are called a bonding pair of electrons. A discrete group of atoms connected by covalent bonds is called a molecule—the smallest part of a compound that retains the chemical identity of that compound.

Chemists frequently use Lewis diagrams to represent covalent bonding in molecular substances. For example, the Lewis diagrams of two separate hydrogen atoms are as follows:



The Lewis diagram of two hydrogen atoms sharing electrons looks like this:



This depiction of molecules is simplified further by using a dash to represent a covalent bond. The hydrogen molecule is then represented as follows:

H—H

Remember that the dash, also referred to as a single bond, represents a *pair* of electrons.

The bond in a hydrogen molecule, measured as the distance between the two nuclei, is about 7.4×10^{-11} m, or 74 picometers (pm; 1 pm = 1×10^{-12} m). This particular bond length represents a balance between several forces: the attractions between oppositely charged electrons and nuclei, the repulsion between two negatively charged electrons, and the repulsion between two positively charged nuclei. If the nuclei were closer together, they would repel each other more strongly; if the nuclei were farther apart, there would be less attraction between the positive and negative particles.

Fluorine is another element whose atoms bond together in pairs to form *diatomic* (two-atom) molecules. Two separate fluorine atoms have the following electron dot diagrams:

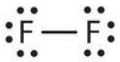


Each fluorine atom contributes one valence electron, making a single bond and giving each atom a complete valence shell, which fulfills the **octet** rule:



Two F's with two dots in between them, and two dots on the top, left/right side, and bottoms of each F.

The circles show that each fluorine atom has eight electrons around it. As with hydrogen, we can represent the fluorine molecule with a dash in place of the bonding electrons:



Two F's with a long dash in between them, and two dots on the top, left/right side, and bottoms of each F.

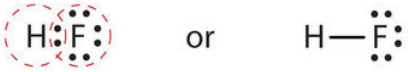
Each fluorine atom has six electrons, or three pairs of electrons, that are not participating in the covalent bond. Rather than being shared, they are considered to belong to a single atom. These are called nonbonding pairs (or lone pairs) of electrons.

Covalent Bonds between Different Atoms

Now that we have looked at electron sharing between atoms of the same element, let us look at covalent bond formation between atoms of different elements. Consider a molecule composed of one hydrogen atom and one fluorine atom:



Each atom needs one additional electron to complete its valence shell. By each contributing one electron, they make the following molecule:



An H and F connected by two dots, and the F has 2 dots on the top, right, and bottom. It also shows the same combination but with a long dash in between the H and F rather than two dots.

In this molecule, the hydrogen atom does not have nonbonding electrons, while the fluorine atom has six nonbonding electrons (three lone electron pairs). The circles show how the valence electron shells are filled for both atoms.

Example 4.2.1

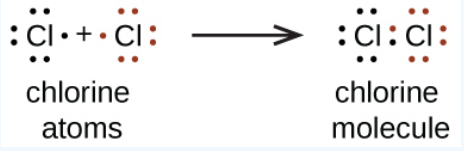
Use Lewis diagrams to indicate the formation of the following:

a. Cl_2
b. HBr

Solution

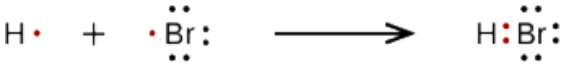
a. When two chlorine atoms form a chlorine molecule, they share one pair of electrons. In Cl_2 molecule, each chlorine atom is surrounded by an **octet** number of electrons.

The Lewis diagram for a Cl_2 molecule is similar to the one for F_2 (shown above).



Cl with 7 dots surrounding it plus Cl with 7 dots surrounding it means they are chlorine atoms. To turn into a chlorine molecule, have two dots in between each Cl and 6 dots surrounding each Cl on the sides that aren't connected.

b. When a hydrogen atom and a bromine atom form HBr, they share one pair of electrons. In the HBr molecule, H achieves a full valence of two electrons (**duet**) while Br achieves an **octet**. The Lewis diagram for HBr is similar to that for HF shown above.

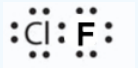

H with one dot plus Br with 7 dots turns into H connected to Br by two dots, with 6 other dots surrounding Br.

? Exercise 4.2.1

Draw the Lewis diagram for each compound.

a. a molecule composed of one chlorine atom and one fluorine atom
b. a molecule composed of one hydrogen atom and one iodine atom

Answer a:

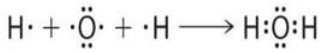


Answer b:

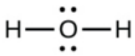


Covalent Bonds in Larger Molecules

The formation of a water molecule from two hydrogen atoms and an oxygen atom can be illustrated using Lewis dot symbols (shown below).

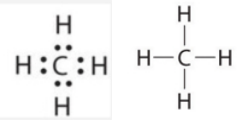

H with one dot + O with 6 dots + H with one dot turns into H connected to O with two dots connected to H with two dots. O also has two dots on top and top dots on bottom.

The structure on the right is the *Lewis electron structure*, or *Lewis structure*, for H_2O. With two bonding pairs and two lone pairs, the oxygen atom has now completed its **octet**. Moreover, by sharing a bonding pair with oxygen, each hydrogen atom now has a full valence shell of two electrons. Chemists usually indicate a bonding pair by a single line, as shown (below).



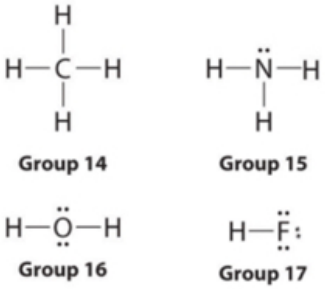
Water

Other large molecules are constructed in a similar fashion, with some atoms participating in more than one covalent bond. For example, methane (CH_4), the central carbon atom bonded to four hydrogen atoms, can be represented using either of the Lewis structures below. Again, sharing electrons between C and H atoms results in C achieving and octet while H achieving a duet number of electrons.



How Many Covalent Bonds Are Formed?

The number of bonds that an atom can form can often be predicted from the number of electrons needed to reach an octet (eight valence electrons). In the Lewis structure, the number of bonds formed by an element in a neutral compound is the same as the number of unpaired electrons it must share with other atoms to complete its octet of electrons. For example, each atom of a **group 4A** (14) element has four electrons in its outermost shell and therefore requires four more electrons to reach an octet. These four electrons can be gained by forming **four covalent bonds**, as illustrated here for carbon in CH_4 (methane). **Group 5A** (15) elements such as nitrogen have five valence electrons in the atomic Lewis symbol: one lone pair and three unpaired electrons. To obtain an octet, these atoms form **three covalent bonds**, as in NH_3 (ammonia). Oxygen and other atoms in **group 6A** (16) obtain an octet by forming **two covalent bonds**. Fluorine and the other halogens in **group 7A** (17) have seven valence electrons and can obtain an octet by forming **one covalent bond**.



Typically, the atoms of group 4A form 4 covalent bonds; group 5A form 3 bonds; group 6A form 2 bonds; and group 7A form one bond. The number of electrons required to obtain an octet determines the number of covalent bonds an atom can form.This is summarized in the table below. In each case, the sum of the number of bonds and the number of lone pairs is 4, which is equivalent to eight (octet) electrons.

This table shows atoms and their group numbers, and how many bonds and lone pairs each has.

Atom (Group number)	Number of Bonds	Number of Lone Pairs
Carbon (Group 14 or 4A)	4	0
Nitrogen (Group 15 or 5A)	3	1
Oxygen (Group 16 or 6A)	2	2
Fluorine (Group 17 or 7A)	1	3

Because hydrogen only needs two electrons to fill its valence shell, it follows the duet rule. It is an **exception to the octet rule.** Hydrogen only needs to form one bond. This is the reason why H is always a terminal atom and never a central atom. Figure 4.2.1 shows the number of covalent bonds various atoms typically form.

The transition elements and inner transition elements also do not follow the octet rule since they have d and f electrons involved in their valence shells.

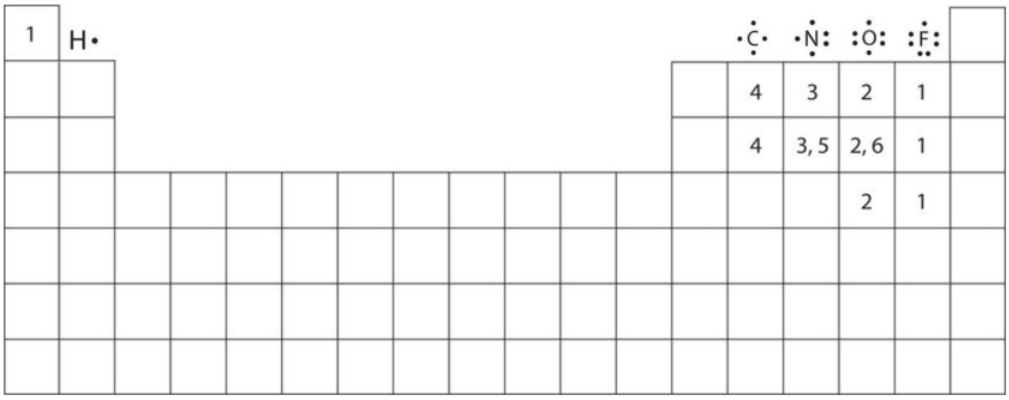
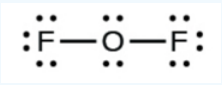


Figure 4.2.1: How Many Covalent Bonds Are Formed? In molecules, there is a pattern to the number of covalent bonds that different atoms can form. Each block with a number indicates the number of covalent bonds formed by that atom in neutral compounds.

Example 4.2.2

Examine the Lewis structure of OF_2 below. Count the number of bonds formed by each element. Based on the element's location in the periodic table, does it correspond to the expected number of bonds shown in Table 4.1? Does the Lewis structure below follow the octet rule?



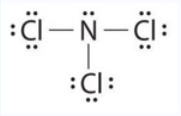
F surrounded by 6 dots, connected to O with a long dash. O surrounded by 4 dots and connects to another F with a long dash. F surrounded by 6 dots.

Solution

Yes. F (group 7A) forms one bond and O (group 6A) forms 2 bonds. Each atom is surrounded by 8 electrons. This structure satisfies the octet rule.

4.2.2Exercise

Examine the Lewis structure of NCl_3 below. Count the number of bonds formed by each element. Based on the element's location in the periodic table, does it correspond to the expected number of bonds shown in Table 4.1? Does the Lewis structure below follow the octet rule?



Answer

Both Cl and N form the expected number of bonds. Cl (group 7A) has one bond and 3 lone pairs. The central atom N (group 5A) has 3 bonds and one lone pair. Yes, the Lewis structure of NCl_3 follows the octet rule.

Key Takeaways

- A covalent bond is formed between two atoms by sharing electrons.
- The number of bonds an element forms in a covalent compound is determined by the number of electrons it needs to reach octet.
- Hydrogen is an exception to the octet rule. H forms only one bond because it needs only two electrons.

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4.3: Polarity and Intermolecular Forces

Learning Outcomes

- Define electronegativity.
- Describe how the electronegativity difference between two atoms in a covalent bond results in the formation of a nonpolar covalent, polar covalent, or ionic bond.
- Predict polarity of a molecule.
- Describe how molecular geometry plays a role in determining whether a molecule is polar or nonpolar.
- Distinguish between the following three types of intermolecular forces: dipole-dipole forces, London dispersion forces, and hydrogen bonds.
- Identify types of intermolecular forces in a molecule.
- Describe how chemical bonding and intermolecular forces influence the properties of various compounds.

In an ionic bond, one or more electrons are transferred from one atom to another. In a covalent bond, one or more pairs of electrons are shared between atoms. However, bonding between atoms of different elements is rarely purely ionic or purely covalent.

Bond Polarity

Bond polarity is determined by the difference in electronegativity and is defined as the relative ability of an atom to attract electrons when present in a compound. The electronegativities of various elements are shown below. Note that elecronegativity values increase from left to right and from bottom to top on the periodic table. The degree to which a given bond is ionic or covalent is determined by calculating the difference in electronegativity between the two atoms involved in the bond.

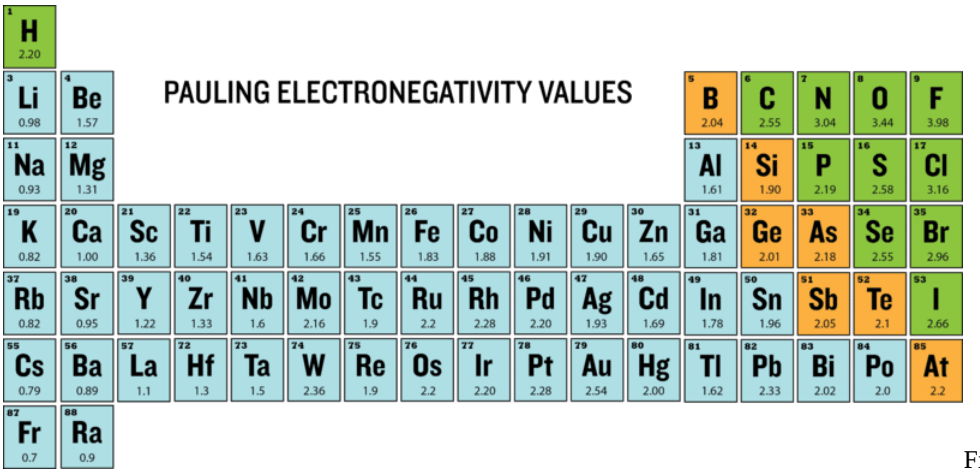


Figure 4.3.1: Electronegativities of the elements.

As an example, consider the bond that occurs between an atom of potassium and an atom of fluorine. Using the table, the difference in electronegativity is $4.0 - 0.8 = 3.2$. Because the difference in electronegativity is relatively large, the bond between the two atoms is primarily ionic. Since the fluorine atom has a much larger attraction for electrons than the potassium atom does, the valence electron from the potassium atom is considered to have completely transferred to the fluorine atom. The figure below shows how the difference in electronegativity relates to the ionic or covalent character of a chemical bond.

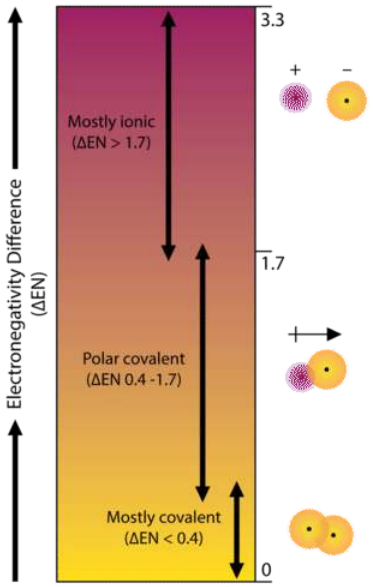


Figure 4.3.2: The difference in electronegativity between the two elements involved in a chemical bond is predictive of the type of bond made by those two atoms. A small difference (<0.4) results in a nonpolar covalent bond, an intermediate difference (0.4 - 1.7) results in a polar covalent bond, and a large difference (>1.7) results in an ionic bond.

According to the figure above, a difference in electronegativity (Δ EN) greater than 1.7 results in a bond that is mostly ionic in character.

Nonpolar Covalent Bonds

A bond in which the electronegativity difference is less than 1.7 is considered to be mostly covalent in character. However, a distinction is often made between two general types of covalent bonds. A **nonpolar covalent bond** *is a covalent ond in which the onding electrons are shared equally between the two atoms.* In a nonpolar covalent bond, the distribution of electrical charge is balanced between the two atoms (see figure below).

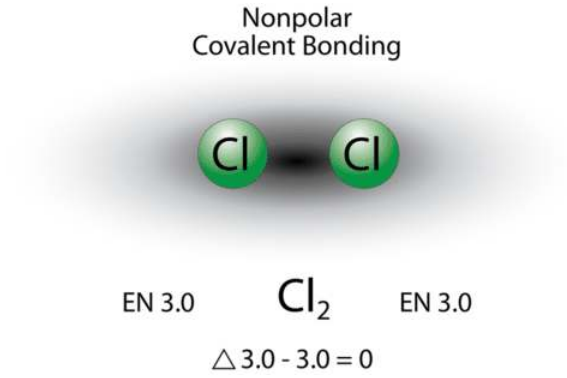


Figure 4.3.3: A nonpolar covalent bond is one in which the shared electrons are distributed equally between the two atoms.

The two chlorine atoms share the pair of electrons in the single covalent bond equally, and the electron density surrounding the Cl_2 molecule is symmetrical. Any diatomic molecule in which the two atoms are the same element must be joined by a nonpolar covalent bond.

There are seven **diatomic elements**, which are *elements whose natural form is of a diatomic molecule.* They are hydrogen (H_2), nitrogen (N_2), oxygen (O_2), fluorine (F_2), chorine (Cl_2), bromine (Br_2), and iodine (I_2). By forming a diatomic molecule, both atoms in each of these molecules satisfy the octet rule, resulting in a structure that is much more stable than the isolated atoms

Notice from the figure above that molecules in which the electronegativity difference is very small (<0.4) are also considered nonpolar covalent. An example would be a bond between chlorine and bromine (Δ EN $= 3.16 - 2.96 = 0.20$).

Polar Covalent Bonds

A bond in which the electronegativity difference between the atoms is between 0.4 and 1.7 is called a polar covalent bond. A **polar covalent bond** *is a covalent bond in which the atoms have an unequal attraction for electrons, so the sharing is unequal.* In a polar covalent bond, sometimes simply called a polar bond, the distribution of shared electrons within the molecule is no longer symmetrical (see figure below).

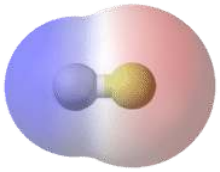
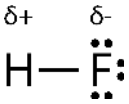


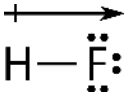
Figure 4.3.4: In the polar covalent bond of HF, the electron density is unevenly distributed. There is a higher density (red) near the fluorine atom, and a lower density (blue) near the hydrogen atom.

The hydrogen fluoride molecule has an electronegativity difference of 1.9, which places it in the category of being slightly ionic. However, the hydrogen ion (H^+) is so very small that it is not capable of adopting the crystal lattice structure of an ionic compound. Hydrogen fluoride is a highly polar molecule. Because of its greater electronegativity, the electron density around the fluorine atom is much higher than the electron density around the hydrogen atom.

An easy way to illustrate the uneven electron distribution in a polar covalent bond is to use the Greek letter delta (δ) along with a positive or negative sign to indicate that an atom has a partial positive or negative charge.



The atom with the greater electronegativity acquires a partial negative charge, while the atom with the lesser electronegativity acquires a partial positive charge. The delta symbol is used to indicate that the quantity of charge is less than one. A crossed arrow can also be used to indicate the direction of greater electron density.



Example 4.3.1

Which type of bond will form between each of the following pairs of atoms?

a. C and O
b. Na and N
c. B and H

Solution

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

Known

Using the electronegativity chart:

- $C = 2.5,\ O = 3.5$
- $Na = 0.9,\ N = 3.0$
- $B = 2.0,\ H = 2.1$

Step 2: Solve.

Calculate the difference and use the diagram above to identify the bond type.

$$3.5 - 2.5 = 1.0 \rightarrow \text{C–O bond is polar covalent} \tag{4.3.1}$$

$$3.0 - 0.9 = 2.1 \rightarrow \text{Na–N bond is ionic} \tag{4.3.2}$$

$$2.1 - 2.0 = 0.1 \rightarrow \text{B—H bond is nonpolar covalent} \tag{4.3.3}$$

Step 3: Think about your result.

Bonds between nonmetal atoms are generally covalent in nature (A and C), while bond between a metal atom and a nonmetal atom are generally ionic.

Molecular Polarity

A **polar molecule** *is a molecule in which one end of the molecule is slightly positive, while the other end is slightly negative*. A diatomic molecule that consists of a polar covalent bond, such as HF, is a polar molecule. The two electrically charged regions on either end of the molecule are called poles, similar to a magnet having a north and a south pole. *A molecule with two poles is called a* **dipole**. Hydrogen fluoride is a dipole. A simplified way to depict molecules is pictured below (see figure below).

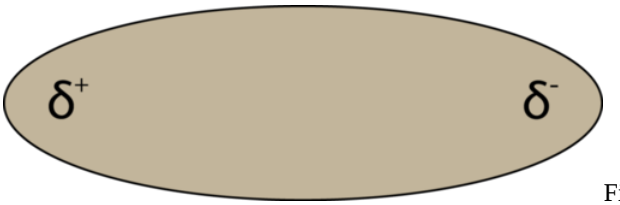


Figure 4.3.5: A molecular dipole results from the unequal distribution of electron density throughout a molecule.

When placed between oppositely charged plates, polar molecules orient themselves so that their positive ends are closer to the negative plate and their negative ends are closer to the positive plate (see figure below).

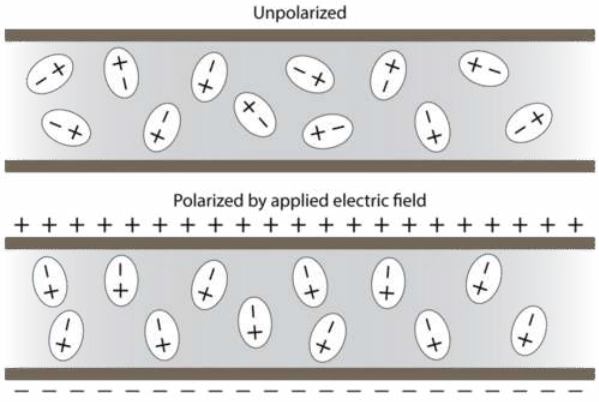


Figure 4.3.6: Polar molecules are randomly oriented in the absence of an applied electric field (top). In an electric field, the molecules orient themselves to maximize the attraction between opposite charges (bottom).

Experimental techniques involving electric fields can be used to determine if a certain substance is composed of polar molecules and to measure the degree of polarity.

For molecules with more than two atoms, the molecular geometry must also be taken into account when determining if the molecule is polar or nonpolar. Pictured below (see figure below) is a comparison between carbon dioxide and water. Carbon dioxide (CO_2) is a linear molecule. The oxygen atoms are more electronegative than the carbon atom, so there are two individual dipoles pointing outward from the C atom to each O atom. However, since the dipoles are of equal strength and are oriented in this way, they cancel each other out, and the overall molecular polarity of CO_2 is zero.

Water is a bent molecule because of the two lone pairs on the central oxygen atom. The individual dipoles point from the H atoms toward the O atom. Because of the shape the dipoles do not cancel each other out, and the water molecule is polar. In the figure below, the net dipole is shown in blue and points upward.

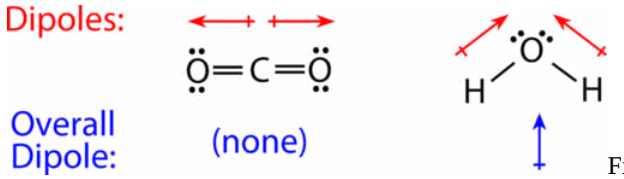


Figure 4.3.7: The molecular geometry of a molecule affects its polarity. In CO_2, the two polar bonds cancel each other out, and the result is a nonpolar molecule. Water is polar because its bent shape means that the two polar bonds do not cancel.

Some other molecules are shown below (see figure below). Notice that a tetrahedral molecule such as CH_4 is nonpolar. However, if one of the peripheral H atoms is replaced by another atom that has a different electronegativity, the molecule becomes polar. A trigonal planar molecule (BF_3) may be nonpolar if all three peripheral atoms are the same, but a trigonal pyramidal molecule (NH_3) is polar because of the pair of electrons in the nitrogen atoms.

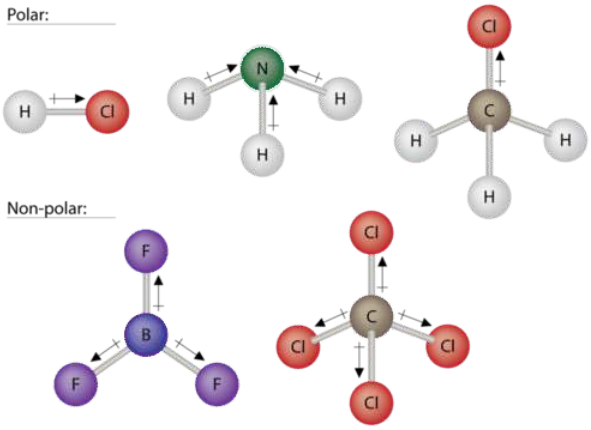


Figure 4.3.8: Some examples of polar and nonpolar molecules with various molecular geometries.

Intermolecular Forces

Covalent and ionic bonds can be called intramolecular forces: forces that act within a molecule or crystal. Molecules also attract other molecules. **Intermolecular forces** *are attractions that occur between molecules.* Intermolecular forces are weaker than either ionic or covalent bonds. However, the varying strengths of different types of intermolecular forces are responsible for physical properties of molecular compounds such as melting and boiling points and the amount of energy needed for changes in state.

London Dispersion Forces

Dispersion forces are the weakest of all intermolecular forces. They are often called London forces after Fritz London (1900 - 1954), who first proposed their existence in 1930. **London dispersion forces** *are intermolecular forces that occur between all atoms and molecules due to the random motion of electrons.*

For example, the electron cloud of a helium atom contains two electrons, and, when averaged over time, these electrons will distribute themselves evenly around the nucleus. However, at any given moment, the electron distribution may be uneven, resulting in an *instantaneous dipole*. This weak and temporary dipole can subsequently influence neighboring helium atoms through electrostatic attraction and repulsion. The formation of an induced dipole is illustrated below.

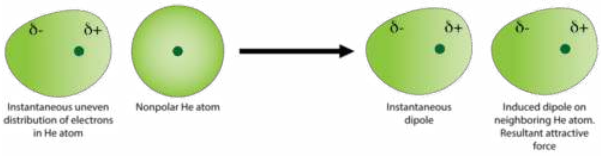


Figure 4.3.9: Random fluctuations in the electron density within the electron cloud of a helium atom results in a short-lived ("instantaneous") dipole. The attractive force between instantaneous dipoles and the resulting induced dipoles in neighboring molecules is called the London dispersion force.

The instantaneous and induced dipoles are weakly attracted to one another. The strength of dispersion forces increases as the total number of electrons in the atoms or nonpolar molecules increases. The halogen group consists of four elements that all take the form of nonpolar diatomic molecules. Listed below is a comparison of the melting and boiling points for each.

Table 4.3.1: Melting and Boiling Points of Halogens

Molecule	Total Number of Electrons	Melting Point (°C)	Boiling Point (°C)	Physical State at Room Temperature
F_2	18	-220	-188	gas
Cl_2	34	-102	-34	gas
Br_2	70	-7	59	liquid
I_2	106	114	184	solid

The dispersion forces are strongest for iodine molecules because they have the greatest number of electrons. The relatively stronger forces result in melting and boiling points which are the highest of the halogen group. These forces are strong enough to hold iodine molecules close together in the solid state at room temperature. The dispersion forces are progressively weaker for bromine, chlorine, and fluorine, as illustrated by their steadily lower melting and boiling points. Bromine is a liquid at room temperature, while chlorine and fluorine are gases. Because gaseous molecules are so far apart from one another, intermolecular forces are nearly nonexistent in the gas state, and so the dispersion forces in chlorine and fluorine only become measurable as the temperature decreases and they condense into the liquid state.

Dipole-Dipole Forces

Dipole-dipole forces *are the attractive forces that occur between polar molecules* (see figure below). A molecule of hydrogen chloride has a partially positive hydrogen atom and a partially negative chlorine atom. A collection of many hydrogen chloride molecules will align themselves so that the oppositely charged regions of neighboring molecules are near each other.

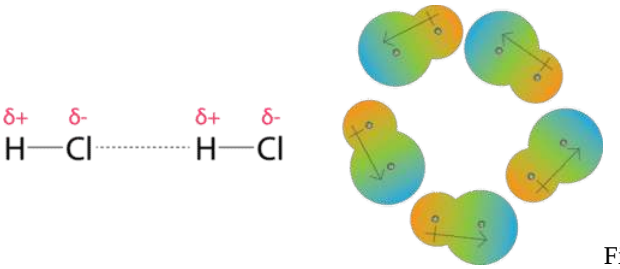


Figure 4.3.10: Dipole-dipole forces result from the attraction between the positive end of one dipole and the negative end of a neighboring dipole. Dipole-dipole forces are similar to ionic bonds, but because they involve only partial charges, they are much weaker.

Hydrogen Bonding

The attractive force between water molecules is an unusually strong type of dipole-dipole interaction. Water contains hydrogen atoms that are bound to a highly electronegative oxygen atom, making for very polar bonds. The partially positive hydrogen atom of one molecule is then attracted to the oxygen atom of a nearby water molecule (see figure below).

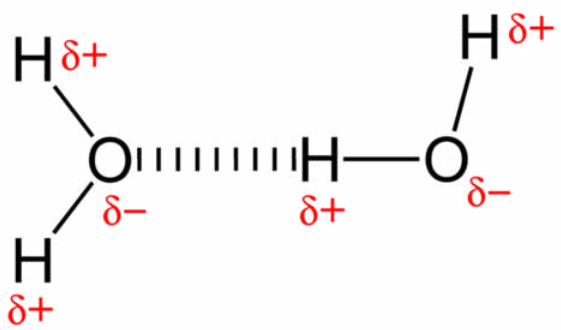


Figure 4.3.11: A hydrogen bond in water occurs between the hydrogen atom of one water molecule and the lone pair of electrons on the oxygen atom of a neighboring water molecule.

A **hydrogen bond** *is an intermolecular attractive force in which a hydrogen atom, that is covalently bonded to a small, highly electronegative atom, is attracted to a lone pair of electrons on an atom in a neighboring molecule.* Hydrogen bonds are very strong compared to other dipole-dipole interactions, but still much weaker than a covalent bond. A typical hydrogen bond is about 5% as strong as a covalent bond.

Hydrogen bonding occurs only in molecules where hydrogen is covalently bonded to one of three elements: fluorine, oxygen, or nitrogen. These three elements are so electronegative that they withdraw the majority of the electron density from the covalent bond with hydrogen, leaving the H atom very electron-deficient. Because the hydrogen atom does not have any electrons other than the ones in the covalent bond, its positively charged nucleus is almost completely exposed, allowing strong attractions to other nearby lone pairs of electrons.

The hydrogen bonding that occurs in water leads to some unusual, but very important properties. Most molecular compounds that have a mass similar to water are gases at room temperature. However, because of the strong hydrogen bonds, water molecules are able to stay condensed in the liquid state. The figure below shows how its bent shape and the presence of two hydrogen atoms per molecule allows each water molecule to hydrogen bond with several other molecules.

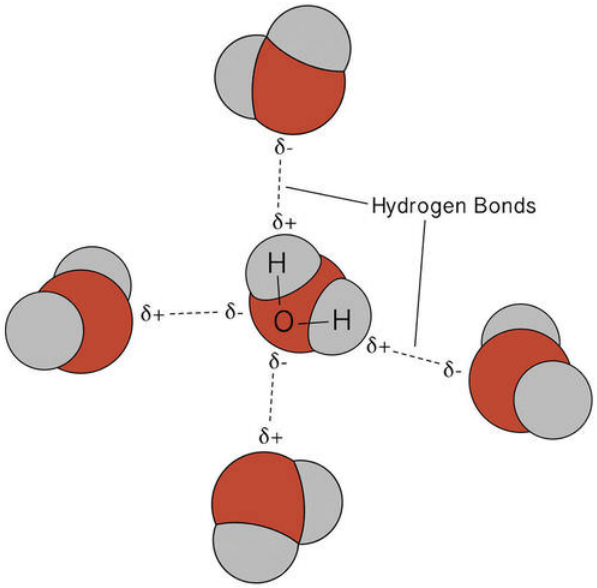


Figure 4.3.12: Multiple hydrogen bonds occur simultaneously in water because of its bent shape and the presence of two hydrogen atoms per molecule.

In the liquid state, the hydrogen bonds of water can break and reform as the molecules flow from one place to another. When water is cooled, the molecules begin to slow down. Eventually, when water is frozen to ice, the hydrogen bonds become more rigid and form a well-defined network (see figure below).

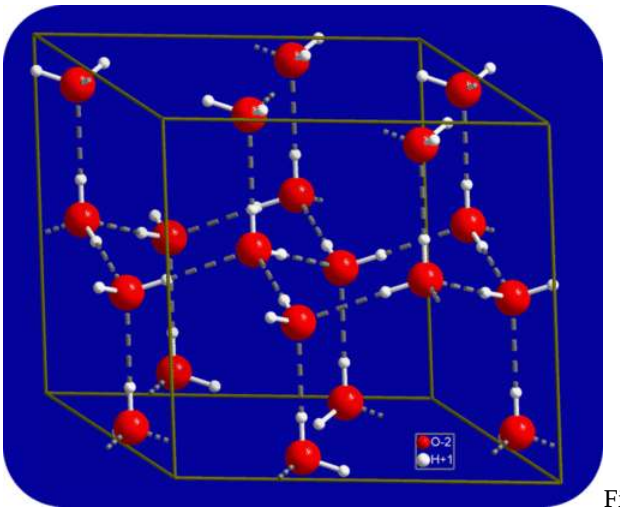


Figure 4.3.13: When water freezes to ice, the hydrogen bonding network becomes fixed until the ice melts. Each oxygen atom has an approximately tetrahedral geometry that includes two covalent bonds and two hydrogen bonds.

The bent shape of the molecules leads to gaps in the hydrogen bonding network of ice. Ice has the very unusual property that its solid state is less dense than its liquid state. As a result, ice floats in liquid water. Virtually all other substances are denser in the solid state than in the liquid state. Hydrogen bonds also play a very important biological role in the physical structures of proteins and nucleic acids.

Boiling Points and Bonding Types

In order for a substance to enter the gas phase, its particles must completely overcome the intermolecular forces holding them together. Therefore, a comparison of boiling points is essentially equivalent to comparing the strengths of the attractive intermolecular forces exhibited by the individual molecules. For small molecular compounds, London dispersion forces are the weakest intermolecular forces. Dipole-dipole forces are somewhat stronger, and hydrogen bonding is a particularly strong form of dipole-dipole interaction. However, when the mass of a nonpolar molecule is sufficiently large, its dispersion forces can be stronger than the dipole-dipole forces in a lighter polar molecule. Thus, nonpolar Cl_2 has a higher boiling point than polar HCl.

Table 4.3.2: Intermolecular Forces and Boiling Points

Substance	Strongest Intermolecular Force	Boiling Point (°C)
H_2	dispersion	-253
Ne	dispersion	-246
O_2	dispersion	-183
Cl_2	dispersion	-34
HCl	dipole-dipole	-85
HBr	dipole-dipole	-66
H_2S	dipole-dipole	-61
NH_3	hydrogen bonding	-33
HF	hydrogen bonding	20
H_2O	hydrogen bonding	100

Supplemental Resources

- Electronegativity: www.chemguideco.uk/atoms/bond...elecroneg.html
- Intermolecular Bonding - van der Waals Forces: www.chemguidecouk/atoms/bonding/vdw.html

- Intermolecular Bonding - Hydrogen Bonds: www.chemguide.co.uk/bonding/hbond.html
- Ionic bond formation: www.dlt.ncssm/edu/core/Chapte...icBonding.html
- Polar covalent bond formation: http://www.dlt.ncssm.edu/core/Chapte...arBonding.html
- Nonpolar covalent bond formation: www.dlt.ncssm/edu/core/Chapte...ntBonding.html

Contributors and Attributions

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4.4: Carbon

Skills to Develop

- Explain why carbon is important for life
- Describe the role of functional groups in biological molecules

Cells are made of many complex molecules called macromolecules, such as proteins, nucleic acids (RNA and DNA), carbohydrates, and lipids. The macromolecules are a subset of organic molecules (any carbon-containing liquid, solid, or gas) that are especially important for life. The fundamental component for all of these macromolecules is carbon. The carbon atom has unique properties that allow it to form covalent bonds to as many as four different atoms, making this versatile element ideal to serve as the basic structural component, or "backbone," of the macromolecules.

Individual carbon atoms have an incomplete outermost electron shell. With an atomic number of 6 (six electrons and six protons), the first two electrons fill the inner shell, leaving four in the second shell. Therefore, carbon atoms can form up to four covalent bonds with other atoms to satisfy the octet rule. The methane molecule provides an example: it has the chemical formula CH_4. Each of its four hydrogen atoms forms a single covalent bond with the carbon atom by sharing a pair of electrons. This results in a filled outermost shell.

Hydrocarbons

Hydrocarbons are organic molecules consisting entirely of carbon and hydrogen, such as methane (CH_4) described above. We often use hydrocarbons in our daily lives as fuels—like the propane in a gas grill or the butane in a lighter. The many covalent bonds between the atoms in hydrocarbons store a great amount of energy, which is released when these molecules are burned (oxidized). Methane, an excellent fuel, is the simplest hydrocarbon molecule, with a central carbon atom bonded to four different hydrogen atoms, as illustrated in Figure 4.4.1. The geometry of the methane molecule, where the atoms reside in three dimensions, is determined by the shape of its electron orbitals. The carbons and the four hydrogen atoms form a shape known as a tetrahedron, with four triangular faces; for this reason, methane is described as having tetrahedral geometry.

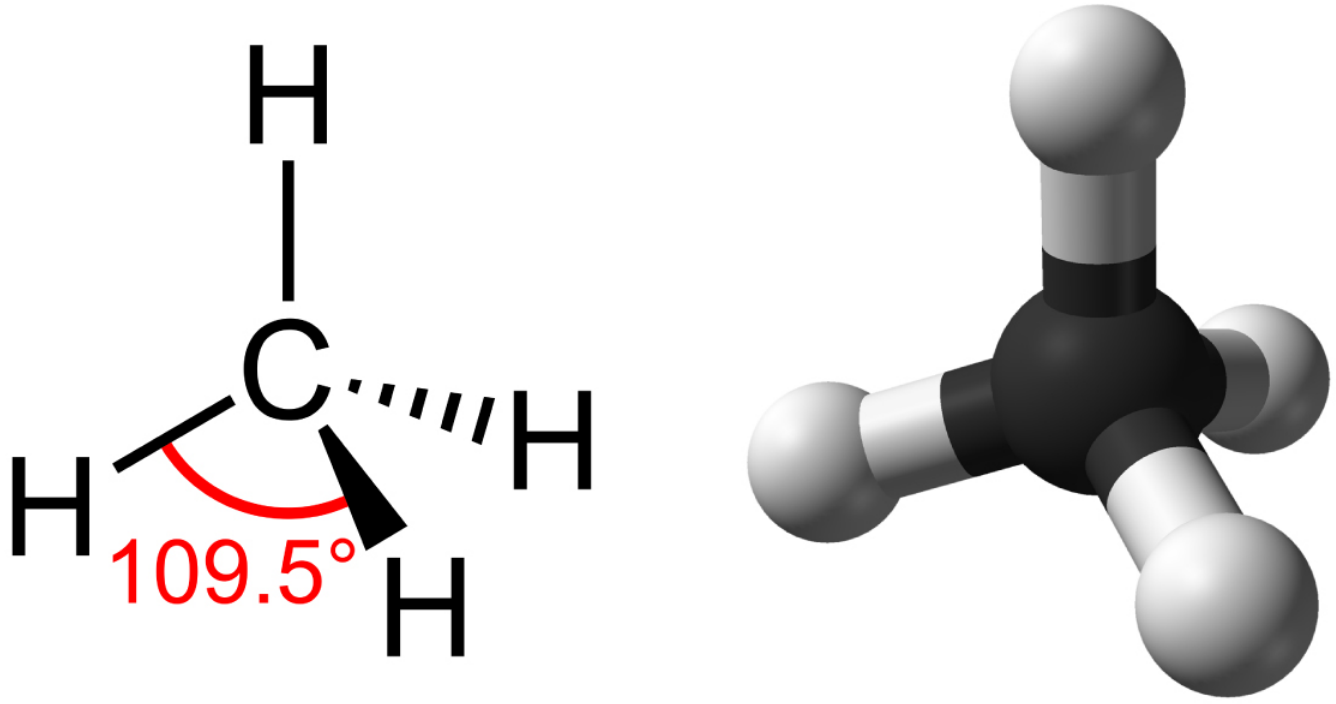


Figure 4.4.1: Methane has a tetrahedral geometry, with each of the four hydrogen atoms spaced 109.5° apart.

As the backbone of the large molecules of living things, hydrocarbons may exist as linear carbon chains, carbon rings, or combinations of both. Furthermore, individual carbon-to-carbon bonds may be single, double, or triple covalent bonds, and each

type of bond affects the geometry of the molecule in a specific way. This three-dimensional shape or conformation of the large molecules of life (macromolecules) is critical to how they function.

Hydrocarbon Chains

Hydrocarbon chains are formed by successive bonds between carbon atoms and may be branched or unbranched. Furthermore, the overall geometry of the molecule is altered by the different geometries of single, double, and triple covalent bonds, illustrated in Figure 4.4.2. The hydrocarbons ethane, ethene, and ethyne serve as examples of how different carbon-to-carbon bonds affect the geometry of the molecule. The names of all three molecules start with the prefix "eth-," which is the prefix for two carbon hydrocarbons. The suffixes "-ane," "-ene," and "-yne" refer to the presence of single, double, or triple carbon-carbon bonds, respectively. Thus, propane, propene, and propyne follow the same pattern with three carbon molecules, butane, butane, and butyne for four carbon molecules, and so on. Double and triple bonds change the geometry of the molecule: single bonds allow rotation along the axis of the bond, whereas double bonds lead to a planar configuration and triple bonds to a linear one. These geometries have a significant impact on the shape a particular molecule can assume.

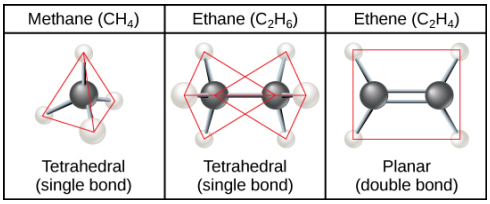


Figure 4.4.2: When carbon forms single bonds with other atoms, the shape is tetrahedral. When two carbon atoms form a double bond, the shape is planar, or flat. Single bonds, like those found in ethane, are able to rotate. Double bonds, like those found in ethene cannot rotate, so the atoms on either side are locked in place.

Hydrocarbon Rings

So far, the hydrocarbons we have discussed have been aliphatic hydrocarbons, which consist of linear chains of carbon atoms. Another type of hydrocarbon, aromatic hydrocarbons, consists of closed rings of carbon atoms. Ring structures are found in hydrocarbons, sometimes with the presence of double bonds, which can be seen by comparing the structure of cyclohexane to benzene in Figure 4.4.3. Examples of biological molecules that incorporate the benzene ring include some amino acids and cholesterol and its derivatives, including the hormones estrogen and testosterone. The benzene ring is also found in the herbicide 2,4-D. Benzene is a natural component of crude oil and has been classified as a carcinogen. Some hydrocarbons have both aliphatic and aromatic portions; beta-carotene is an example of such a hydrocarbon.

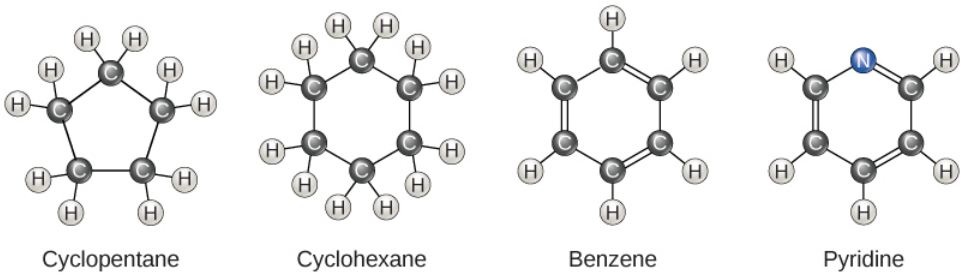


Figure 4.4.3: Carbon can form five-and six membered rings. Single or double bonds may connect the carbons in the ring, and nitrogen may be substituted for carbon.

Isomers

The three-dimensional placement of atoms and chemical bonds within organic molecules is central to understanding their chemistry. Molecules that share the same chemical formula but differ in the placement (structure) of their atoms and/or chemical bonds are known as isomers. Structural isomers (like butane and isobutene shown in Figure 4.4.4a differ in the placement of their covalent bonds: both molecules have four carbons and ten hydrogens (C_4H_{10}), but the different arrangement of the atoms within the molecules leads to differences in their chemical properties. For example, due to their different chemical properties, butane is suited for use as a fuel for cigarette lighters and torches, whereas isobutene is suited for use as a refrigerant and a propellant in spray cans.

Geometric isomers, on the other hand, have similar placements of their covalent bonds but differ in how these bonds are made to the surrounding atoms, especially in carbon-to-carbon double bonds. In the simple molecule butene (C_4H_8), the two methyl groups (CH_3) can be on either side of the double covalent bond central to the molecule, as illustrated in Figure 4.4.4b. When the carbons are bound on the same side of the double bond, this is the *cis* configuration; if they are on opposite sides of the double bond, it is a *trans* configuration. In the *trans* configuration, the carbons form a more or less linear structure, whereas the carbons in the *cis* configuration make a bend (change in direction) of the carbon backbone.

Art Connection

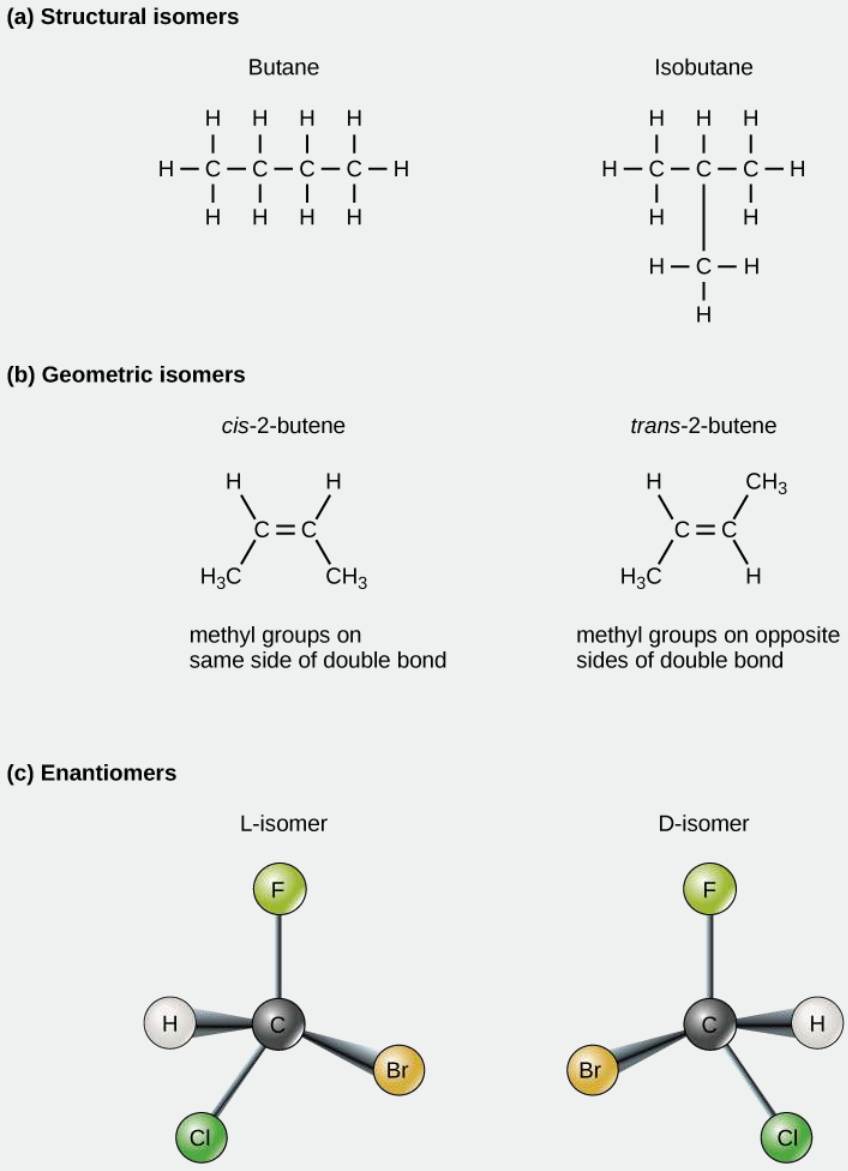
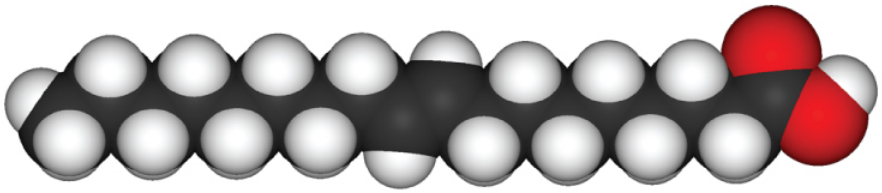


Figure 4.4.4: Molecules that have the same number and type of atoms arranged differently are called isomers. (a) Structural isomers have a different covalent arrangement of atoms. (b) Geometric isomers have a different arrangement of atoms around a double bond. (c) Enantiomers are mirror images of each other.

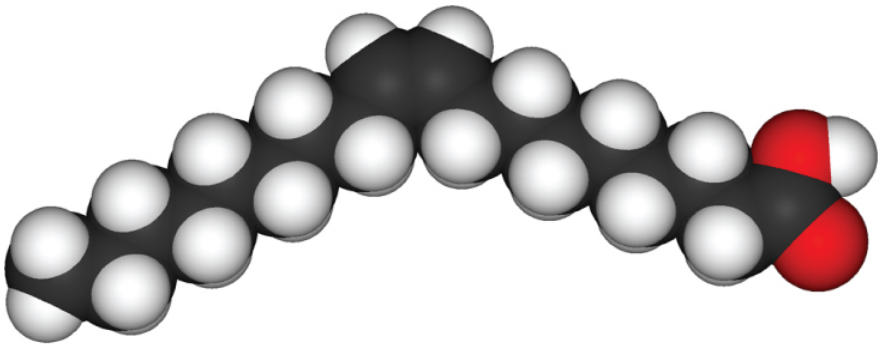
Which of the following statements is false?

A. Molecules with the formulas CH_3CH_2COOH and $C_3H_6O_2$ could be structural isomers.
B. Molecules must have a double bond to be *cis-trans* isomers.
C. To be enantiomers, a molecule must have at least three different atoms or groups connected to a central carbon.
D. To be enantiomers, a molecule must have at least four different atoms or groups connected to a central carbon.

In triglycerides (fats and oils), long carbon chains known as fatty acids may contain double bonds, which can be in either the *cis* or *trans* configuration, illustrated in Figure 4.4.5. Fats with at least one double bond between carbon atoms are unsaturated fats. When some of these bonds are in the *cis* configuration, the resulting bend in the carbon backbone of the chain means that triglyceride molecules cannot pack tightly, so they remain liquid (oil) at room temperature. On the other hand, triglycerides with *trans* double bonds (popularly called trans fats), have relatively linear fatty acids that are able to pack tightly together at room temperature and form solid fats. In the human diet, trans fats are linked to an increased risk of cardiovascular disease, so many food manufacturers have reduced or eliminated their use in recent years. In contrast to unsaturated fats, triglycerides without double bonds between carbon atoms are called saturated fats, meaning that they contain all the hydrogen atoms available. Saturated fats are a solid at room temperature and usually of animal origin.



Eliadic acid



Oleic acid

Figure 4.4.5: These space-filling models show a *cis* (oleic acid) and a *trans* (eliadic acid) fatty acid. Notice the bend in the molecule cause by the *cis* configuration.

Enantiomers

Enantiomers are molecules that share the same chemical structure and chemical bonds but differ in the three-dimensional placement of atoms so that they are mirror images. As shown in Figure 4.4.6, an amino acid alanine example, the two structures are non-superimposable. In nature, only the L-forms of amino acids are used to make proteins. Some D forms of amino acids are seen in the cell walls of bacteria, but never in their proteins. Similarly, the D-form of glucose is the main product of photosynthesis and the L-form of the molecule is rarely seen in nature.

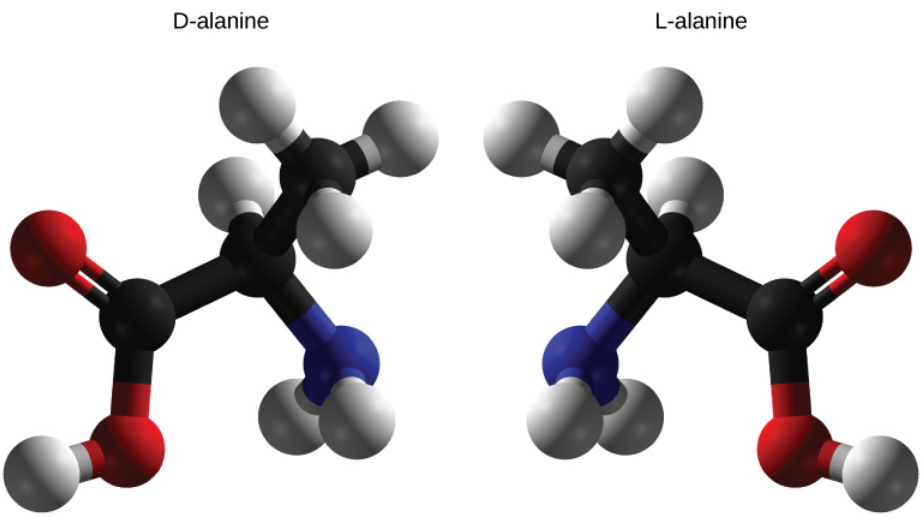


Figure 4.4.6: D-alanine and L-alanine are examples of enantiomers or mirror images. Only the L-forms of amino acids are used to make proteins.

Functional Groups

Functional groups are groups of atoms that occur within molecules and confer specific chemical properties to those molecules. They are found along the “carbon backbone” of macromolecules. This carbon backbone is formed by chains and/or rings of carbon atoms with the occasional substitution of an element such as nitrogen or oxygen. Molecules with other elements in their carbon backbone are substituted hydrocarbons.

The functional groups in a macromolecule are usually attached to the carbon backbone at one or several different places along its chain and/or ring structure. Each of the four types of macromolecules—proteins, lipids, carbohydrates, and nucleic acids—has its own characteristic set of functional groups that contributes greatly to its differing chemical properties and its function in living organisms.

A functional group can participate in specific chemical reactions. Some of the important functional groups in biological molecules are shown in Figure 4.4.7; they include: hydroxyl, methyl, carbonyl, carboxyl, amino, phosphate, and sulfhydryl. These groups play an important role in the formation of molecules like DNA, proteins, carbohydrates, and lipids. Functional groups are usually classified as hydrophobic or hydrophilic depending on their charge or polarity characteristics. An example of a hydrophobic group is the non-polar methane molecule. Among the hydrophilic functional groups is the carboxyl group found in amino acids, some amino acid side chains, and the fatty acids that form triglycerides and phospholipids. This carboxyl group ionizes to release hydrogen ions (H^+) from the COOH group resulting in the negatively charged COO^- group; this contributes to the hydrophilic nature of whatever molecule it is found on. Other functional groups, such as the carbonyl group, have a partially negatively charged oxygen atom that may form hydrogen bonds with water molecules, again making the molecule more hydrophilic.

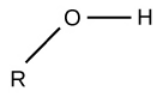
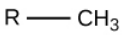
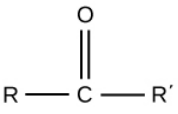
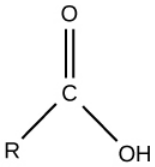
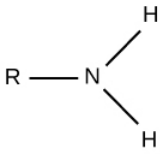
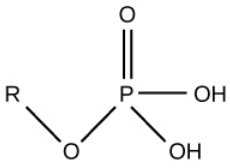
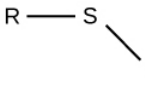
Functional Group	Structure	Properties
Hydroxyl		Polar
Methyl		Nonpolar
Carbonyl		Polar
Carboxyl		Charged, ionizes to release H^+. Since carboxyl groups can release H^+ ions into solution, they are considered acidic.
Amino		Charged, accepts H^+ to form NH_3^+. Since amino groups can remove H^+ from solution, they are considered basic.
Phosphate		Charged, ionizes to release H^+. Since phosphate groups can release H^+ ions into solution, they are considered acidic.
Sulfhydryl		Polar

Figure 4.4.7: The functional groups shown here are found in many different biological molecules.

Hydrogen bonds between functional groups (within the same molecule or between different molecules) are important to the function of many macromolecules and help them to fold properly into and maintain the appropriate shape for functioning. Hydrogen bonds are also involved in various recognition processes, such as DNA complementary base pairing and the binding of an enzyme to its substrate, as illustrated in Figure 4.4.8.

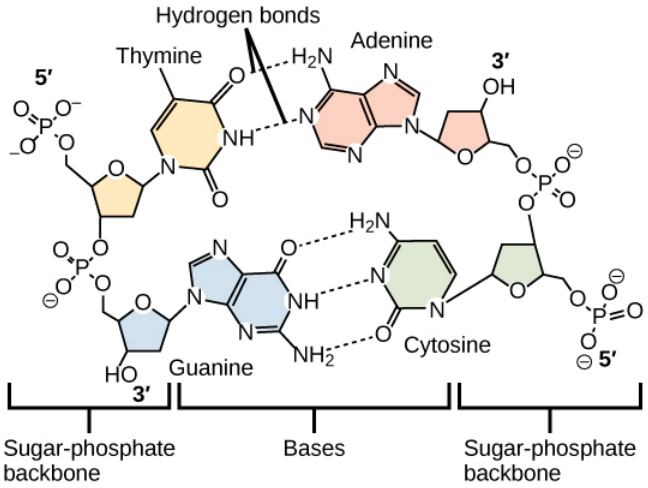


Figure 4.4.8: Hydrogen bonds connect two strands of DNA together to create the double-helix structure.

Summary

The unique properties of carbon make it a central part of biological molecules. Carbon binds to oxygen, hydrogen, and nitrogen covalently to form the many molecules important for cellular function. Carbon has four electrons in its outermost shell and can form four bonds. Carbon and hydrogen can form hydrocarbon chains or rings. Functional groups are groups of atoms that confer specific properties to hydrocarbon (or substituted hydrocarbon) chains or rings that define their overall chemical characteristics and function.

Art Connections

Figure 4.4.4: Which of the following statements is false?

A. Molecules with the formulas CH_3CH_2COOH and $C_3H_6O_2$ could be structural isomers.
B. Molecules must have a double bond to be *cis-trans* isomers.
C. To be enantiomers, a molecule must have at least three different atoms or groups connected to a central carbon.
D. To be enantiomers, a molecule must have at least four different atoms or groups connected to a central carbon.

Answer

C

Glossary

aliphatic hydrocarbon
hydrocarbon consisting of a linear chain of carbon atoms

aromatic hydrocarbon
hydrocarbon consisting of closed rings of carbon atoms

enantiomers
molecules that share overall structure and bonding patterns, but differ in how the atoms are three dimensionally placed such that they are mirror images of each other

functional group
group of atoms that provides or imparts a specific function to a carbon skeleton

geometric isomer
isomer with similar bonding patterns differing in the placement of atoms alongside a double covalent bond

hydrocarbon
molecule that consists only of carbon and hydrogen

isomers
molecules that differ from one another even though they share the same chemical formula

organic molecule
any molecule containing carbon (except carbon dioxide)

structural isomers
molecules that share a chemical formula but differ in the placement of their chemical bonds

substituted hydrocarbon
hydrocarbon chain or ring containing an atom of another element in place of one of the backbone carbons

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4.5: Functional Groups

Learning Outcomes

- Describe the importance and purpose of functional groups in organic reactions.
- Identify and name functional groups in compounds.

With over twenty million known organic compounds in existence, it would be very challenging to memorize chemical reactions for each one. Fortunately, molecules with similar functional groups tend to undergo similar reactions. A **functional group** is defined as an atom or group of atoms within a molecule that has similar chemical properties whenever it appears in various compounds. Even if other parts of the molecule are quite different, certain functional groups tend to react in certain ways.

We've already looked at alkanes, but they are generally unreactive. We primarily use alkanes as a source of energy when they are combusted. While the majority of functional groups involve atoms other than carbon and hydrogen, we will also look at some that include only carbon and hydrogen. Some of the most common functional groups are presented in the following sections.

Organic molecules vary greatly in size and when focusing on functional groups, we want to direct our attention to the atoms involved in the functional group. As a result, the abbreviation R is used in some examples. The letter R is used in molecular structures to represent the "**R**est of the molecule". It consists of a group of carbon and hydrogen atoms of any size. It is used as an abbreviation since a group of carbon and hydrogen atoms does not affect the functionality of the compound. In some molecules, you will see R, R', or R'' which indicates that the R groups in the molecule can be different from one another. For example, R might be $–CH_2CH_3$ while R' is $–CH_2CH_2CH_2CH_3$.

Alkenes and Alkynes

Alkenes are hydrocarbons that contain one or more double bonds between neighboring carbon atoms. Alkynes contain one or more triple bonds between neighboring carbon atoms. The presence of a double or triple bond results in reactivity not present in alkane and alkynes (see figure below) undergo characteristic reactions which will be covered later.



Figure 4.5.1: Alkenes (left) contain one or more double bonds while alkynes (right) contain one or more triple bonds.

Aromatics

The additional functional group that contains only carbon and hydrogen is an aromatic ring which is a six-carbon ring with alternative double bonds. The aromatic ring is also shown as a ring with a circle in the middle representing the double bonds. Aromatic rings (see figure below) are found in many compounds including steroids and medications.


Figure 4.5.2: Aromatic rings contain alternating double bonds.

Alcohols

The **alcohol** functional group involves an oxygen atom that is bonded to one hydrogen atom and one carbon atom. The carbon atom will be part of a larger organic structure. One way to indicate a generic alcohol would be with the formula $\mathrm{R{-}OH}$. R represents any organic fragment in which a carbon atom is directly bonded to the explicitly indicated functional group (in this case, OH). The R group is typically a chain of carbon atoms.

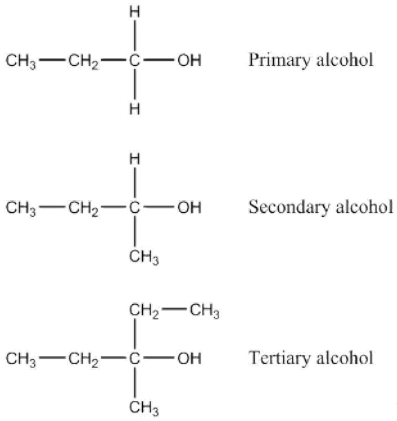


Figure 4.5.3: Primary, secondary, and tertiary alcohols.

Alcohols can be classified as primary, secondary, or tertiary based on the characteristics of the carbon to which it is attached. In a primary alcohol, the carbon bonded directly to the oxygen atom is also bonded to exactly one carbon atom, with the other bonds generally going to hydrogen atoms. In a secondary alcohol, the carbon is attached to two other carbon atoms, and in a tertiary alcohol, the carbon is bonded to three other carbon atoms. The type of alcohol being used will determine the product of certain reactions. Note the naming of alcohols as illustrated in the figure above. The location of the $-\mathrm{OH}$ group is indicated with the number of the carbon to which it is attached.

We are already familiar with several common alcohols. For example, ethanol $(\mathrm{CH_3CH_2OH})$ is the alcohol present in alcoholic beverages. It is also widely used in the industrial manufacture of other chemicals. Methanol $(\mathrm{CH_3OH})$ is used as a gasoline additive or alternative. Additionally, methanol can be used to manufacture formaldehyde, which is employed in the production of plastics, paints, and other useful substances. Isopropanol is commonly known as rubbing alcohol. In addition to its industrial uses, isopropanol is used to clean various surfaces, including computer monitors, whiteboards, and even skin (e.g., before getting blood drawn).

Ethers

The **ether** functional group consists of an oxygen atom that forms single bonds with two carbon atoms.

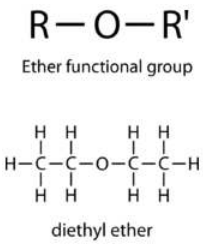


Figure 4.5.4: Ethers

Ethers are good solvents for other organic compounds because of their low reactivity. They readily dissolve nonpolar molecules. Diethyl ether is perhaps the best known ether. It is widely used as a solvent and has been used as an inhalable anesthetic.

Although ethers themselves are relatively unreactive, they can be converted to peroxides after prolonged exposure to oxygen. Peroxides are very reactive and are often explosive at elevated temperatures. Many commercially available ethers come with a small amount of a peroxide scavenger dissolved in them to help prevent this type of safety hazard.

Thiol

The **thiol** functional group contains a sulfur atom bonded to a hydrogen atom. It is very similar to an alcohol functional group with the sulfur replacing the O.

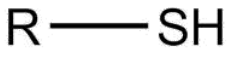


Figure 4.5.5: Thiol

Thiols are also called mercaptans which is derived from the Latin phrase for "capturing mercury" because of the strong bonds it forms with mercury-containing compounds. Some thiol compounds have a distinctive smell similar to rotten eggs. They are often

added to natural gas, which itself has no odor, as a way to detect leaks since its odor can be detected by humans in very small amounts. A thiol group is also present in the amino acid cysteine which will be discussed later.

Amines

An **amine** consists of a nitrogen atom bonded to some combination of carbons and hydrogens.

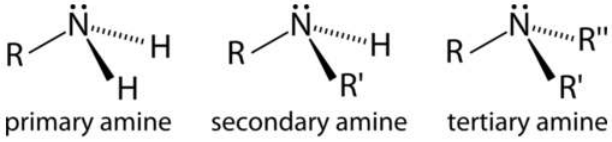


Figure 4.5.6: Amines

Like alcohols, amines can be classified as primary, secondary, or tertiary. However, the rules for assigning these categories are slightly different. In an alcohol, the oxygen atom is always bonded to exactly one carbon atom, so we look at the branching on the adjacent carbon, not the oxygen atom itself. In a neutral amine, the nitrogen can be bonded to one, two, or three carbon atoms, and this is how we decide whether it is called a primary, secondary, or tertiary amine.

Neutral amines are weak bases, because the lone pair on nitrogen can act as a proton acceptor. Many smaller amines have very strong and offensive odors. For example, the aptly-named compounds cadaverine and putrescine are foul-smelling amines, formed as a part of the decay process after death.

Amines serve a wide variety of uses. Diphenylamine acts as a stabilizer for certain types of explosives. Amines are found as components in some lubricating materials, in developers, and are a part of waterproofing textiles. Some amines, such as novocaine, are used as anesthetics. Many pharmaceutical compounds contain amines, including 8 of the 10 most prescribed medications in 2012.

Aldehydes

A very common structural component of organic structures is the **carbonyl**, which is simply a carbon atom and an oxygen atom connected by a double bond. The reactivity of carbonyls is primarily dictated by the polarization of the C=O bond, but the surrounding atoms also play a role in its specific reaction pathways. While carbonyl is a component of many functional groups, it is not itself a functional group.

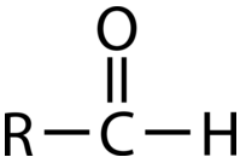


Figure 4.5.7: Aldehyde

An **aldehyde** is a carbonyl in which the carbon atom is bonded to at least one hydrogen atom. The other group attached to the carbonyl may be an R-group or a hydrogen atom. Because the hydrogen atom is so small, the partial positive charge on the carbonyl carbon is very easy for other molecules to approach, making aldehydes a particularly reactive type of carbonyl. Aldehydes are versatile reactants for a wide variety of organic syntheses. Many aldehydes also have distinctive flavors and aromas. For example, the flavor of cinnamon is primarily due to the molecule cinnamaldehyde, and vanillin is the aldehyde most responsible for the smell and taste of vanilla extract.

A special aldehyde is the molecule in which the carbonyl is bonded to two hydrogen atoms. This molecule, called formaldehyde, has a wide variety of uses. By itself, it can be used as a tissue preservative or as a very harsh disinfectant. It is also used as a precursor to various materials, including plastics, resins, and other polymers.

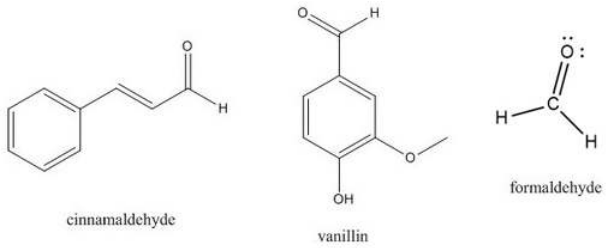


Figure 4.5.8: Examples of molecules with aldehyde functional groups.

Ketones

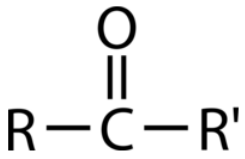


Figure 4.5.9: Ketone

A **ketone** involves a carbonyl in which the carbon atom makes single bonds with two R-groups. Ketones undergo most of the same reactions as aldehydes, but they tend to be slightly less reactive. The simplest ketone is acetone, in which the carbonyl carbon is bonded to two CH_3 groups. This ketone is commonly used to remove fingernail polish and serves as an industrial solvent. Methyl ethyl ketone is used as a paint stripper and a solvent. Ketones are also used in the production of various polymers, either as a building block or as a solvent. The R-group in a ketone can be the same or different as seen in the example.



Figure 4.5.10: Two examples of ketones.

Carboxylic Acids

Carboxylic acids are another carbonyl-containing functional group, in which the carbon atom is bonded to an OH group on one side and either a carbon or hydrogen atom on the other.

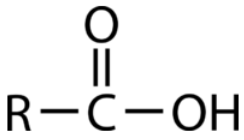


Figure 4.5.11: *Carboxylic acid*

As the name implies, carboxylic acids are weak acids. An OH group that is directly connected to a carbonyl will ionize to a small extent when dissolved in water. The reason for this is the relative stability of the resulting anion. A carboxylate ion (see figure below), in which the negative charge is spread over two different oxygen atoms through resonance structures, is more stable than an isolated oxygen-centered anion. The carboxylic acid and carboxylate ion are interchangeable. Carboxylate ions are often present in amino acids.

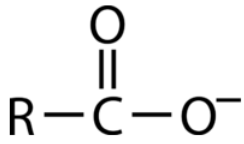


Figure 4.5.12: Carboxylate ion

Carboxylic acids are used in a variety of environments. Formic acid acts as a protective chemical for many stinging insects and plants. Acetic acid gives vinegar its characteristic smell and flavor and is a fundamental biological and industrial building block. Carboxylic acids with longer carbon chains (fatty acids) are used by animals as a way of storing energy and are widely used in the manufacture of soaps. Some compounds contain multiple carboxylic acids within a single molecule. For example, citric acid (three carboxyl groups) is especially abundant in citrus fruits and it used as a flavoring and preservative in many foods and beverages.

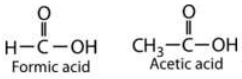
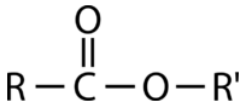


Figure 4.5.13: Carboxylic acids

Esters

An **ester** is similar to a carboxylic acid, in that it contains a carbonyl where the carbon is bonded to one additional oxygen atom and one carbon or hydrogen atom. However, the second oxygen atom is bonded to another carbon instead of to an acidic hydrogen atom. Structurally, carboxylic acids and esters are related to one another in the same way as alcohols and ethers.

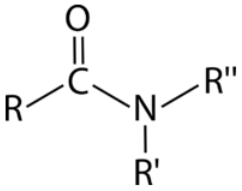

Figure 4.5.14: Ester

Esters can be formed by heating carboxylic acids and alcohols in the presence of an acid catalyst. This process is reversible, and the starting materials can be regenerated by reacting an ester with water in the presence of a weak base.

Some esters have very pleasant odors, so they are used in the manufacture of many perfumes. Propyl acetate contributes to the odor of pears, while isoamyl acetate gives bananas their smell. This ester also serves as an alarm signal for honeybees. Esters are employed in the manufacture of fabrics (polyesters) and Plexiglass. Anesthetics such as procaine and benzocaine also contain esters.

Amides

An **amide** is a carbonyl in which the carbon is attached to one nitrogen atom and one carbon or hydrogen atom. Alternatively, we could define an amide as an amine in which one of the carbon atoms attached to the nitrogen is part of a carbonyl.


Figure 4.5.15: Amide

An amide can be formed by combining a carboxylic acid and an amine. Only primary and secondary amines can be sued to form amides, since they have a hydrogen that can be replaced with the carbonyl carbon; tertiary amines will not form amides. The amide shown in the figure above was formed from a carboxylic acid and a primary amine.

Amides are used as coloring agents in crayons, pencils, and ink. They are employed in the paper, plastic, and rubber industries. Polyacrylamide is a very widely used amide; it is involved in t he treatment of drinking water and sewage, and in plastics manufacture. The amide Kevlar is widely employed for the production of body armor, and nylon is another type of amide-based polymer.

Haloalkanes

The haloalkanes, also known as alkyl halides, are a group of chemical compounds comprised of an alkane with one or more hydrogens replaced by a halogen atom (Group 17 atom). There is a fairly large distinction between the structural and physical properties of haloalkanes and the structural and physical properties of alkanes. A


Figure 4.5.16: Amide

Haloalkanes are found in fire extinguishers, refrigerants, propellants, solvents, and medications. They are also a significant source of pollution and their use has been reduced or eliminated in some products. Chlorofluorocarbons (CFCs) were used as refrigerants in air-conditioners but were found to be a major cause of the depletion of the ozone layer. Research and development of alternatives began in the 1970s. Hydrochlorofluorocarbons (HCFCs) have been used for many years since they cause less damage to the ozone layer, but many countries agreed to eliminate HCFCs by 2020.

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4.E: Covalent Bonding and Simple Molecular Compounds (Exercises)

4.1: Covalent Bonds

Concept Review Exercises

1. How is a covalent bond formed between two atoms?
2. How does covalent bonding allow atoms in group 6A to satisfy the octet rule?

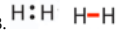
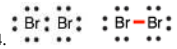
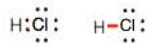
Answers

1. Covalent bonds are formed by two atoms sharing electrons.
2. The atoms in group 6A make two covalent bonds.

Exercises

1. Define *covalent bond*.
2. What is electron sharing?
3. Draw the Lewis diagram for the covalent bond in the H_2 molecule.
4. Draw the Lewis diagram for the covalent bond in the Br_2 molecule.
5. Draw the Lewis diagram for the covalent bond in the HCl molecule.
6. What is the difference between a molecule and a formula unit?
7. Why do hydrogen atoms not follow the octet rule when they form covalent bonds?
8. Draw the Lewis diagram for the covalent bonding in H_2S. How many bonding electrons and nonbonding electrons are in the molecule?
9. Draw the Lewis diagram for the covalent bonding in CF_4. How many bonding electrons and nonbonding electrons are in the molecule?
10. Draw the Lewis diagram for the covalent bonding in PCl_3. How many bonding electrons and nonbonding electrons are in the molecule?
11. How many covalent bonds does a hydrogen atom typically form? Why?
12. How many covalent bonds does an oxygen atom typically form? Why?
13. Tellurium atoms make covalent bonds. How many covalent bonds would a tellurium atom make? Predict the formula of a compound between tellurium and hydrogen.
14. Tin atoms make covalent bonds. How many covalent bonds would a tin atom make? Predict the formula of a compound between tin and hydrogen.
15. Astatine is a synthetic element, made one atom at a time in huge “atom-smasher” machines. It is in the halogen group on the periodic table. How many covalent bonds would an atom of this element form?
16. There have been reports that atoms of element 116 (Lv) were made by smashing smaller atoms together. Using the periodic table, determine what column element 116 would be in and suggest how many covalent bonds an atom of this element would form.

Answers

1. A covalent bond is formed when two atoms share electrons.
2. Electron sharing joins two atoms in a covalent bond. This is a more stable arrangement than 2 individual atoms.
3. 
4. 
5. 

6. A molecule is a discrete combination of atoms; a formula unit is the lowest ratio of ions in a crystal. 7. Hydrogen atoms follow the duet rule (not the octet rule). This is because it has only one shell and this shell can only hold 2 electrons.

8. 

bonding electrons: 4; nonbonding electrons: 4

9. 

bonding electrons: 8; nonbonding electrons: 24

10. 

bonding electrons: 6; nonbonding electrons: 20

11. Hydrogen atoms form only one covalent bond because they have only one valence electron to pair.
12. Oxygen atoms form 2 covalent bonds because oxygen atoms have 6 valence electrons (2 lone pairs plus 2 unpaired electrons that are shared to achieve octet).
13. two; H_2Te
14. four: SnH_4

15. one
16. two

4.2: Covalent Compounds - Formulas and Names

Concept Review Exercises

1. How do you recognize a covalent compound?
2. What are the rules for writing the molecular formula of a simple covalent compound?
3. What are the rules for naming a simple covalent compound?

Answers

1. A covalent compound is usually composed of two or more nonmetal elements.
2. It is just like an ionic compound except that the element further down and to the left on the periodic table is listed first and is named with the element name.
3. Name the first element first and then the second element by using the stem of the element name plus the suffix -ide. Use numerical prefixes if there is more than one atom of the first element; always use numerical prefixes for the number of atoms of the second element.

Exercises

1. Identify whether each compound has covalent bonds.
   a. NaI
   b. Na_2CO_3
   c. N_2O
   d. SiO_2
2. Identify whether each compound has covalent bonds.
   a. C_2H_6
   b. C_6H_5Cl
   c. $KC_2H_3O_2$
   d. $Ca(OH)_2$
3. Identify whether each compound has ionic bonds, covalent bonds, or both.
   a. Na_3PO_4
   b. K_2O
   c. $COCl_2$
   d. $CoCl_2$
4. Identify whether each compound has ionic bonds, covalent bonds, or both.
   a. $FeCl_3$
   b. $Fe(NO_3)_3$
   c. $(NH_2)_2CO$
   d. SO_3
5. Which is the correct molecular formula—H_4Si or SiH_4? Explain.
6. Which is the correct molecular formula—SF_6 or F_6S? Explain.
7. Write the name for each covalent compound.
   a. SiF_4
   b. NO_2
   c. CS_2
   d. P_2O_5
8. Write the name for each covalent compound.
   a. CO
   b. S_2O_3
   c. BF_3
   d. GeS_2
9. Write the formula for each covalent compound.
   a. iodine trichloride
   b. disulfur dibromide
   c. arsenic trioxide
   d. xenon hexafluoride
10. Write the formula for each covalent compound.
    a. boron trichloride
    b. carbon dioxide
    c. tetraphosphorus decoxide
    d. germanium dichloride
11. Write two covalent compounds that have common rather than systematic names.
12. What is the name of the simplest organic compound? What would its name be if it followed the nomenclature for binary covalent compounds?

Answers

1. a. no
   b. yes
   c. yes
   d. yes
2.

a. yes
b. yes
c. yes
d. yes

3. a. both
   b. ionic
   c. covalent
   d. ionic

4.

   a. ionic
   b. both
   c. covalent
   d. covalent

5. SiH_4; except for water, hydrogen is almost never listed first in a covalent compound.

6. SF_6; the less electronegative atom (S) is written first

7. a. silicon tetrafluoride
   b. nitrogen dioxide
   c. carbon disulfide
   d. diphosphorus pentoxide

8.

   a. carbon monoxide
   b. disulfur trioxide
   c. boron trifluoride
   d. germanium disulfide

9. a. ICl_3
   b. S_2Br_2
   c. AsO_3
   d. XeF_6

10.

    a. BCl_3
    b. CO_2
    c. P_4O_{10}
    d. $GeCl_2$

11. H_2O and NH_3 (water and ammonia) (answers will vary)
12. CH_4; carbon tetrahydride

4.3: Drawing Lewis Structures

Exercises

1. What is one clue that a molecule has a multiple bond?

2. Draw the Lewis diagram for each of the following.

   a. H_2O

   b. NH_3

   c. C_2H_6

   d. CCl_4

3. Each molecule contains double bonds. Draw the Lewis diagram for each. The first element is the central atom.

   a. CS_2
   b. C_2F_4
   c. $COCl_2$

4. Each molecule contains multiple bonds. Draw the Lewis diagram for each. Assume that the first element is the central atom, unless otherwise noted.

   a. N_2
   b. CO
   c. HCN (The carbon atom is the central atom.)
   d. POCl (The phosphorus atom is the central atom.)

5. Explain why hydrogen atoms do not form double bonds.

6. Why is it incorrect to draw a double bond in the Lewis diagram for MgO?

Answers

1. If single bonds between all atoms do not give all atoms (except hydrogen) an octet, multiple covalent bonds may be present.
2. a.

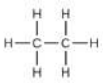


b.



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c.



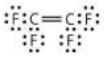
d.



3. a.



b.



c.

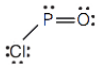


4. a. $\ddot{N} \equiv \ddot{N}$

b. $:C \equiv O:$

c. $H:C \equiv \ddot{N}$

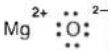
d.



5. Hydrogen can accept only one more electron; multiple bonds require more than one electron pair to be shared.

6. MgO is an ionic compound (Mg transfers two electrons to O). The electrons are not shared hence it's incorrect to draw a double bond.

This is the Lewis dot structure of MgO.



4.4: Characteristics of Covalent Bonds

Concept Review Exercises

1. What is the name for the distance between two atoms in a covalent bond?
2. What does the electronegativity of an atom indicate?
3. What type of bond is formed between two atoms if the difference in electronegativities is small? Medium? Large?

Answers

1. bond length
2. Electronegativity is a qualitative measure of how much an atom attracts electrons in a covalent bond.
3. nonpolar; polar; ionic

Exercises

1. Which is longer—a C–H bond or a C–O bond? (Refer to Table $4.E.1$.)
2. Which is shorter—an N–H bond or a C–H bond? (Refer to Table $4.E.1$.)
3. A nanometer is 10^{-9} m. Using the data in Table $4.E.1$ and Table $4.E.2$, determine the length of each bond in nanometers.
   a. a C–O bond
   b. a C=O bond
   c. an H–N bond
   d. a C≡N bond
4. An angstrom (Å) is defined as 10^{-10} m. Using Table $4.E.1$ and Table $4.E.2$, determine the length of each bond in angstroms.
   a. a C–C bond
   b. a C=C bond
   c. an N≡N bond
   d. an H–O bond
5. Refer to Exercise 3. Why is the nanometer unit useful as a unit for expressing bond lengths?
6. Refer to Exercise 4. Why is the angstrom unit useful as a unit for expressing bond lengths?
7. Using Figure $4.E.3$, determine which atom in each pair has the higher electronegativity.
   a. H or C
   b. O or Br

c. Na or Rb
d. I or Cl

8. Using Figure 4.E.3, determine which atom in each pair has the lower electronegativity.

a. Mg or O
b. S or F
c. Al or Ga
d. O or I

9. Will the electrons be shared equally or unequally across each covalent bond? If unequally, to which atom are the electrons more strongly drawn?

a. a C–O bond
b. an F–F bond
c. an S–N bond
d. an I–Cl bond

10. Will the electrons be shared equally or unequally across each covalent bond? If unequally, to which atom are the electrons more strongly drawn?

a. a C–C bond
b. a S–Cl bond
c. an O–H bond
d. an H–H bond

11. Arrange the following bonds from least polar to most polar: H-F, H-N, H-O, H-C

12. Arrange the following bonds from least polar to most polar: C-F, C-N, C-O, C-C

Answers

1. A C–O bond is longer.

2. An H-N bond is shorter than an H-C bond.

3. a. 0.143 nm
b. 0.120 nm
c. 0.100 nm
d. 0.116 nm

4.

a. 1.54 Å
b. 1.34 Å
c. 1.10 Å
d. 0.97 Å

5. Actual bond lengths are very small, so the nanometer unit makes the expression of length easier to understand.

6. Actual bond lengths are very small, so the angstrom unit makes the expression of length easier to understand.

7. a. C
b. O
c. Na
d. Cl

8.

a. Mg
b. S
c. Al
d. I

9.

a. unequally toward the O
b. equally
c. unequally toward the N
d. unequally toward the Cl

10.

a. equally
b. unequally toward the Cl
c. unequally toward the O
d. equally

11. The electronegativity difference increases from 0.4; 0.9; 1.4; 1.9. Hence, the least to most polar: H-C, H-N, H-O, H-F

12. The electronegativity difference increases from 0; 0.5; 1.0; 1.5. Hence, the least to most polar: C-C, C-N, C-O, C-F

4.5: Characteristics of Molecules

Concept Review Exercises

1. How do you determine the molecular mass of a covalent compound?
2. How do you determine the shape of a molecule?
3. How do you determine whether a molecule is polar or nonpolar?

Answers

1. The molecular mass is the sum of the masses of the atoms in the formula.

2. The shape of a molecule is determined by the position of the atoms, which in turn is determined by the repulsion of the bonded and lone electron pairs around the central atom.

3. If all the bonds in a molecule are nonpolar, the molecule is nonpolar. If it contains identical polar bonds that are oriented symmetrically opposite each other (linear, trigonal planar or tetrahedral) then the molecule is nonpolar. If it contains polar bonds that don't cancel each other's effects, the molecule is polar.

Exercises

1. What is the molecular mass of each compound?
    a. H_2S
    b. N_2O_4
    c. ICl_3
    d. HCl
2. What is the molecular mass of each compound?
    a. O_2F_2
    b. CCl_4
    c. C_6H_6
    d. SO_3
3. Aspirin ($C_9H_8O_4$) is a covalent compound. What is its molecular mass?
4. Cholesterol ($C_{27}H_{46}O$) is a biologically important compound. What is its molecular mass?
5. What is the shape of each molecule? State whether it is polar or nonpolar.
    a. H_2S
    b. $COCl_2$
    c. SO_2
6. What is the shape of each molecule? State whether it is polar or nonpolar.
    a. NBr_3
    b. SF_2
    c. SiH_4
7. Predict the shape of nitrous oxide (N_2O), which is used as an anesthetic. A nitrogen atom is in the center of this three-atom molecule. Is this polar?
8. Predict the shape of acetylene (C_2H_2), which has the two carbon atoms in the middle of the molecule with a triple bond. What generalization can you make about the shapes of molecules that have more than one central atom?

Answers

1. a. 34.08 amu
    b. 92.02 amu
    c. 233.25 amu
    d. 36.46 amu
2. What is the molecular mass of each compound?
    a. 70.00 amu
    b. 153.81 amu
    c. 78.12 amu
    d. 80.06 amu
3. 180.17 amu
4. 386.73 amu
5. a. bent; polar
    b. trigonal planar; nonpolar
    c. bent; polar
6.
    a. pyramidal; polar
    b. bent; polar
    c. tetrahedral; nonpolar
7. linear; polar
8. linear; in a molecule with more than one central atom, the geometry around each central atom needs to be examined.

4.6: Organic Chemistry

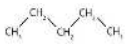
Concept Review Exercises

1. What is organic chemistry?
2. What is a functional group? Give at least two examples of functional groups.

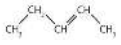
Answers

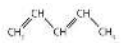
1. Organic chemistry is the study of the chemistry of carbon compounds.
2. A functional group is a specific structural arrangement of atoms or bonds that imparts a characteristic chemical reactivity to the molecule; alcohol group and carboxylic group (answers will vary).

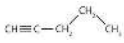
Exercises

1. Give three reasons why carbon is the central element in organic chemistry.
2. Are organic compounds based more on ionic bonding or covalent bonding? Explain.
3. Identify the type of hydrocarbon in each structure.
    a. 

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b. 

c. 

d. 

4. Identify the type of hydrocarbon in each structure.

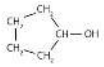
a. 

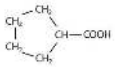
b. 

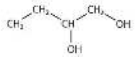
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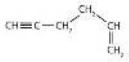
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5. Identify the functional group(s) in each molecule.

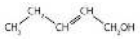
a. 

b. 

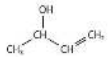
c. 

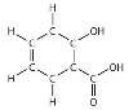
d. 

6. Identify the functional group(s) in each molecule.

a. 

b. 

c. 

d. 

7. How many functional groups described in this section contain carbon and hydrogen atoms only? Name them.

8. What is the difference in the ways the two oxygen atoms in the carboxyl group are bonded to the carbon atom?

Answers

1. Carbon atoms bond reasonably strongly with other carbon atoms. Carbon atoms bond reasonably strongly with atoms of other elements. Carbon atoms make a large number of covalent bonds (four).

2. Organic compounds are based on covalent bonding or electron sharing. The atoms C, H, O, N that make up organic compounds are all nonmetals.

3.

a. alkane
b. alkene
c. alkene
d. alkyne

4.

a. alkene
b. alkane
c. alkyne
d. alkene

5.

a. alcohol
b. carboxyl
c. alcohol
d. alkene and alkyne

6.

a. a carbon-carbon double bond and alcohol
b. carboxyl group
c. carbon-carbon double bond and alcohol
d. carbon-carbon double bond; alcohol and carboxyl group

7. two; carbon-carbon double bonds and carbon-carbon triple bonds

8. There are two oxygen atoms in a carboxyl group: one is double-bonded while the other is OH, single bonded to the same carbon atom.

Additional Exercises

Use the atomic masses found in Figure 2.7.1

1. An atomic mass unit equals 1.661×10^{-24} g. what is the mass in grams of each molecule of (a) H_2S (b) N_2O_4 (c) ICl_3 (d) NCl_3?
2. An atomic mass unit equals 1.661×10^{-24} g. What is the mass in grams of (a) O_2F_2 (b) CCl_4 (c) C_6H_6 (d) SO_3?
3. An atomic mass unit equals 1.661×10^{-24} g. What is the mass in grams of 5.00×10^{22} molecules of $C_9H_8O_4$?
4. An atomic mass unit equals 1.661×10^{-24} g. What is the mass in grams of 1.885×10^{20} molecules of $C_{27}H_{46}O$?
5. Acetic acid has the following structure:

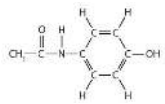


This molecule can lose a hydrogen ion (H^+) and the resulting anion can combine with other cations, such as Na^+:



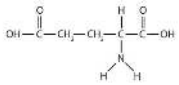
Name this ionic compound.

6. Formic acid (HCOOH) loses a hydrogen ion to make the formate ion ($HCOO^-$). Write the formula for each ionic compound: potassium formate, calcium formate, and ferric formate.
7. Cyanogen has the formula C_2N_2. Propose a bonding scheme that gives each atom the correct number of covalent bonds. (Hint: the two carbon atoms are in the center of a linear molecule.)
8. How many carbon–carbon single bonds, linked together, are needed to make a carbon chain that is 1.000 cm long?
9. How many carbon–carbon double bonds, linked together, are needed to make a carbon chain that is 1.000 cm long?
10. In addition to themselves, what other atoms can carbon atoms bond with and make covalent bonds that are nonpolar (or as nonpolar as possible)?
11. What is the greatest possible electronegativity difference between any two atoms? Use Figure 4.4 to find the answer.
12. Acetaminophen, a popular painkiller, has the following structure:



Name the recognizable functional groups in this molecule. Do you think there are other groups of atoms in this molecule that might qualify as functional groups?

13. Glutamic acid is the parent compound of monosodium glutamate (known as MSG), which is used as a flavor enhancer. Glutamic acid has the following structure:



Name the functional groups you recognize in this molecule. Do you think there are other groups of atoms in this molecule that might qualify as functional groups?

Answers

1.

a: 5.661×10^{-23} g

b: 1.528×10^{-22} g

c: 3.874×10^{-22} g

d: 1.999×10^{-22} g

2.

a: 1.163×10^{-22} g

b: 2.555×10^{-22} g

c: 1.298×10^{-22} g

d: 1.330×10^{-22} g

3. 14.96 g

4. 0.1211 g

5. sodium acetate

6.

a. KHCOO

b. $Ca(HCOO)_2$

c. $Fe(HCOO)_3$

7. :N≡C–C≡N:
8. 6.49×10^7 C-C bonds
9. 7.46×10^7 C=C bonds
10. Hydrogen atoms make relatively nonpolar bonds with carbon atoms.
11. The greatest electronegativity difference is 3.2, between F and Rb.
12. alcohol; the ring with double bonds, and the O=C-NH are also likely functional groups.
13. carboxyl and $-NH_2$ functional groups

Additional Questions

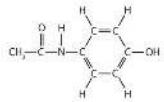
1. An atomic mass unit equals 1.661×10^{-24} g. What is the mass in grams of each molecule of (a) H_2S (b) N_2O_4 (c) ICl_3 (d) NCl_3?
2. An atomic mass unit equals 1.661×10^{-24} g. What is the mass in grams of (a) O_2F_2 (b) CCl_4 (c) C_6H_6 (d) SO_3?
3. An atomic mass unit equals 1.661×10^{-24} g. What is the mass in grams of 5.00×10^{22} molecules of $C_9H_8O_4$?
4. An atomic mass unit equals 1.661×10^{-24} g. What is the mass in grams of 1.885×10^{20} molecules of $C_{27}H_{46}O$?
5. Acetic acid has the following structure:



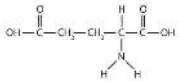
   This molecule can lose a hydrogen ion (H^+) and the resulting anion can combine with other cations, such as Na^+:



   Name this ionic compound.
6. Formic acid (HCOOH) loses a hydrogen ion to make the formate ion ($HCOO^-$). Write the formula for each ionic compound: potassium formate, calcium formate, and ferric formate.
7. Cyanogen has the formula C_2N_2. Propose a bonding scheme that gives each atom the correct number of covalent bonds. (Hint: the two carbon atoms are in the center of a linear molecule.)
8. The molecular formula C_3H_6 represents not only propene, a compound with a carbon–carbon double bond, but also a molecule that has all single bonds. Draw the molecule with formula C_3H_6 that has all single bonds.
9. How many carbon–carbon single bonds, linked together, are needed to make a carbon chain that is 1.000 cm long?
10. How many carbon–carbon double bonds, linked together, are needed to make a carbon chain that is 1.000 cm long?
11. In addition to themselves, what other atoms can carbon atoms bond with and make covalent bonds that are nonpolar (or as nonpolar as possible)?
12. What is the greatest possible electronegativity difference between any two atoms? Use Figure 4.4 to find the answer.
13. Acetaminophen, a popular painkiller, has the following structure:



   Name the recognizable functional groups in this molecule. Do you think there are other groups of atoms in this molecule that might qualify as functional groups?
14. Glutamic acid is the parent compound of monosodium glutamate (known as MSG), which is used as a flavor enhancer. Glutamic acid has the following structure:



   Name the functional groups you recognize in this molecule. Do you think there are other groups of atoms in this molecule that might qualify as functional groups?

Answers

1. 1a: 5.75×10^{-23} g; 1b: 1.53×10^{-22} g; 1c: 3.88×10^{-22} g; 1d: 6.06×10^{-23} g

3. 14.96 g

5. sodium acetate

7. N≡C–C≡N

9. 6.49×10^7 bonds

11. Hydrogen atoms make relatively nonpolar bonds with carbon atoms.

13. alcohol; the N–H group, the ring with double bonds, and the C=O are also likely functional groups.

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CHAPTER OVERVIEW

5: Chemical Reactions

5.1: Physical and Chemical Changes

5.2: Chemical Equations

5.3: Organic Reactions

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5.1: Physical and Chemical Changes

Learning Outcomes

- Distinguish between physical and chemical changes.
- Give examples of physical and chemical changes.

Physical Changes

As an ice cube melts, its shape changes as it acquires the ability to flow. However, its composition does not change. **Melting**is an example of a **physical change**. A physical change is a change to a sample of matter in which some properties of the material change, but the identity of the matter does not. Physical changes can further be classified as reversible or irreversible. The melted ice cube may be refrozen, so melting is a reversible physical change. Physical changes that involve a change of state are all reversible. Other changes of state include **vaporization** (liquid to gas), **freezing** (liquid to solid), and **condensation** (gas to liquid). Dissolving is also a reversible physical change. When salt is dissolved into water, the salt is said to have entered the aqueous state. The salt may be regained by boiling off the water, leaving the salt behind.



Figure 5.1.1: Melting ice in the Beaufort Sea.

When a piece of wood is ground into sawdust, that change is irreversible since the sawdust could not be reconstituted into the same piece of wood that it was before. Cutting the grass or pulverizing a rock would be other irreversible physical changes. Firewood also represents an irreversible physical change since the pieces cannot be put back together to form the tree.



Figure 5.1.2: Firewood being cut is a physical change because the composition doesn't change when being cut.

Chemical Changes

When exposed to air, an object made of iron will eventually begin to rust (see figure below).



Figure 5.1.3: Rust (iron oxide) forms on an unprotected iron surface.

As the rust forms on the surface of the iron, it flakes off to expose more iron, which will continue to rust. Rust is clearly a substance that is different from iron. Rusting is an example of a chemical change.

A **chemical property** *describes the ability of a substance to undergo a specific chemical change*. A chemical property of iron is that it is capable of combining with oxygen to form iron oxide, the chemical name of rust. A more general term for rusting and other similar processes is corrosion. Other terms that are commonly used in descriptions of chemical changes are *burn*, *rot*, *explode*, and *ferment*. Chemical properties are very useful as a way of identifying substances. However, unlike physical properties, chemical properties can only be observed as the substance is in the process of being changed into a different substance.

A chemical change is also called a chemical reaction. A **chemical reaction** *is a process that occurs when one or more substances are changed into one or more new substances*. Zinc (Zn) is a silver-gray element that can be ground into a powder. If zinc is mixed at room temperature with powdered sulfur (S), a bright yellow element, the result will simply be a mixture of zinc and sulfur. No chemical reaction occurs. However, if energy is provided to the mixture in the form of heat, the zinc will chemically react with the sulfur to form the compound zinc sulfide (ZnS). Pictured below are the substances involved in this reaction.

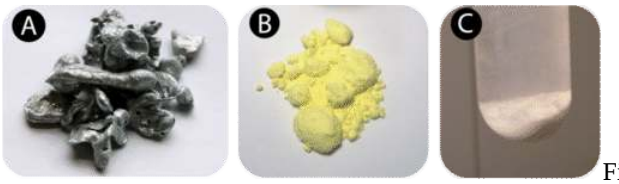


Figure 5.1.4: Zinc (A) and sulfur (B) are two elements that undergo a chemical reaction when heated to form the the compound zinc sulfide (C).

The reaction between zinc and sulfur can be depicted in something called a chemical equation. In words, we could write the reaction as:

$$\text{zinc} + \text{sulfur} \rightarrow \text{zinc sulfide} \tag{5.1.1}$$

A more convenient way to express a chemical reaction is to use the symbols and formulas of the substances involved:

$$\mathrm{Zn} + \mathrm{S} \rightarrow \mathrm{ZnS} \tag{5.1.2}$$

The substance(s) to the left of the arrow in a chemical equation are called reactants. A **reactant** *is a substance that is present at the start of a chemical reaction.* The substance(s) to the right of the arrow are called products. A **product** *is a substance that is present at the end of a chemical reaction*. In the equation above, zinc and sulfur are the reactants that chemically combine to form zinc sulfide as a product.

Recognizing Chemical Reactions

How can you tell if a chemical reaction is taking place? Certain visual clues indicate that a chemical reaction is likely (but not necessarily) occurring, including the following examples:

1. A change of color occurs during the reaction.
2. A gas is produced during the reaction.
3. A solid product, called a precipitate, is produced in the reaction.
4. A visible transfer of energy occurs in the form of light as a result of the reaction.

When zinc reacts with hydrochloric acid, the reaction bubbles vigorously as hydrogen gas is produced (see figure below). The production of a gas is also an indication that a chemical reaction may be occurring.


Figure 5.1.5: Zinc reacts with hydrochloric acid to produce bubbles of hydrogen gas.

When a colorless solution of lead (II) nitrate is added to a colorless solution of potassium iodide, a yellow solid called a precipitate is instantly produced (see figure below). A **precipitate** *is a solid product that forms from a reaction and settles out of a liquid mixture*. The formation of a precipitate may also indicate the occurrence of a chemical reaction.

$$\mathrm{Pb(NO_3)_2}\,(aq) + 2\mathrm{KI}\,(aq) \rightarrow \mathrm{PbI_2}\,(s) + 2\mathrm{KNO_3}\,(aq) \tag{5.1.3}$$

 Figure 5.1.6: A yellow precipitate of solid lead (II) iodide forms immediately when solutions of lead (II) nitrate and potassium iodide are mixed.

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5.2: Chemical Equations

Learning Outcomes

- Describe chemical reactions using word equations.
- Write equations for chemical reactions.
- Use coefficients to balance chemical equations.

Chemical reactions are occurring all around you. 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 inside you as well, especially 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 substance, called products. The general form of the equation for such a process looks like this.

$$\text{Reactants} \rightarrow \text{Products} \tag{5.2.1}$$

Unlike in 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 food such as eggs. The word equation for the process is:

$$\text{Silver} + \text{sulfur} \rightarrow \text{Silver sulfide} \tag{5.2.2}$$

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



Figure 5.2.1: The coffee percolator on the left has been tarnished from exposure to sulfur. Tarnish is the chemical compound silver sulfide. The same percolator on the right has been polished with a tarnish removal product in order to restore its silver finish.

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 (see 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:

$$\text{Methane} + \text{oxygen} \rightarrow \text{carbon dioxide} + \text{water} \tag{5.2.3}$$



Figure 5.2.2 *A Bunsen burner is commonly used to heat substances in a chemistry lab. Methane is reacted with oxygen to form carbon dioxide and water.*

Chemical Equations

Word equations are time-consuming to write and will 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:

$$\mathrm{CH_4 + O_2 \rightarrow CO_2 + H_2O} \tag{5.2.4}$$

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. At room temperature, the components of the previous reaction are in the following states:

$$\mathrm{CH_4\,(g) + O_2\,(g) \rightarrow CO_2\,(g) + H_2O\,(l)} \tag{5.2.5}$$

The table below shows a listing of symbols used in chemical equations.

Table 5.2.1: Symbols Used in Chemical Equations

Symbol	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 gas state
(aq)	reactant or product in an aqueous solution (dissolved in water)
$\overset{\mathrm{Pt}}{\rightarrow}$	formula written above the arrow is used as a catalyst in the reaction
$\overset{\Delta}{\rightarrow}$	triangle indicates that the reaction is being heated

Balancing Chemical Equations

Suppose you were to write a word equation for building the ideal ham sandwich (see figure below). Perhaps you might come up with this:

$$\mathrm{Ham + cheese + tomato + pickles + bread \rightarrow ham\ sandwich} \tag{5.2.6}$$

The reactants are the "parts" or ingredients of the ham sandwich while the sandwich itself is the product. There is something missing from your equation, however. There is no indication how many of each "reactant" is required to make the "product". For one thing, you would certainly need two slices of bread to make a conventional sandwich.



Figure 5.2.3: A ham sandwich can be thought of as the product of a reaction while all of the individual ingredients are the reactants.

Let's say that the perfect ham sandwich (HS) is composed of 2 slices of ham (H), a slice of cheese (C), 1 slice of tomato (T), 5 pickles (P), and 2 slices of bread (B). Accounting for the numbers of each reactant, as well as substituting symbols for words, your equation would become:

$$2\mathrm{H} + \mathrm{C} + \mathrm{T} + 5\mathrm{P} + 2\mathrm{B} \rightarrow \mathrm{HS} \tag{5.2.7}$$

This now shows the correct quantities of the reactants. As one final improvement, we will change the "formula" of the product. Since the final sandwich contains all the reactants that went into it, its formula should reflect that.

$$2\mathrm{H} + \mathrm{C} + \mathrm{T} + 5\mathrm{P} + 2\mathrm{B} \rightarrow \mathrm{H_2CTP_5B_2} \tag{5.2.8}$$

The subscript after each symbol in the product stands for the number of that particular reactant found on the reactant side of the equation: 2 for H, 1 for C, etc.

Since the equation now shows equal numbers of each sandwich part on both sides of the equation, we say that the equation is balanced. Chemical equations must also be balanced in a similar way. 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 $(\mathrm{CH_4})$.

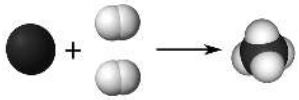
$$\underset{1\text{ C atom}}{\mathrm{C}\,(s)} \quad + \quad \underset{2\text{ H atoms}}{\mathrm{H_2}\,(g)} \quad \rightarrow \quad \underset{1\text{ C atom},\ 4\text{ H atoms}}{\mathrm{CH_4}\,(g)} \tag{5.2.9}$$

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. This violates the law of conservation of mass, which states that mass must be conserved in any chemical reaction or physical process. Another common way to express the law of conservation of mass is that matter cannot be created or destroyed.

John Dalton's atomic theory stated that chemical reactions are separations, combinations, or rearrangements of atoms. Atoms themselves cannot be created or destroyed. Dalton's theory explains the law of conservation of mass and the process of balancing an equation ensures that the law is followed. We can balance the above equation by adding a coefficient of 2 in front of the formula for hydrogen.

$$\mathrm{C}\,(s) + 2\mathrm{H_2}\,(g) \rightarrow \mathrm{CH_4}\,(g) \tag{5.2.10}$$

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:



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 by placing the reactant(s) on the left side of the yield sign $(\rightarrow)$ and the product(s) on the right side. If there is more than one reactant or product, separate with plus signs.
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 formula. No coefficient is written for a 1. It is best to begin by balancing elements that only appear in one formula on each side of the equation. You can only balance equations by using coefficients, NEVER change the subscripts in a chemical formula.
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.

Example 5.2.1

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 chemical equation for this reaction.

Solution

Step 1: Plan the problem.

Follow the steps for writing and balancing a chemical equation.

Step 2: Solve.

Write the skeleton equation with the correct formulas.

$$\mathrm{Pb(NO_3)_2}\,(aq) + \mathrm{NaCl}\,(aq) \rightarrow \mathrm{NaNO_3}\,(aq) + \mathrm{PbCl_2}\,(s) \tag{5.2.11}$$

Count the number of each atom or polyatomic ion on both sides of the equation (see table below).

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:

$$\mathrm{Pb(NO_3)_2}\,(aq) + 2\mathrm{NaCl}\,(aq) \rightarrow 2\mathrm{NaNO_3}\,(aq) + \mathrm{PbCl_2}\,(s) \tag{5.2.12}$$

The new count for each atom and polyatomic ion becomes (see table below).

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.

Count the number of each atom or polyatomic ion on both sides of the equation.

Table 5.2.2: Unbalanced Reactants/Products

Reactants	Products
1 Pb atom	1 Pb atom
2 $\mathrm{NO_3^-}$	1 $\mathrm{NO_3^-}$
2 Na atoms	2 Na atoms
2 Cl atoms	1 Cl atom

The new count for each atom and polyatomic ion becomes:

Table 5.2.3: Balanced Reactants/Products

Reactants	Products
1 Pb atom	1 Pb atom
2 NO_3^-	2 NO_3^-
2 Na atoms	2 Na atoms
2 Cl atoms	2 Cl atoms

Some equations provide a challenge to balancing when one or more of the elements can't be balanced simply by using one coefficient. Aluminum reacts with oxygen gas to form aluminum oxide according to the equation:

$$\mathrm{Al}\,(s) + \mathrm{O_2}\,(g) \rightarrow \mathrm{Al_2O_3}\,(s) \tag{5.2.13}$$

Since there are two oxygen atoms on the reactant side and 3 oxygen atoms on the product side, no single whole-number coefficient will balance the oxygen atoms. Find the lowest common multiple of 2 and 3, which is 6. Placing a 3 in front of the O_2 and a 2 in front of the Al_2O_3 will result in 6 oxygen atoms on both sides. Finish by balancing the aluminum with a 4.

$$4\mathrm{Al}\,(s) + 3\mathrm{O_2}\,(g) \rightarrow 2\mathrm{Al_2O_3}\,(s) \tag{5.2.14}$$

The equation is balanced with 4 Al atoms and 6 O atoms on each side.

Finally, we will return to the equation from earlier where methane was reacted with oxygen to form carbon dioxide and water.

$$\mathrm{CH_4}\,(g) + \mathrm{O_2}\,(g) \rightarrow \mathrm{CO_2}\,(g) + \mathrm{H_2O}\,(l) \tag{5.2.15}$$

The element oxygen appears in two different places on the product side of the equation, so you should not start by trying to balance the oxygen. Instead, balance the carbon and the hydrogen first. The carbon is already balanced, but the hydrogen is balanced by placing a 2 in front of the water.

$$\mathrm{CH_4}\,(g) + \mathrm{O_2}\,(g) \rightarrow \mathrm{CO_2}\,(g) + 2\mathrm{H_2O}\,(l) \tag{5.2.16}$$

Now count the total number of oxygen atoms on the product side: two from the CO_2 and two from the 2 H_2O to give a total of four. Place a 2 in front of the O_2.

$$\mathrm{CH_4}\,(g) + 2\mathrm{O_2}\,(g) \rightarrow \mathrm{CO_2}\,(g) + 2\mathrm{H_2O}\,(l) \tag{5.2.17}$$

Balancing difficult equations can be a trial-and-error process and is a skill that requires practice. If you find that one particular strategy with a tough equation isn't working, start over and balance a different element first. Persistence will lead you to the correct balanced equation.

Supplemental Resources

- http://phet.colorado.edu/en/simulati...ical-equations
- "Balancing Act": http://education.jlab.org/elementbalancing/index.html
- Balancing Chemical Equations: www.sciencegeek.net/Chemistry...nBalancing.htm

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5.3: Organic Reactions

Learning Outcomes

- Identify and describe substitution, elimination, addition, hydrolysis, and condensation reactions.
- Predict products of each reaction type.
- Predict products of hydration reactions based on Markovnikov's rule.
- Explain why condensation reactions are also called dehydration reactions.
- Define "polymer".

Organic reactions require the breaking of strong covalent bonds, which takes a considerable input of energy. In order for relatively stable organic molecules to react at a reasonable rate, they often must be modified with the use of highly reactive materials or in the presence of a catalyst. In this lesson, you will learn about several general categories of organic reactions.

Substitution Reactions

A **substitution reaction**, which is the same as a single replacement reaction in inorganic reactions, *is a reaction in which one or more atoms in a molecule are replaced with another atom or group of atoms.* Alkyl halides are formed by the substitution of a halogen atom for a hydrogen atom. When methane reacts with chlorine gas, ultraviolet light can act as a catalyst for the reaction.

$$\mathrm{CH_4\,(g) + Cl_2\,(g) \overset{\text{UV light}}{\rightarrow} CH_3Cl\,(g) + HCl\,(g)} \tag{5.3.1}$$

The reaction produces chloromethane and hydrogen chloride. When the mixture is allowed to react for longer periods of time, further substitution reactions may occur.

$$\mathrm{CH_3Cl\,(g) + Cl_2\,(g) \overset{\text{UV light}}{\rightarrow} CH_2Cl_2\,(g) + HCl\,(g)} \tag{5.3.2}$$

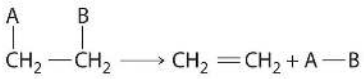
The product above is dichloromethane. Further substitution products trichloromethane and tetrachloromethane, commonly called carbon tetrachloride. A mixture of products occurs in the reaction, with the relative amounts dependent upon the time that the reaction is allowed to proceed. Chlorofluorocarbons are produced by reacting chloroalkanes with HF, because the fluorine atom makes a stronger bond to the carbon atom than chlorine does.

$$\mathrm{CCl_4\,(g) + HF\,(g) \overset{SbF_5}{\rightarrow} CCl_3F\,(g) + HCl\,(g)} \tag{5.3.3}$$

The fluorine atom substitutes for a chlorine atom in the reaction.

Elimination Reactions

An **elimination reaction** involves the removal of adjacent atoms from a molecule. This results in the formation of a multiple bond and the release of a small molecule, so they are called elimination reactions. They have the general form



A typical example is the conversion of ethyl chloride to ethylene:

$$CH_3CH_2Cl \rightarrow CH_2 = CH_2 + HCl \tag{5.3.4}$$

Much of the approximately 26 million tons of ethylene produced per year in the United States is used to synthesize plastics, such as polyethylene. In the above reaction, the A–B molecule eliminated is HCl, whose components are eliminated as H^+ from the carbon atom on the left and Cl^- from the carbon on the right. When an acid is produced, as occurs here, the reaction is generally carried out in the presence of a base (such as NaOH) to neutralize the acid. Other elimination reactions will produce H_2, X_2 (where X = halogen), or H_2O. These reactions are often referred to by more descriptive terms such as dehydrogenation (removing hydrogen) or dechlorination (removing chlorine).

Addition Reactions

An **addition reaction** *is a reaction in which an atom or molecule is added to an unsaturated molecule, making a single product.* An addition reaction can often be thought of as adding a molecule across the double bond of an alkene or across the triple bond of an alkyne. Knowing that "ation" means to add, the specific names of these reactions, such as hydrogenation, hydration, or chlorination, should make sense. Note that hydrogenation (adding H_2) and hydration (adding H_2O) are very different processes.

One type of addition reaction is called hydrogenation. **Hydrogenation** *is a reaction that occurs when molecular hydrogen is added to an alkene to produce an alkane* or *hydrogen is added to an alkyne to produce an alkene or alkane.* The reaction is typically performed with the use of a transition metal catalyst. For example, ethene reacts with hydrogen to form ethane.

$$\mathrm{CH_2{=}CH_2\,(g) + H_2\,(g) \overset{Pt}{\rightarrow} CH_3CH_3\,(g)} \tag{5.3.5}$$

Note that the hydrogenation reaction is also a redox reaction. Ethene is reduced, because the oxidation numbers of the carbon atoms change from -2 to -3 as a result of the reaction.

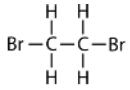
Vegetable oils consist of long carbon chains with carboxyl groups on the end; these molecules are referred to as fatty acids. The carbon chains of the fatty acids in vegetable oils are unsaturated, usually containing multiple double bonds. When hydrogen gas is blown through a sample of the oil, hydrogen atoms add across the double bonds. This conversion changes the substance from a liquid oil into a solid fat. The "hydrogenated" on a food product is an indication that oil (liquid) has been converted into fat (solid) by this process. Margarine is manufactured from unsaturated vegetable oil in this way by hydrogenating some of the double bonds making it a "partially hydrogenated vegetable oil".

Addition reactions are also useful ways to introduce a new functional group into an organic molecule. Alkyl halides can be produced from an alkene by the addition of either the elemental halogen or the hydrogen halide. A monosubstituted alkyl halide can be produced by the addition of a hydrogen halide to an alkene. Shown below is the formation of chloroethane.

$$\mathrm{CH_2{=}CH_2\,(g) + HCl\,(g) \rightarrow CH_3CH_2Cl\,(g)} \tag{5.3.6}$$

When the reactant is the diatomic halogen, the product is a disubstituted alkyl halide as in the addition of bromine to ethene.

$$\mathrm{CH_2{=}CH_2\,(g) + Br_2\,(l) \rightarrow CH_2BrCH_2Br\,(g)} \tag{5.3.7}$$



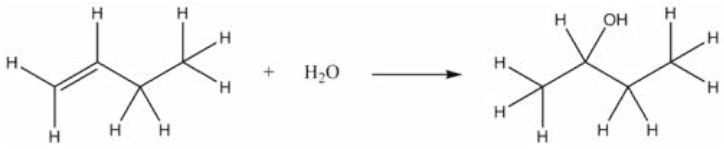
1,2-dibromoethane

The addition of bromine to an unknown organic compound can be used as a test for unsaturation in the compound. Bromine has a distinctive brownish-orange color, while most bromoalkanes are colorless. When bromine is slowly added to a solution of the compound, the orange color will fade if it undergoes an addition reaction to produce an alkyl halide. If the orange color remains, then the original compound was already saturated, and no reaction occurred.

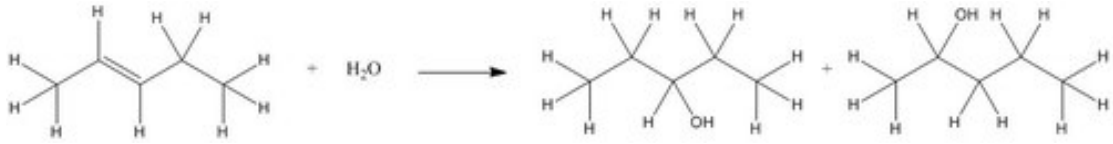
A **hydration reaction** *is a reaction in which water is added to an alkene*. Hydration reactions can take place when the alkene and water are heated to near $100°C$ in the presence of a strong acid, which acts as a catalyst. Shown below is the hydration of ethene to produce ethanol.

$$\mathrm{CH_2{=}CH_2\,(g) + H_2O\,(l) \rightarrow CH_3CH_2OH\,(g)} \tag{5.3.8}$$

Unlike addition reactions involving H_2 or Br_2, the addition of water can have two possible products because an $-H$ and an $-OH$ are being added to the carbons in the double bond. **Markovnikov's rule** helps predict the main product in a hydration reaction. The rule states that the hydrogen atom from water will add to the carbon that originally had more hydrogen atoms. For example, look at the hydration of 1-butene.



Note that the first carbon in 1-butene started with two hydrogen atoms and the second carbon started with one hydrogen. Therefore, the hydrogen from water adds to the first carbon and the $-OH$ group adds to the second carbon. When there are equal numbers of hydrogen atoms on both carbons in a double bond then the two products will form in approximately equal amounts. For example, the hydration of 2-pentene results in two products. In the first product, the $-OH$ group is on the third carbon and in the second product, the $-OH$ group is on the second carbon. While these two molecules will have similar properties, there will be differences.



Condensation Reactions

A **condensation reaction** *is a reaction in which two molecules combine to form a single molecule.* A small molecule, often water, is usually removed during a condensation reaction. Amino acids are important biological molecules that have an amine functional group on one end of the molecule and a carboxylic acid functional group on the other end. When two amino acids combine in a condensation reaction, a covalent bond forms between the amine nitrogen of one amino acid and the carboxyl carbon of the second amino acid. A molecule of water is then removed as a second product (see figure below).

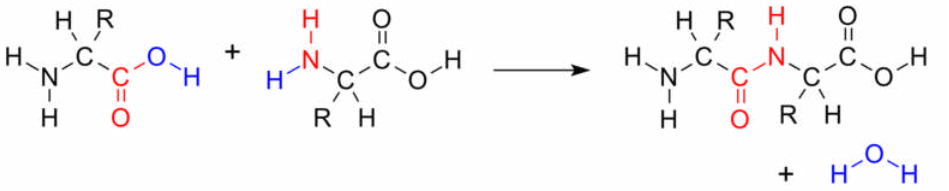
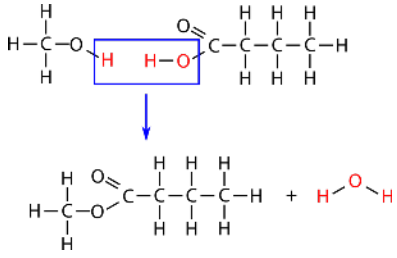


Figure 5.3.1: Amino acids join together to form a molecule called a dipeptide. The $-OH$ from the carboxyl group of one amino acid combines with a hydrogen atom from the amine group of the other amino group to produce water (blue).

This reaction forms a molecule called a dipeptide, and the resulting carbon-nitrogen covalent bond is often called a peptide bond. When repeated numerous times, a long molecule called a protein is eventually produced.

An **esterification** *is a condensation reaction in which an ester is formed from an alcohol and a carboxylic acid.* Esterification is a subcategory of condensation reactions because a water molecule is produced in the reaction. The reaction can be catalyzed by a strong acid, usually sulfuric acid. When the carboxylic acid, butanoic acid, is heated with an excess of methanol and a few drops of sulfuric acid, the ester methyl butanoate is produced. Methyl butanoate has the scent of pineapples. The reaction is shown below with both molecular and structural formulas. Esterification reactions are reversible.

$$CH_3CH_2CH_2COOH + HOCH_3 \overset{H_2SO_4}{\rightarrow} CH_3CH_2CH_2COOCH_3 + H_2O \tag{5.3.9}$$

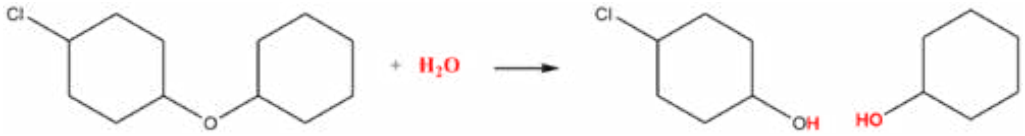


Saponification *describes the alkaline hydrolysis reaction of an ester*. The term saponification originally described the hydrolysis of long-chain esters called fatty acid esters to produce soap molecules, which are the salts of fatty acids. One such soap molecule is sodium stearate, formed from the hydrolysis of ethyl stearate.

$$\underset{\text{ethyl stearate}}{C_{17}H_{35}COOC_2H_5} + NaOH \rightarrow \underset{\text{sodium stearate (soap)}}{C_{17}H_{35}COO^-Na^+} + C_2H_5OH \tag{5.3.10}$$

Hydrolysis Reactions

Hydrolysis is the reverse of condensation. "Hydro" indicates that water is involved and "lysis" means to break apart. In a hydrolysis reaction, water is added and the molecule breaks apart, usually at a C–O–C linkage.



Polymerization

Polymers are very different than the other kinds of organic molecules that you have seen so far. Whereas other compounds are of relatively low molar mass, polymers are giant molecules of very high molar mass. Polymers are the primary components of all sorts of plastics and related compounds. A **polymer** *is a large molecule formed of many smaller molecules covalently bonded to one another in a repeating pattern*. The *small molecules that make up the polymer are called* **monomers**. Polymers are generally formed by either addition or condensation reactions. Teflon (see figure below) is a non-reactive, non-stick coating used on cookware as well as in containers and pipes for reactive or corrosive chemicals.

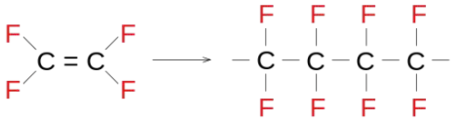


Figure 5.3.2: Polytetrafluoroethylene (also known as Teflon) is formed from the polymerization of tetrafluoroethylene.

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CHAPTER OVERVIEW

6: Water and Solutions

6.1: Water

6.2: Solutions

6.3: Concentration

6.4: The Dissolution Process

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6.1: Water

Skills to Develop

- Describe the properties of water that are critical to maintaining life
- Explain why water is an excellent solvent
- Provide examples of water's cohesive and adhesive properties
- Discuss the role of acids, bases, and buffers in homeostasis

Why do scientists spend time looking for water on other planets? Why is water so important? It is because water is essential to life as we know it. Water is one of the more abundant molecules and the one most critical to life on Earth. Approximately 60–70 percent of the human body is made up of water. Without it, life as we know it simply would not exist.

The polarity of the water molecule and its resulting hydrogen bonding make water a unique substance with special properties that are intimately tied to the processes of life. Life originally evolved in a watery environment, and most of an organism's cellular chemistry and metabolism occur inside the watery contents of the cell's cytoplasm. Special properties of water are its high heat capacity and heat of vaporization, its ability to dissolve polar molecules, its cohesive and adhesive properties, and its dissociation into ions that leads to the generation of pH. Understanding these characteristics of water helps to elucidate its importance in maintaining life.

Water's Polarity

One of water's important properties is that it is composed of polar molecules: the hydrogen and oxygen within water molecules (H_2O) form polar covalent bonds. While there is no net charge to a water molecule, the polarity of water creates a slightly positive charge on hydrogen and a slightly negative charge on oxygen, contributing to water's properties of attraction. Water's charges are generated because oxygen is more electronegative than hydrogen, making it more likely that a shared electron would be found near the oxygen nucleus than the hydrogen nucleus, thus generating the partial negative charge near the oxygen.

As a result of water's polarity, each water molecule attracts other water molecules because of the opposite charges between water molecules, forming hydrogen bonds. Water also attracts or is attracted to other polar molecules and ions. A polar substance that interacts readily with or dissolves in water is referred to as hydrophilic (hydro- = "water"; -philic = "loving"). In contrast, non-polar molecules such as oils and fats do not interact well with water, as shown in Figure 6.1.1 and separate from it rather than dissolve in it, as we see in salad dressings containing oil and vinegar (an acidic water solution). These nonpolar compounds are called hydrophobic (hydro- = "water"; -phobic = "fearing").

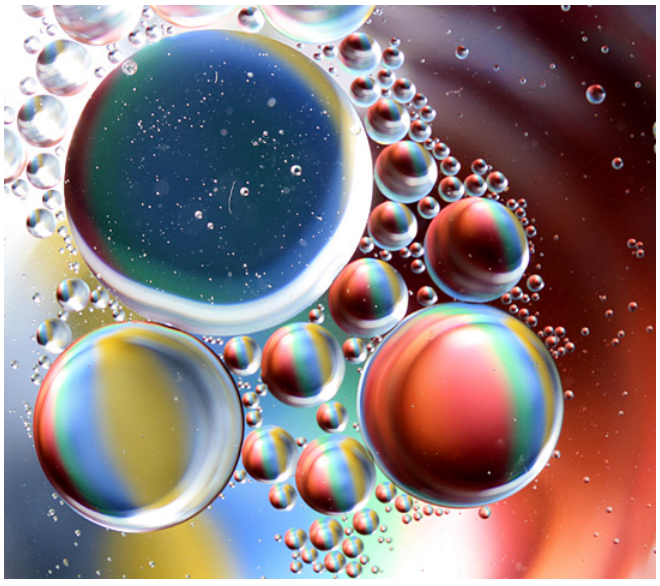


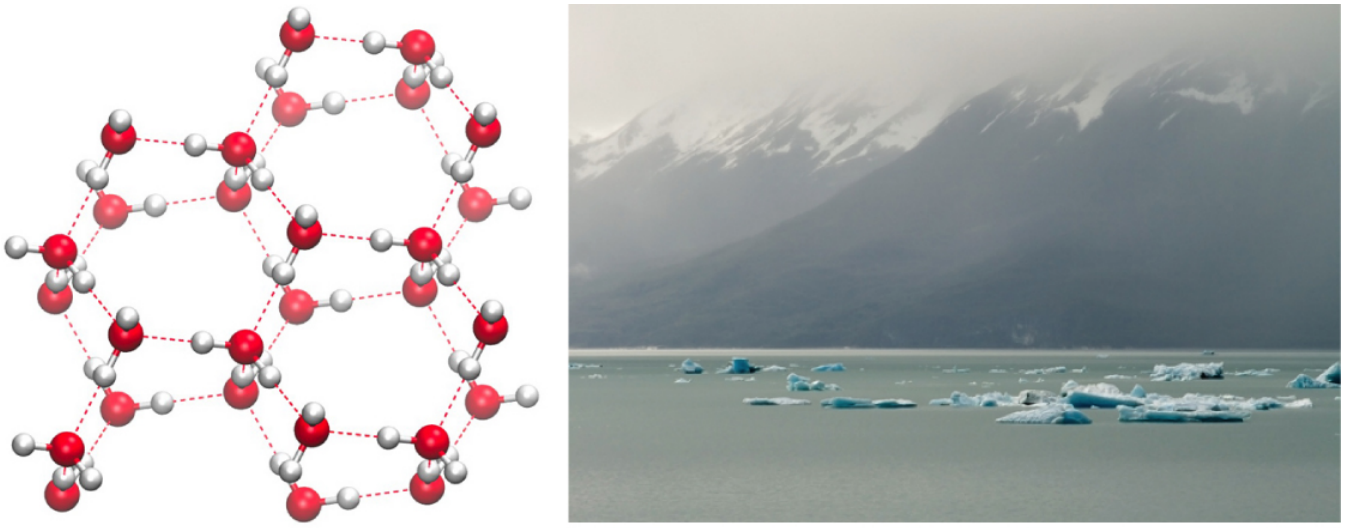
Figure 6.1.1: Oil and water do not mix. As this macro image of oil and water shows, oil does not dissolve in water but forms droplets instead. This is due to it being a nonpolar compound. (credit: Gautam Dogra).

Water's States: Gas, Liquid, and Solid

The formation of hydrogen bonds is an important quality of the liquid water that is crucial to life as we know it. As water molecules make hydrogen bonds with each other, water takes on some unique chemical characteristics compared to other liquids and, since living things have a high water content, understanding these chemical features is key to understanding life. In liquid water, hydrogen bonds are constantly formed and broken as the water molecules slide past each other. The breaking of these bonds is caused by the motion (kinetic energy) of the water molecules due to the heat contained in the system. When the heat is raised as water is boiled, the higher kinetic energy of the water molecules causes the hydrogen bonds to break completely and allows water molecules to escape into the air as gas (steam or water vapor). On the other hand, when the temperature of water is reduced and water freezes, the water molecules form a crystalline structure maintained by hydrogen bonding (there is not enough energy to break the hydrogen bonds) that makes ice less dense than liquid water, a phenomenon not seen in the solidification of other liquids.

Water's lower density in its solid form is due to the way hydrogen bonds are oriented as it freezes: the water molecules are pushed farther apart compared to liquid water. With most other liquids, solidification when the temperature drops includes the lowering of kinetic energy between molecules, allowing them to pack even more tightly than in liquid form and giving the solid a greater density than the liquid.

The lower density of ice, illustrated and pictured in Figure 6.1.2, an anomaly, causes it to float at the surface of liquid water, such as in an iceberg or in the ice cubes in a glass of ice water. In lakes and ponds, ice will form on the surface of the water creating an insulating barrier that protects the animals and plant life in the pond from freezing. Without this layer of insulating ice, plants and animals living in the pond would freeze in the solid block of ice and could not survive. The detrimental effect of freezing on living organisms is caused by the expansion of ice relative to liquid water. The ice crystals that form upon freezing rupture the delicate membranes essential for the function of living cells, irreversibly damaging them. Cells can only survive freezing if the water in them is temporarily replaced by another liquid like glycerol.



(a) (b)

Figure 6.1.2: Hydrogen bonding makes ice less dense than liquid water. The (a) lattice structure of ice makes it less dense than the freely flowing molecules of liquid water, enabling it to (b) float on water. (credit a: modification of work by Jane Whitney, image created using Visual Molecular Dynamics (VMD) software[1]; credit b: modification of work by Carlos Ponte)

Link to Learning



Video: Click here to see a 3-D animation of the structure of an ice lattice. (Image credit: Jane Whitney. Image created using Visual Molecular Dynamics VMD software.[2])

Water's High Heat Capacity

Water's high heat capacity is a property caused by hydrogen bonding among water molecules. Water has the highest specific heat capacity of any liquids. Specific heat is defined as the amount of heat one gram of a substance must absorb or lose to change its temperature by one degree Celsius. For water, this amount is one calorie. It therefore takes water a long time to heat and long time to cool. In fact, the specific heat capacity of water is about five times more than that of sand. This explains why the land cools faster than the sea. Due to its high heat capacity, water is used by warm blooded animals to more evenly disperse heat in their bodies: it acts in a similar manner to a car's cooling system, transporting heat from warm places to cool places, causing the body to maintain a more even temperature.

Water's Heat of Vaporization

Water also has a high heat of vaporization, the amount of energy required to change one gram of a liquid substance to a gas. A considerable amount of heat energy (586 cal) is required to accomplish this change in water. This process occurs on the surface of water. As liquid water heats up, hydrogen bonding makes it difficult to separate the liquid water molecules from each other, which is required for it to enter its gaseous phase (steam). As a result, water acts as a heat sink or heat reservoir and requires much more heat to boil than does a liquid such as ethanol (grain alcohol), whose hydrogen bonding with other ethanol molecules is weaker than water's hydrogen bonding. Eventually, as water reaches its boiling point of 100° Celsius (212° Fahrenheit), the heat is able to break the hydrogen bonds between the water molecules, and the kinetic energy (motion) between the water molecules allows them to escape from the liquid as a gas. Even when below its boiling point, water's individual molecules acquire enough energy from other water molecules such that some surface water molecules can escape and vaporize: this process is known as evaporation.

The fact that hydrogen bonds need to be broken for water to evaporate means that a substantial amount of energy is used in the process. As the water evaporates, energy is taken up by the process, cooling the environment where the evaporation is taking place. In many living organisms, including in humans, the evaporation of sweat, which is 90 percent water, allows the organism to cool so that homeostasis of body temperature can be maintained.

Water's Solvent Properties

Since water is a polar molecule with slightly positive and slightly negative charges, ions and polar molecules can readily dissolve in it. Therefore, water is referred to as a solvent, a substance capable of dissolving other polar molecules and ionic compounds. The charges associated with these molecules will form hydrogen bonds with water, surrounding the particle with water molecules. This is referred to as a sphere of hydration, or a hydration shell, as illustrated in Figure 6.1.3 and serves to keep the particles separated or dispersed in the water.

When ionic compounds are added to water, the individual ions react with the polar regions of the water molecules and their ionic bonds are disrupted in the process of dissociation. Dissociation occurs when atoms or groups of atoms break off from molecules and form ions. Consider table salt (NaCl, or sodium chloride): when NaCl crystals are added to water, the molecules of NaCl dissociate into Na^+ and Cl^- ions, and spheres of hydration form around the ions, illustrated in Figure 6.1.3. The positively charged sodium ion is surrounded by the partially negative charge of the water molecule's oxygen. The negatively charged chloride ion is surrounded by the partially positive charge of the hydrogen on the water molecule.

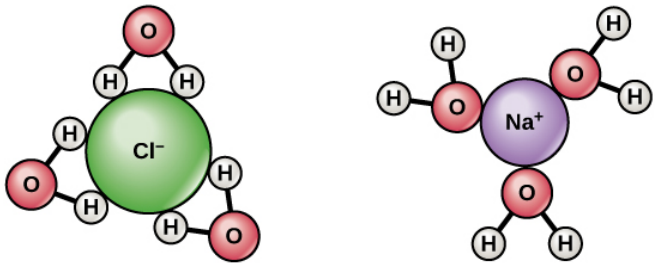


Figure 6.1.3: When table salt (NaCl) is mixed in water, spheres of hydration are formed around the ions.

Water's Cohesive and Adhesive Properties

Have you ever filled a glass of water to the very top and then slowly added a few more drops? Before it overflows, the water forms a dome-like shape above the rim of the glass. This water can stay above the glass because of the property of cohesion. In cohesion, water molecules are attracted to each other (because of hydrogen bonding), keeping the molecules together at the liquid-gas (water-air) interface, although there is no more room in the glass.

Cohesion allows for the development of surface tension, the capacity of a substance to withstand being ruptured when placed under tension or stress. This is also why water forms droplets when placed on a dry surface rather than being flattened out by gravity. When a small scrap of paper is placed onto the droplet of water, the paper floats on top of the water droplet even though paper is denser (heavier) than the water. Cohesion and surface tension keep the hydrogen bonds of water molecules intact and support the item floating on the top. It's even possible to "float" a needle on top of a glass of water if it is placed gently without breaking the surface tension, as shown in Figure 6.1.4.

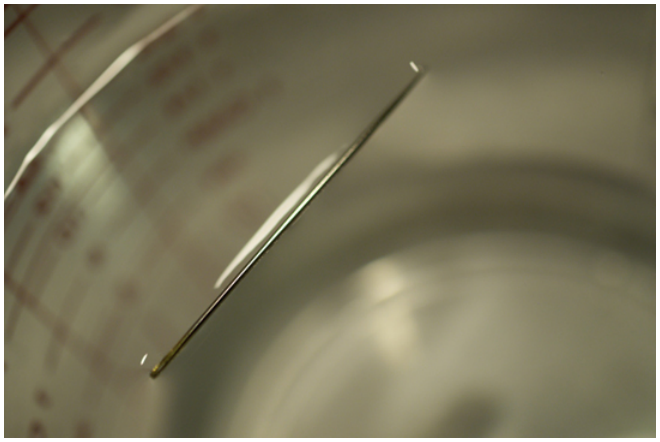


Figure 6.1.4: The weight of the needle is pulling the surface downward; at the same time, the surface tension is pulling it up, suspending it on the surface of the water and keeping it from sinking. Notice the indentation in the water around the needle. (credit: Cory Zanker)

These cohesive forces are related to water's property of adhesion, or the attraction between water molecules and other molecules. This attraction is sometimes stronger than water's cohesive forces, especially when the water is exposed to charged surfaces such as those found on the inside of thin glass tubes known as capillary tubes. Adhesion is observed when water "climbs" up the tube placed in a glass of water: notice that the water appears to be higher on the sides of the tube than in the middle. This is because the water molecules are attracted to the charged glass walls of the capillary more than they are to each other and therefore adhere to it. This type of adhesion is called capillary action, and is illustrated in Figure 6.1.5.

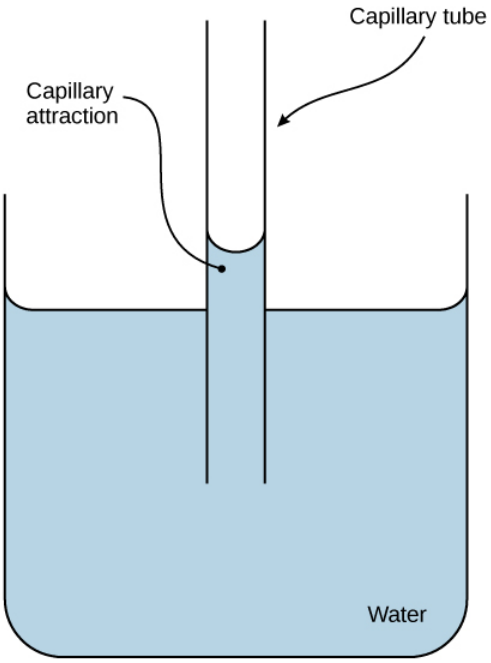


Figure 6.1.5: Capillary action in a glass tube is caused by the adhesive forces exerted by the internal surface of the glass exceeding the cohesive forces between the water molecules themselves. (credit: modification of work by Pearson-Scott Foresman, donated to the Wikimedia Foundation)

Why are cohesive and adhesive forces important for life? Cohesive and adhesive forces are important for the transport of water from the roots to the leaves in plants. These forces create a "pull" on the water column. This pull results from the tendency of water molecules being evaporated on the surface of the plant to stay connected to water molecules below them, and so they are pulled along. Plants use this natural phenomenon to help transport water from their roots to their leaves. Without these properties of water, plants would be unable to receive the water and the dissolved minerals they require. In another example, insects such as the water strider, shown in Figure 6.1.6, use the surface tension of water to stay afloat on the surface layer of water and even mate there.

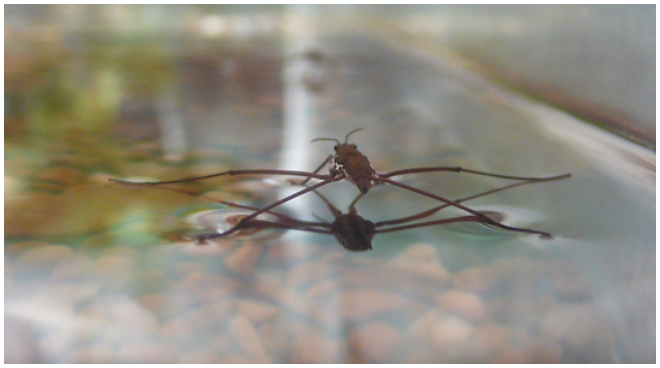


Figure 6.1.6: Water's cohesive and adhesive properties allow this water strider (*Gerris* sp.) to stay afloat. (credit: Tim Vickers)

pH, Buffers, Acids, and Bases

The pH of a solution indicates its acidity or alkalinity.

$$H_2O(I) \rightleftharpoons H^+(aq) + O^-(aq)$$

litmus or pH paper, filter paper that has been treated with a natural water-soluble dye so it can be used as a pH indicator, to test how much acid (acidity) or base (alkalinity) exists in a solution. You might have even used some to test whether the water in a swimming pool is properly treated. In both cases, the pH test measures the concentration of hydrogen ions in a given solution.

Hydrogen ions are spontaneously generated in pure water by the dissociation (ionization) of a small percentage of water molecules into equal numbers of hydrogen (H^+) ions and hydroxide (OH^-) ions. While the hydroxide ions are kept in solution by their

hydrogen bonding with other water molecules, the hydrogen ions, consisting of naked protons, are immediately attracted to un-ionized water molecules, forming hydronium ions (H_30^+). Still, by convention, scientists refer to hydrogen ions and their concentration as if they were free in this state in liquid water.

The concentration of hydrogen ions dissociating from pure water is 1×10^{-7} moles H^+ ions per liter of water. Moles (mol) are a way to express the amount of a substance (which can be atoms, molecules, ions, etc), with one mole being equal to 6.02×10^{23} particles of the substance. Therefore, 1 mole of water is equal to 6.02×10^{23} water molecules. The pH is calculated as the negative of the base 10 logarithm of this concentration. The log10 of 1×10^{-7} is -7.0, and the negative of this number (indicated by the "p" of "pH") yields a pH of 7.0, which is also known as neutral pH. The pH inside of human cells and blood are examples of two areas of the body where near-neutral pH is maintained.

Non-neutral pH readings result from dissolving acids or bases in water. Using the negative logarithm to generate positive integers, high concentrations of hydrogen ions yield a low pH number, whereas low levels of hydrogen ions result in a high pH. An acid is a substance that increases the concentration of hydrogen ions (H^+) in a solution, usually by having one of its hydrogen atoms dissociate. A base provides either hydroxide ions ($OH^–$) or other negatively charged ions that combine with hydrogen ions, reducing their concentration in the solution and thereby raising the pH. In cases where the base releases hydroxide ions, these ions bind to free hydrogen ions, generating new water molecules.

The stronger the acid, the more readily it donates H^+. For example, hydrochloric acid (HCl) completely dissociates into hydrogen and chloride ions and is highly acidic, whereas the acids in tomato juice or vinegar do not completely dissociate and are considered weak acids. Conversely, strong bases are those substances that readily donate $OH^–$ or take up hydrogen ions. Sodium hydroxide (NaOH) and many household cleaners are highly alkaline and give up $OH^–$ rapidly when placed in water, thereby raising the pH. An example of a weak basic solution is seawater, which has a pH near 8.0, close enough to neutral pH that marine organisms adapted to this saline environment are able to thrive in it.

The pH scale is, as previously mentioned, an inverse logarithm and ranges from 0 to 14 (Figure 6.1.7). Anything below 7.0 (ranging from 0.0 to 6.9) is acidic, and anything above 7.0 (from 7.1 to 14.0) is alkaline. Extremes in pH in either direction from 7.0 are usually considered inhospitable to life. The pH inside cells (6.8) and the pH in the blood (7.4) are both very close to neutral. However, the environment in the stomach is highly acidic, with a pH of 1 to 2. So how do the cells of the stomach survive in such an acidic environment? How do they homeostatically maintain the near neutral pH inside them? The answer is that they cannot do it and are constantly dying. New stomach cells are constantly produced to replace dead ones, which are digested by the stomach acids. It is estimated that the lining of the human stomach is completely replaced every seven to ten days.

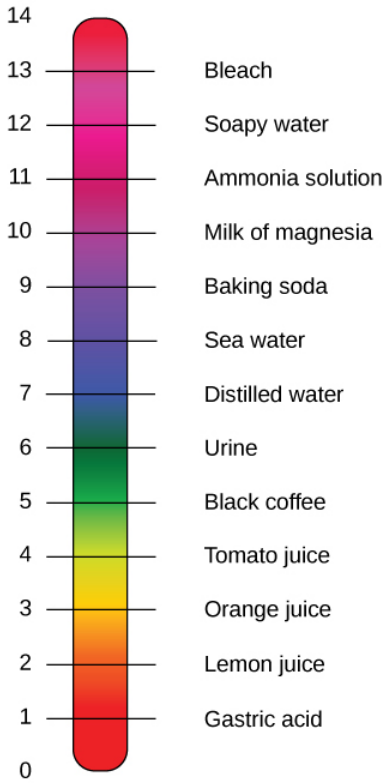


Figure 6.1.7: The pH scale measures the concentration of hydrogen ions (H^+) in a solution. (credit: modification of work by Edward Stevens)

Link to Learning



Watch this video for a straightforward explanation of pH and its logarithmic scale.

So how can organisms whose bodies require a near-neutral pH ingest acidic and basic substances (a human drinking orange juice, for example) and survive? Buffers are the key. Buffers readily absorb excess H^+ or OH^-, keeping the pH of the body carefully maintained in the narrow range required for survival. Maintaining a constant blood pH is critical to a person's well-being. The buffer maintaining the pH of human blood involves carbonic acid (H_2CO_3), bicarbonate ion (HCO_3^-), and carbon dioxide (CO_2). When bicarbonate ions combine with free hydrogen ions and become carbonic acid, hydrogen ions are removed, moderating pH

changes. Similarly, as shown in Figure 6.1.8, excess carbonic acid can be converted to carbon dioxide gas and exhaled through the lungs. This prevents too many free hydrogen ions from building up in the blood and dangerously reducing the blood's pH. Likewise, if too much OH^- is introduced into the system, carbonic acid will combine with it to create bicarbonate, lowering the pH. Without this buffer system, the body's pH would fluctuate enough to put survival in jeopardy.

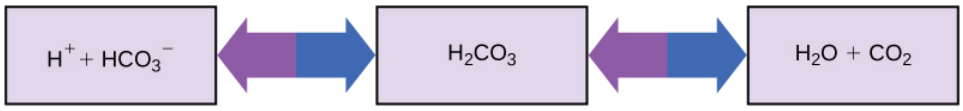


Figure 6.1.8: This diagram shows the body's buffering of blood pH levels. The blue arrows show the process of raising pH as more CO_2 is made. The purple arrows indicate the reverse process: the lowering of pH as more bicarbonate is created.

Other examples of buffers are antacids used to combat excess stomach acid. Many of these over-the-counter medications work in the same way as blood buffers, usually with at least one ion capable of absorbing hydrogen and moderating pH, bringing relief to those that suffer "heartburn" after eating. The unique properties of water that contribute to this capacity to balance pH—as well as water's other characteristics—are essential to sustaining life on Earth.

Link to Learning

To learn more about water. Visit the U.S. Geological Survey Water Science for Schools All About Water! website.

Summary

Water has many properties that are critical to maintaining life. It is a polar molecule, allowing for the formation of hydrogen bonds. Hydrogen bonds allow ions and other polar molecules to dissolve in water. Therefore, water is an excellent solvent. The hydrogen bonds between water molecules cause the water to have a high heat capacity, meaning it takes a lot of added heat to raise its temperature. As the temperature rises, the hydrogen bonds between water continually break and form anew. This allows for the overall temperature to remain stable, although energy is added to the system. Water also exhibits a high heat of vaporization, which is key to how organisms cool themselves by the evaporation of sweat. Water's cohesive forces allow for the property of surface tension, whereas its adhesive properties are seen as water rises inside capillary tubes. The pH value is a measure of hydrogen ion concentration in a solution and is one of many chemical characteristics that is highly regulated in living organisms through homeostasis. Acids and bases can change pH values, but buffers tend to moderate the changes they cause. These properties of water are intimately connected to the biochemical and physical processes performed by living organisms, and life would be very different if these properties were altered, if it could exist at all.

Footnotes

1. 1 W. Humphrey W., A. Dalke, and K. Schulten, "VMD—Visual Molecular Dynamics," *Journal of Molecular Graphics* 14 (1996): 33-38.
2. 2 W. Humphrey W., A. Dalke, and K. Schulten, "VMD—Visual Molecular Dynamics," *Journal of Molecular Graphics* 14 (1996): 33-38.

Glossary

acid

molecule that donates hydrogen ions and increases the concentration of hydrogen ions in a solution

adhesion

attraction between water molecules and other molecules

base
molecule that donates hydroxide ions or otherwise binds excess hydrogen ions and decreases the concentration of hydrogen ions in a solution

buffer
substance that prevents a change in pH by absorbing or releasing hydrogen or hydroxide ions

calorie
amount of heat required to change the temperature of one gram of water by one degree Celsius

capillary action
occurs because water molecules are attracted to charges on the inner surfaces of narrow tubular structures such as glass tubes, drawing the water molecules to the sides of the tubes

cohesion
intermolecular forces between water molecules caused by the polar nature of water; responsible for surface tension

dissociation
release of an ion from a molecule such that the original molecule now consists of an ion and the charged remains of the original, such as when water dissociates into H^+ and OH^-

evaporation
separation of individual molecules from the surface of a body of water, leaves of a plant, or the skin of an organism

heat of vaporization of water
high amount of energy required for liquid water to turn into water vapor

hydrophilic
describes ions or polar molecules that interact well with other polar molecules such as water

hydrophobic
describes uncharged non-polar molecules that do not interact well with polar molecules such as water

litmus paper
(also, pH paper) filter paper that has been treated with a natural water-soluble dye that changes its color as the pH of the environment changes so it can be used as a pH indicator

pH paper
see litmus paper

pH scale
scale ranging from zero to 14 that is inversely proportional to the concentration of hydrogen ions in a solution

solvent
substance capable of dissolving another substance

specific heat capacity
the amount of heat one gram of a substance must absorb or lose to change its temperature by one degree Celsius

sphere of hydration
when a polar water molecule surrounds charged or polar molecules thus keeping them dissolved and in solution

surface tension

tension at the surface of a body of liquid that prevents the molecules from separating; created by the attractive cohesive forces between the molecules of the liquid

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6.2: Solutions

Learning Objectives

- To understand what causes solutions to form.

A solution is another name for a homogeneous mixture. A *mixture* as a material composed of two or more substances. In a solution, the combination is so intimate that the different substances cannot be differentiated by sight, even with a microscope. Compare, for example, a mixture of salt and pepper and another mixture consisting of salt and water. In the first mixture, we can readily see individual grains of salt and the flecks of pepper. A mixture of salt and pepper is not a solution. However, in the second mixture, no matter how carefully we look, we cannot see two different substances. Salt dissolved in water is a solution.

The major component of a solution, called the **solvent**, is typically the same phase as the solution itself. Each minor component of a solution (and there may be more than one) is called the **solute**. In most of the solutions we will describe in this textbook, there will be no ambiguity about whether a component is the solvent or the solute. For example, in a solution of salt in water, the solute is salt, and solvent is water.

Solutions come in all phases, and the solvent and the solute do not have to be in the same phase to form a solution (such as salt and water). For example, air is a gaseous solution of about 80% nitrogen and about 20% oxygen, with some other gases present in much smaller amounts. An alloy is a solid solution consisting of a metal (like iron) with some other metals or nonmetals dissolved in it. Steel, an alloy of iron and carbon and small amounts of other metals, is an example of a solid solution. Table 6.2.1 lists some common types of solutions, with examples of each.

Table 6.2.1: Types of Solutions

Solvent Phase	Solute Phase	Example
gas	gas	air
liquid	gas	carbonated beverages
liquid	liquid	ethanol (C_2H_5OH) in H_2O (alcoholic beverages)
liquid	solid	saltwater
solid	gas	H_2 gas absorbed by Pd metal
solid	liquid	Hg(ℓ) in dental fillings
solid	solid	steel alloys

What causes a solution to form? The simple answer is that the solvent and the solute must have similar intermolecular interactions. When this is the case, the individual particles of solvent and solute can easily mix so intimately that each particle of solute is surrounded by particles of solvent, forming a solution. However, if two substances have very different intermolecular interactions, large amounts of energy are required to force their individual particles to mix intimately, so a solution does not form. Thus two alkanes like *n*-heptane, C_7H_{16}, and *n*-hexane, C_6H_{14}, are completely miscible in all proportions. The C_7H_{16} and C_6H_{14} molecules are so similar (recall Section 4.6) that there are only negligible differences in intermolecular forces.

For a similar reason, methanol, CH_3OH, is completely miscible with water. In this case both molecules are polar and can form hydrogen bonds among themselves, and so there are strong intermolecular attractions within each liquid. However, CH_3OH dipoles can align with H_2O dipoles, and CH_3OH molecules can hydrogen bond to H_2O molecules, and so the attractions among unlike molecules in the solution are similar to those among like molecules in each pure liquid.

This process leads to a simple rule of thumb: *like dissolves like*. Solvents that are very polar will dissolve solutes that are very polar or even ionic. Solvents that are nonpolar will dissolve nonpolar solutes. Thus water, being polar, is a good solvent for ionic

compounds and polar solutes like ethanol (C_2H_5OH). However, water does not dissolve nonpolar solutes, such as many oils and greases (Figure 6.2.1).



Figure 6.2.1: A beaker holds water with blue food dye (upper liquid layer) and a much more dense perfluoroheptane (a fluorocarbon) lower liquid layer. The two fluids cannot mix and the dye cannot dissolve in fluorocarbon. A goldfish and a crab have been introduced into the water. The goldfish cannot penetrate the dense fluorocarbon. The crab floats at the liquid boundary with only parts of his legs penetrating the fluorocarbon fluid, unable to sink to the bottom of the beaker. Quarter coins rest on the bottom of the beaker. Animals were rescued from their predicament after the photo was taken. Figure used with permission from Wikipedia (Sbharris (Steven B. Harris)).

We use the word soluble to describe a solute that dissolves in a particular solvent, and the word insoluble for a solute that does not dissolve in a solvent. Thus, we say that sodium chloride is soluble in water but insoluble in hexane (C_6H_{14}). If the solute and the solvent are both liquids and soluble in any proportion, we use the word miscible, and the word immiscible if they are not.

✔ Example 6.2.1

Water is considered a polar solvent. Which substances should dissolve in water?

1. methanol (CH_3OH)
2. sodium sulfate (Na_2SO_4)
3. octane (C_8H_{18})

Solution

Because water is polar, substances that are polar or ionic will dissolve in it.

1. Because of the OH group in methanol, we expect its molecules to be polar. Thus, we expect it to be soluble in water. As both water and methanol are liquids, the word *miscible* can be used in place of *soluble*.
2. Sodium sulfate is an ionic compound, so we expect it to be soluble in water.
3. Like other hydrocarbons, octane is nonpolar, so we expect that it would not be soluble in water.

? Exercise 6.2.1

Toluene ($C_6H_5CH_3$) is widely used in industry as a nonpolar solvent. Which substances should dissolve in toluene?

a. water (H_2O)
b. sodium sulfate (Na_2SO_4)
c. octane (C_8H_{18})

Answer

Octane only.

Example 6.2.2

Predict which of the following compounds will be most soluble in water:

a. $\underset{\text{Ethanol}}{CH_3CH_2OH}$

b. $\underset{\text{Hexanol}}{CH_3CH_2CH_2CH_2CH_2CH_2OH}$

Solution

Since ethanol contains an **OH** group, it can hydrogen bond to water. Although the same is true of hexanol, the OH group is found only at one end of a fairly large molecule. The rest of the molecule can be expected to behave much as though it were a nonpolar alkane. This substance should thus be much less soluble than the first. Experimentally we find that ethanol is completely miscible with water, while only 0.6 g hexanol dissolves in 100 g water.

6.2.2Exercise

Would I_2 be more soluble in CCl_4 or H_2O?

Answer

I_2 is nonpolar. Of the two solvents, CCl_4 is nonpolar and H_2O is polar, so I_2 would be expected to be more soluble in CCl_4.

Key Takeaway

- Solutions form because a solute and a solvent experience similar intermolecular interactions.

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6.3: Concentration

Learning Objectives

- Calculate percentage concentration (m/m, v/v, m/v), ppm and ppb.
- Calculate the molarity of a solution.
- Use concentration units to calculate the amount of solute in a solution.
- Use molarity to determine quantities in chemical reactions.
- Determine the resulting concentration of a diluted solution.

To define a solution precisely, we need to state its concentration: how much solute is dissolved in a certain amount of solvent. Words such as *dilute* or *concentrated* are used to describe solutions that have a little or a lot of dissolved solute, respectively, but these are relative terms whose meanings depend on various factors.

Solubility

There is usually a limit to how much solute will dissolve in a given amount of solvent. This limit is called the **solubility** of the solute. Some solutes have a very small solubility, while other solutes are soluble in all proportions. Table 6.3.1 lists the solubilities of various solutes in water. Solubilities vary with temperature, so Table 6.3.1 includes the temperature at which the solubility was determined.

Table 6.3.1: Solubilities of Various Solutes in Water at 25°C (Except as Noted)

Substance	Solubility (g in 100 mL of H2O)
AgCl(s)	0.019
$C_6H_6(\ell)$ (benzene)	0.178
$CH_4(g)$	0.0023
$CO_2(g)$	0.150
$CaCO_3(s)$	0.058
$CaF_2(s)$	0.0016
$Ca(NO_3)_2(s)$	143.9
$C_6H_{12}O_6$ (glucose)	120.3 (at 30°C)
KBr(s)	67.8
$MgCO_3(s)$	2.20
NaCl(s)	36.0
$NaHCO_3(s)$	8.41
$C_{12}H_{22}O_{11}$ (sucrose)	204.0 (at 20°C)

If a solution contains so much solute that its solubility limit is reached, the solution is said to be **saturated**, and its concentration is known from information contained in Table 6.3.1. If a solution contains less solute than the solubility limit, it is **unsaturated**. Under special circumstances, more solute can be dissolved even after the normal solubility limit is reached; such solutions are called ***supersaturated*** and are not stable. If the solute is solid, excess solute can easily recrystallize. If the solute is a gas, it can bubble out of solution uncontrollably, like what happens when you shake a soda can and then immediately open it.

Precipitation from Supersaturated Solutions

Recrystallization of excess solute from a supersaturated solution usually gives off energy as heat. Commercial heat packs containing supersaturated sodium acetate ($NaC_2H_3O_2$) take advantage of this phenomenon. You can probably find them at your local drugstore.



Video 6.3.1***:*** Watered-down sodium acetate trihydrate. Needle crystal is truly wonderful structures

Most solutions we encounter are unsaturated, so knowing the solubility of the solute does not accurately express the amount of solute in these solutions. There are several common ways of specifying the concentration of a solution.

Percent Composition

There are several ways of expressing the concentration of a solution by using a percentage. The **mass/mass percent** (% m/m) is defined as the mass of a solute divided by the mass of a solution times 100:

$$\%\ \mathrm{m/m} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$$

If you can measure the masses of the solute and the solution, determining the mass/mass percent is easy. Each mass must be expressed in the same units to determine the proper concentration.

Example 6.3.1

A saline solution with a mass of 355 g has 36.5 g of NaCl dissolved in it. What is the mass/mass percent concentration of the solution?

Solution

We can substitute the quantities given in the equation for mass/mass percent:

$$\%\ \mathrm{m/m} = \frac{36.5\ \mathrm{g}}{355\ \mathrm{g}} \times 100\% = 10.3\%$$

Exercise 6.3.1

A dextrose (also called D-glucose, $C_6H_{12}O_6$) solution with a mass of 2.00×10^2 g has 15.8 g of dextrose dissolved in it. What is the mass/mass percent concentration of the solution?

Answer

7.90%

For gases and liquids, volumes are relatively easy to measure, so the concentration of a liquid or a gas solution can be expressed as a **volume/volume percent** (% v/v): the volume of a solute divided by the volume of a solution times 100:

$$\%\ \text{v/v} = \frac{\text{volume of solute}}{\text{volume of solution}} \times 100\%$$

Again, the units of the solute and the solution must be the same. A hybrid concentration unit, **mass/volume percent** (% m/v), is commonly used for intravenous (IV) fluids (Figure 6.3.1). It is defined as the mass in grams of a solute, divided by volume in milliliters of solution times 100:

$$\%\ \text{m/v} = \frac{\text{mass of solute (g)}}{\text{volume of solution (mL)}} \times 100\%$$



Figure 6.3.1: Mass/Volume Percent.The 0.9% NaCl concentration on this IV bag is mass/volume percent (left). Such solution is used for other purposes and available in bottles (right). Figures used with permission from Wikipedia

Using Percent Composition in Calculations

The **percent concentration** can be used to produce a **conversion factor** between the **amount of solute** and the **amount of solution**. As such, concentrations can be useful in a variety of stoichiometry problems as discussed in Chapter 6. In many cases, it is best to use the original definition of the concentration unit; it is that definition that provides the conversion factor.

As an example, if the given concentration is **5% v/v solution of alcohol**, this means that there are 5 mL of alcohol dissolved in every 100 mL solution.

5 mL alcohol = 100 mL solution

The two possible conversion factors are written as follows:

$$\frac{5\ \text{mL alcohol}}{100\ \text{mL solution}} \text{ or } \frac{100\ \text{mL solution}}{5\ \text{mL alcohol}}$$

Use the first conversion factor to convert from a given amount of solution to amount of solute. The second conversion factor is used to convert from a given amount of solute to amount of solution. Given any two quantities in any percent composition, the third quantity can be calculated, as the following example illustrates.

Example 6.3.2

A sample of 45.0% v/v solution of ethanol (C_2H_5OH) in water has a volume of 115 mL. What volume of ethanol solute does the sample contain?

Solution

A percentage concentration is simply the number of parts of solute per 100 parts of solution. Thus, the percent concentration of 45.0% v/v implies the following:

$$45.0\%\ \text{v/v} \rightarrow \frac{45\ \text{mL}\ C_2H_5OH}{100\ \text{mL solution}}$$

That is, there are 45 mL of C_2H_5OH for every 100 mL of solution. We can use this fraction as a **conversion factor** to determine the amount of C_2H_5OH in 115 mL of solution:

$$115 \text{ mL solution} \times \frac{45 \text{ mL } C_2H_5OH}{100 \text{ mL solution}} = 51.8 \text{ mL } C_2H_5OH$$

Exercise 6.3.2

What volume of a 12.75% m/v solution of glucose ($C_6H_{12}O_6$) in water is needed to obtain 50.0 g of $C_6H_{12}O_6$?

Answer

$$50.0 \text{ g } C_6H_12O_6 \times \frac{100 \text{ mL solution}}{12.75 \text{ g } C_6H_12O_6} = 392 \text{ mL solution}$$

Example 6.3.3

A normal saline IV solution contains 9.0 g of NaCl in every liter of solution. What is the mass/volume percent of normal saline?

Solution

We can use the definition of mass/volume percent, but first we have to express the volume in milliliter units:

$$1 \text{ L} = 1{,}000 \text{ mL}$$

Because this is an exact relationship, it does not affect the significant figures of our result.

$$\%\text{ m/v} = \frac{9.0 \text{ g NaCl}}{1{,}000 \text{ mL solution}} \times 100\% = 0.90\%\text{ m/v}$$

Exercise 6.3.3

The chlorine bleach that you might find in your laundry room is typically composed of 27.0 g of sodium hypochlorite (NaOCl), dissolved to make 500.0 mL of solution. What is the mass/volume percent of the bleach?

Answer

$$\%\text{ m/v} = \frac{27.0 \text{ g NaOCl}}{500.0 \text{ mL solution}} \times 100\% = 5.40\%\text{ m/v}$$

In addition to percentage units, the units for expressing the concentration of extremely dilute solutions are parts per million (ppm) and parts per billion (ppb). Both of these units are mass based and are defined as follows:

$$\text{ppm} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 1{,}000{,}000$$

$$\text{ppb} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 1{,}000{,}000{,}000$$

> *Similar to parts per million and parts per billion, related units include parts per thousand (ppth) and parts per trillion (ppt).*

Concentrations of *trace elements* in the body—elements that are present in extremely low concentrations but are nonetheless necessary for life—are commonly expressed in parts per million or parts per billion. Concentrations of poisons and pollutants are also described in these units. For example, cobalt is present in the body at a concentration of 21 ppb, while the State of Oregon's Department of Agriculture limits the concentration of arsenic in fertilizers to 9 ppm.

> *In aqueous solutions, 1 ppm is essentially equal to 1 mg/L, and 1 ppb is equivalent to 1 µg/L.*

Example 6.3.4

If the concentration of cobalt in a human body is 21 ppb, what mass in grams of Co is present in a body having a mass of 70.0 kg?

Solution

A concentration of 21 ppb means "21 g of solute per 1,000,000,000 g of solution." Written as a **conversion factor,** this concentration of Co is as follows:

$$21 \text{ ppb Co} \rightarrow \frac{21 \text{ g Co}}{1,000,000,000 \text{ g solution}}$$

We can use this as a conversion factor, but first we must convert 70.0 kg to gram units:

$$70.0 \text{ kg} \times \frac{1,000 \text{ g}}{1 \text{ kg}} = 7.00 \times 10^4 \text{ g}$$

Now we determine the amount of Co:

$$7.00 \times 10^4 \text{ g solution} \times \frac{21 \text{ g Co}}{1,000,000,000 \text{ g solution}} = 0.0015 \text{ g Co}$$

This is only 1.5 mg.

Exercise 6.3.4

An 85 kg body contains 0.012 g of Ni. What is the concentration of Ni in parts per million?

Answer

0.14 ppm

Molarity

Another way of expressing concentration is to give the number of moles of solute per unit volume of solution. Such concentration units are useful for discussing chemical reactions in which a solute is a product or a reactant. Molar mass can then be used as a conversion factor to convert amounts in moles to amounts in grams.

Molarity is defined as the number of moles of a solute dissolved per liter of solution:

$$\text{molarity} = \frac{\text{number of moles of solute}}{\text{number of liters of solution}}$$

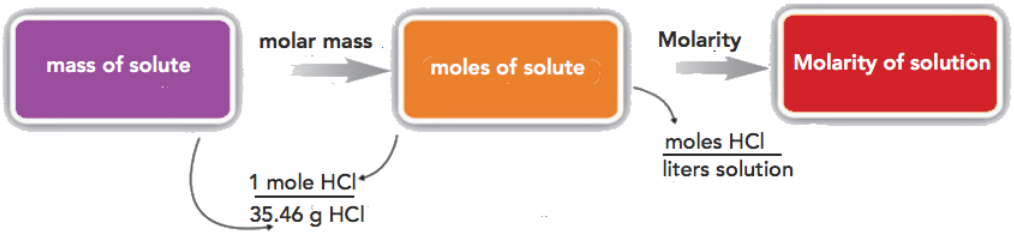
Molarity is abbreviated M (often referred to as "molar"), and the units are often abbreviated as mol/L. It is important to remember that "mol" in this expression refers to moles of solute and that "L" refers to liters of solution. For example, if you have 1.5 mol of NaCl dissolved in 0.500 L of solution, its molarity is therefore

$$\frac{1.5 \text{ mol NaCl}}{0.500 \text{ L solution}} = 3.0 \text{ M NaCl}$$

which is read as "three point oh **molar** sodium chloride." Sometimes (aq) is added when the solvent is water, as in "3.0 M NaCl(aq)."

Before a molarity concentration can be calculated, the amount of the **solute must be expressed in moles**, and the **volume of the solution** must be expressed in **liters**.

If the quantity of the solute is given in mass units, you must convert mass units to mole units before using the definition of molarity to calculate concentration. For example, what is the molar concentration of a solution of 22.4 g of HCl dissolved in 1.56 L?



Step 1: convertthe **mass of solute** to **moles** using the **molar mass of HCl (36.46 g/mol):**

$$22.4\ \cancel{g HCl} \times \frac{1\ mol\ HCl}{36.46\ \cancel{g HCl}} = 0.614\ mol\ HCl$$

Step 2:use the **definition of molarity** to determine the concentration:

$$M\ =\ \frac{0.614\ mol\ HCl}{1.56 L\ solution} = 0.394\ MHCl$$

Example 6.3.5

What is the molarity of an aqueous solution of 25.0 g of NaOH in 750 mL?

Solution

Before we substitute these quantities into the definition of molarity, we must convert them to the proper units. The mass of NaOH must be converted to moles of NaOH. The molar mass of NaOH is 40.00 g/mol:

$$25.0\ \text{g NaOH} \times \frac{1\ \text{mol NaOH}}{40.00\ \text{g NaOH}} = 0.625\ \text{mol NaOH}$$

Next, we convert the volume units from milliliters to liters:

$$750\ \text{mL} \times \frac{1\ \text{L}}{1,000\ \text{mL}} = 0.750\ \text{L}$$

Now that the quantities are expressed in the proper units, we can substitute them into the definition of molarity:

$$\text{M} = \frac{0.625\ \text{mol NaOH}}{0.750\ \text{L}} = 0.833\ \text{M NaOH}$$

Exercise 6.3.5

If a 350 mL cup of coffee contains 0.150 g of caffeine ($C_8H_{10}N_4O_2$), what is the molarity of this caffeine solution?

Answer

0.00221 M

Using Molarity in Calculations

The definition of molarity can also be used to calculate a needed volume of solution, given its concentration and the number of moles desired, or the number of moles of solute (and subsequently, the mass of the solute), given its concentration and volume. As in the percent concentration, molarity can also be expressed as a **conversion factor**.

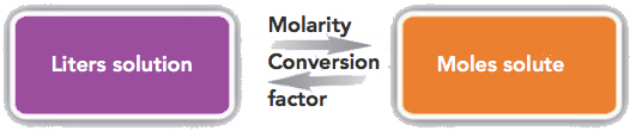
Molarity is defined as moles solute per liter solution. There is an understood 1 in the denominator of the conversion factor. For example, a **3.0 M solution of sucrose** means that there are three moles of sucrose dissolved in every **liter of solution**. Mathematically, this is stated as follows:

3.0 moles sucrose = 1 L solution

Dividing both sides of this expression by either side, we generate two possible conversion factors:

$$\frac{3.0 \text{ mol sucrose}}{1 \text{ L solution}} \text{ or } \frac{1 \text{ L solution}}{3.0 \text{ mol sucrose}}$$

The first conversion factor can be used to convert from *volume (L) of solution to moles solute*, and the *second converts from moles of solute to volume (L) of solution*.



For example, suppose we are asked how many moles of sucrose are present in 0.108 L of a 3.0 M sucrose solution. The given volume (0.108 L) is multiplied by the first conversion factor to cancel the L units, and find that 0.32 moles of sucrose are present.

$$0.108 \cancel{L\ solution} \times \frac{3.0\ mol\ sucrose}{1 \cancel{L\ solution}} = 0.32\ mol\ sucrose$$

How many liters of 3.0 M sucrose solutionare needed to obtain 4.88 mol of sucrose? In such a conversion, we multiply the given (4.88 moles sucrose) with the second conversion factor. This cancels the moles units and converts it to liters of solution.

$$4.88 \cancel{mol\ sucrose} \times \frac{1\ L\ solution}{3.0 \cancel{mol\ sucrose}} = 1.63\ L\ solution$$

Example 6.3.6

1. What volume of a 0.0753 M solution of dimethylamine [$(CH_3)_2NH$] is needed to obtain 0.450 mol of the compound?
2. Ethylene glycol ($C_2H_6O_2$) is mixed with water to make auto engine coolants. How many grams of $C_2H_6O_2$ are in 5.00 L of a 6.00 M aqueous solution?

Solution

1. To solve for the volume, multiply the "given" (0.450 mol of dimethylamine) with the molarity conversion factor (0.0753 M). Use the proper conversion factor to cancel the unit "mol" and get the unit volume (L) of solution:

$$0.450 \text{ mol dimethylamine} \times \frac{1 \text{ L solution}}{0.0753 \text{ mol dimethylamine}} = 5.98 \text{ L solution}$$

2. The strategy in solving this problem is to convert the given volume (5.00 L) using the 6.00 M (conversion factor) to solve for moles of ethylene glycol, which can then be converted to grams.

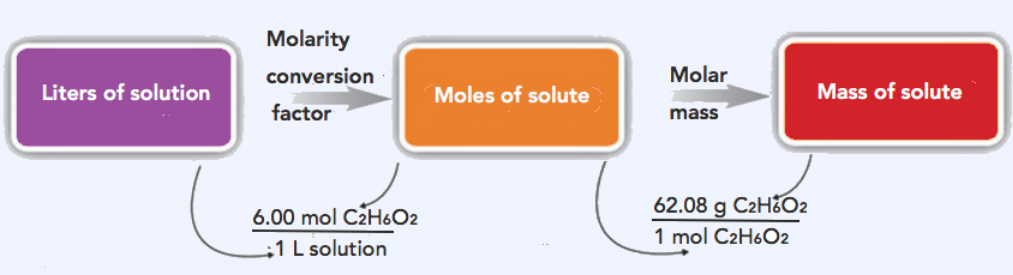
Step 1: Convert the given volume (5.00 L) to moles ethylene glycol.

$$5.00 \text{ L solution} \times \frac{6.00 \text{ mol } C_2H_6O_2}{1 \text{ L solution}} = 30.0 \text{ mol } C_2H_6O_2$$

Step 2: Convert 30.0 mols $C_2H_6O_2$to grams $C_2H_6O_2$. Molar mass of $C_2H_6O_2$= 62.08 g/mol

$$30.0 \text{ mol } C_2H_6O_2 \times \frac{62.08 \text{ g } C_2H_6O_2}{1 \text{ mol } C_2H_6O_2} = 1,860 \text{ g } C_2H_6O_2$$

The same two-step problem can also be worked out in a single line, rather than as two separate steps, as follows:



$$5.00 \text{ L solution} \times \frac{6.00 \text{ mol } C_2H_6O_2}{1 \text{ L solution}} \times \frac{62.08 \text{ g } C_2H_6O_2}{1 \text{ mol } C_2H_6O_2} = 1,860 \text{ g } C_2H_6O_2$$

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The final answer is rounded off to 3 significant figures. Thus, there are 1,860 g of $C_2H_6O_2$ in the specified amount of engine coolant.

Note: Dimethylamine has a “fishy” odor. In fact, organic compounds called amines cause the odor of decaying fish.

Example 6.3.6A

1. What volume of a 0.0753 M solution of dimethylamine [$(CH_3)_2NH$] is needed to obtain 0.450 mol of the compound?
2. Ethylene glycol ($C_2H_6O_2$) is mixed with water to make auto engine coolants. How many grams of $C_2H_6O_2$ are in 5.00 L of a 6.00 M aqueous solution?

Solution

This is an alternative method in case you don't want to use the conversion factor for molarity. In both parts, we will use the definition of molarity to solve for the desired quantity.

1. $$0.0753\ \text{M} = \frac{0.450\ \text{mol}\ (CH_3)_2NH}{\text{volume of solution}}$$

   To solve for the volume of solution, we multiply both sides by volume of solution and divide both sides by the molarity value to isolate the volume of solution on one side of the equation:

   $$\text{volume of solution} = \frac{0.450\ \text{mol}\ (CH_3)_2NH}{0.0753\ \text{M}} = 5.98\ \text{L}$$

   Note that because the definition of molarity is mol/L, the division of mol by M yields L, a unit of volume.

2. The molar mass of $C_2H_6O_2$ is 62.08 g/mol., so

   $$6.00\ \text{M} = \frac{\text{moles of solute}}{5.00\ \text{L}}$$

   To solve for the number of moles of solute, we multiply both sides by the volume:

   $$\text{moles of solute} = (6.00\ \text{M})(5.00\ \text{L}) = 30.0\ \text{mol}$$

   Note that because the definition of molarity is mol/L, the product M × L gives mol, a unit of amount. Now, using the molar mass of $C_3H_8O_3$, we convert mol to g:

   $$30.0\ \text{mol} \times \frac{62.08\ \text{g}}{\text{mol}} = 1,860\ \text{g}$$

   Thus, there are 1,860 g of $C_2H_6O_2$ in the specified amount of engine coolant.

Exercise 6.3.6

a. What volume of a 0.0902 M solution of formic acid (HCOOH) is needed to obtain 0.888 mol of HCOOH?
b. Acetic acid ($HC_2H_3O_2$) is the acid in vinegar. How many grams of $HC_2H_3O_2$ are in 0.565 L of a 0.955 M solution?

Answer

a. 9.84 L

b. 32.4 g

Using Molarity in Stoichiometry Problems

Of all the ways of expressing concentration, molarity is the one most commonly used in stoichiometry problems because it is directly related to the mole unit. Consider the following chemical equation:

$$HCl(aq) + NaOH(s) \rightarrow H_2O(\ell) + NaCl(aq)$$

Suppose we want to know how many liters of aqueous HCl solution will react with a given mass of NaOH. A typical approach to answering this question is as follows:

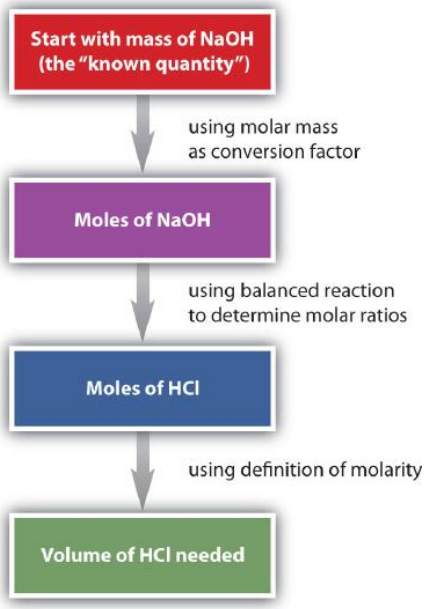


Figure 6.3.2*: Typical approach to solving Molarity problems*

In itself, each step is a straightforward conversion. It is the combination of the steps that is a powerful quantitative tool for problem solving.

Example 6.3.7

How many milliliters of a 2.75 M HCl solution are needed to react with 185 g of NaOH? The balanced chemical equation for this reaction is as follows:

$$HCl(aq) + NaOH(s) \rightarrow H_2O(\ell) + NaCl(aq)$$

Solution

We will follow the flowchart to answer this question. First, we convert the mass of NaOH to moles of NaOH using its molar mass, 40.00 g/mol:

$$185\ \text{g NaOH} \times \frac{1\ \text{mol NaOH}}{40.00\ \text{g NaOH}} = 4.63\ \text{mol NaOH}$$

Using the balanced chemical equation, we see that there is a one-to-one ratio of moles of HCl to moles of NaOH. We use this to determine the number of moles of HCl needed to react with the given amount of NaOH:

$$4.63\ \text{mol NaOH} \times \frac{1\ \text{mol HCl}}{1\ \text{mol NaOH}} = 4.63\ \text{mol HCl}$$

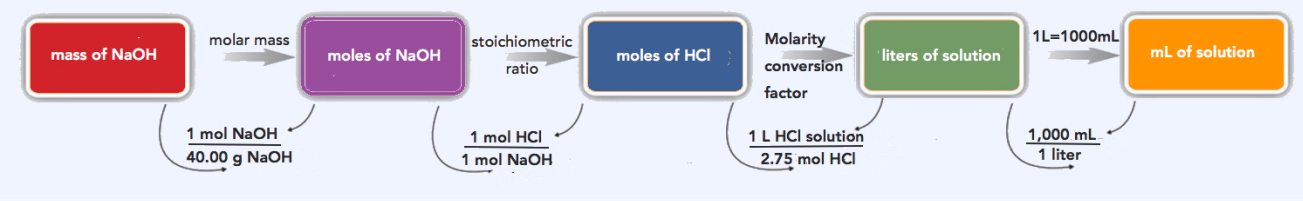
Finally, we use the definition of molarity to determine the volume of 2.75 M HCl needed:

$$2.75\ \text{M HCl} = \frac{4.63\ \text{mol HCl}}{\text{volume of HCl solution}}$$

$$\text{volume of HCl} = \frac{4.63\ \text{mol HCl}}{2.75\ \text{M HCl}} = 1.68\ \text{L} \times \frac{1,000\ \text{mL}}{1\ \text{L}} = 1,680\ \text{mL}$$

We need 1,680 mL of 2.75 M HCl to react with the NaOH.

The same multi-step problem can also be worked out in a single line, rather than as separate steps, as follows:



$$185 \text{ g NaOH} \times \frac{1 \text{ mol NaOH}}{40.00 \text{ g NaOH}} \times \frac{1 \text{ mol HCl}}{1 \text{ mol NaOH}} \times \frac{1 \text{ L HCl solution}}{2.75 \text{ mol HCl}} \times \frac{1000 \text{ mL HCl solution}}{1 \text{ L HCl solution}} = 1,680 \text{ mL HCl solution}$$

Our final answer (rounded off to three significant figures) is 1,680 mL HCl solution.

Exercise 6.3.7

How many milliliters of a 1.04 M H_2SO_4 solution are needed to react with 98.5 g of $Ca(OH)_2$? The balanced chemical equation for the reaction is as follows:

$$H_2SO_{4(aq)} + Ca(OH)_{2(s)} \rightarrow 2H_2O_{(\ell)} + CaSO_{4(aq)}$$

Answer

1,280 mL

The general steps for performing stoichiometry problems such as this are shown in Figure 6.3.3. You may want to consult this figure when working with solutions in chemical reactions. The double arrows in Figure 6.3.3 indicate that you can start at either end of the chart and, after a series of simple conversions, determine the quantity at the other end.

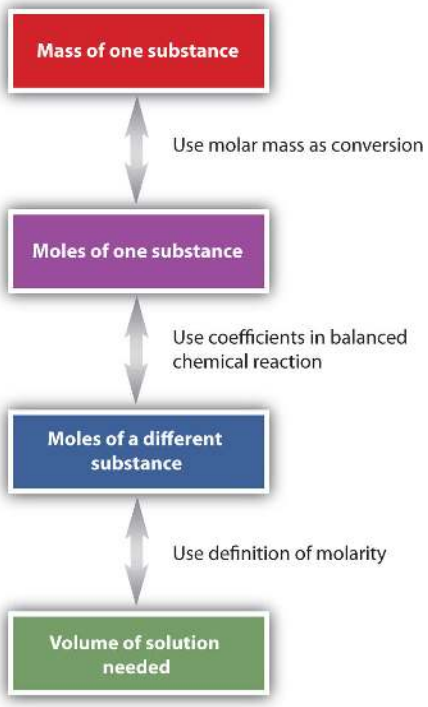


Figure 6.3.3: Diagram of Steps for Using Molarity in Stoichiometry Calculations. When using molarity in stoichiometry calculations, a specific sequence of steps usually leads you to the correct answer.

Many of the fluids found in our bodies are solutions. The solutes range from simple ionic compounds to complex proteins. Table 6.3.2 lists the typical concentrations of some of these solutes.

Table 6.3.2: Approximate Concentrations of Various Solutes in Some Solutions in the Body*

Solution	Solute	Concentration (M)
blood plasma	Na^+	0.138
	K^+	0.005
	Ca^{2+}	0.004
	Mg^{2+}	0.003
	Cl^-	0.110
	HCO_3^-	0.030
stomach acid	HCl	0.10
urine	NaCl	0.15
	PO_4^{3-}	0.05
	NH_2CONH_2 (urea)	0.30

*Note: Concentrations are approximate and can vary widely.

Looking Closer: The Dose Makes the Poison

Why is it that we can drink 1 qt of water when we are thirsty and not be harmed, but if we ingest 0.5 g of arsenic, we might die? There is an old saying: *the dose makes the poison*. This means that what may be dangerous in some amounts may not be dangerous in other amounts.

Take arsenic, for example. Some studies show that arsenic deprivation limits the growth of animals such as chickens, goats, and pigs, suggesting that arsenic is actually an essential trace element in the diet. Humans are constantly exposed to tiny amounts of arsenic from the environment, so studies of completely arsenic-free humans are not available; if arsenic is an essential trace mineral in human diets, it is probably required on the order of 50 ppb or less. A toxic dose of arsenic corresponds to about 7,000 ppb and higher, which is over 140 times the trace amount that may be required by the body. Thus, arsenic is not poisonous in and of itself. Rather, it is the amount that is dangerous: the dose makes the poison.

Similarly, as much as water is needed to keep us alive, too much of it is also risky to our health. Drinking too much water too fast can lead to a condition called water intoxication, which may be fatal. The danger in water intoxication is not that water itself becomes toxic. It is that the ingestion of too much water too fast dilutes sodium ions, potassium ions, and other salts in the bloodstream to concentrations that are not high enough to support brain, muscle, and heart functions. Military personnel, endurance athletes, and even desert hikers are susceptible to water intoxication if they drink water but do not replenish the salts lost in sweat. As this example shows, even the right substances in the wrong amounts can be dangerous!

Equivalents

Concentrations of ionic solutes are occasionally expressed in units called equivalents (Eq). One equivalent equals 1 mol of positive or negative charge. Thus, 1 mol/L of Na^+(aq) is also 1 Eq/L because sodium has a 1+ charge. A 1 mol/L solution of Ca^{2+}(aq) ions has a concentration of 2 Eq/L because calcium has a 2+ charge. Dilute solutions may be expressed in milliequivalents (mEq)—for example, human blood plasma has a total concentration of about 150 mEq/L. (For more information about the ions present in blood plasma, see Chapter 3, Section 3.3.)

Dilutions

When additional water is added to an aqueous solution, the concentration of that solution decreases. This is because the number of **moles of the solute does not change**, while the **volume of the solution increases**. We can set up an equality between the moles of the solute before the dilution (1) and the moles of the solute after the dilution (2).

$$\text{mol}_1 = \text{mol}_2$$

Since the moles of solute in a solution is equal to the molarity multiplied by the liters, we can set those equal.

$$M_1 \times L_1 = M_2 \times L_2$$

Finally, because the two sides of the equation are set equal to one another, the volume can be in any units we choose, as long as that unit is the same on both sides. Our equation for calculating the molarity of a diluted solution becomes:

$$M_1 \times V_1 = M_2 \times V_2$$

Suppose that you have $100.\ \text{mL}$ of a $2.0\ \text{M}$ solution of HCl. You dilute the solution by adding enough water to make the solution volume $500.\ \text{mL}$. The new molarity can easily be calculated by using the above equation and solving for M_2.

$$M_2 = \frac{M_1 \times V_1}{V_2} = \frac{2.0\ \text{M} \times 100.\ \text{mL}}{500.\ \text{mL}} = 0.40\ \text{M HCl}$$

The solution has been diluted by one-fifth since the new volume is five times as great as the original volume. Consequently, the molarity is one-fifth of its original value.

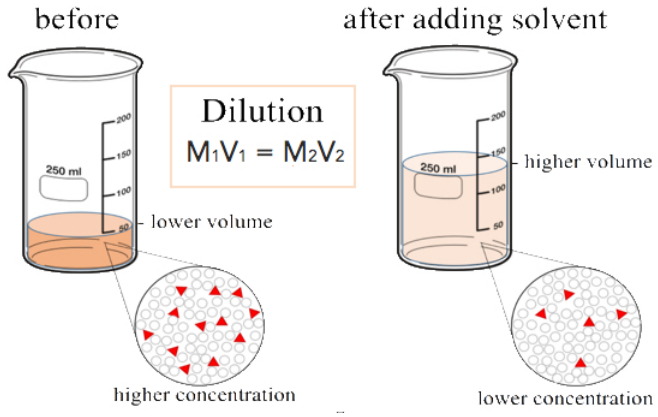


Figure 6.3.1: Figure 6.3.4: Diluting a solution by adding more solvent. Through the dilution process, the volume increases and the concentrations of the solutes decrease. As a consequence, there is more solution in the beaker after dilution, and the color of the solution becomes fainter. The inset shows that at the particular level (picometer to nanometer scale), there are less solute particles (red triangles) per volume. The content in the central box shows the dilution law, i.e. that the product of concentration and volume stays constant upon dilution. CC BY-SA 4.0.

Dilution Equations

Any units of concentration and volume can be used, as long as both concentrations and both volumes have the same unit. For example, if we are using M (molarity), then we can express the equation as follows:

$$\text{Molarity}_{\text{initial}} \times \text{volume}_{\text{initial}} = \text{Molarity}_{\text{final}} \times \text{volume}_{\text{final}} \text{or}$$

$$\boldsymbol{M_1V_1 = M_2V_2}$$

If we are using percent, the dilution equation is as follows:

$$\%_{\text{initial}} \times \text{volume}_{\text{initial}} = \%_{\text{final}} \times \text{volume}_{\text{final}} \text{or}$$

$$\boldsymbol{\%_1V_1 = \%_2V_2}$$

Example 6.3.8

A 125 mL sample of 0.900 M NaCl is diluted to 1,125 mL. What is the final concentration of the diluted solution?

Solution

Because the volume units are the same, and we are looking for the molarity of the final solution, we can use $(\text{concentration} \times \text{volume})_{\text{initial}} = (\text{concentration} \times \text{volume})_{\text{final}}$:

$$(0.900\ \text{M} \times 125\ \text{mL}) = (\text{concentration} \times 1{,}125\ \text{mL})$$

We solve by isolating the unknown concentration by itself on one side of the equation. Dividing by 1,125 mL gives

$$\text{concentration} = \frac{0.900\ \text{M} \times 125\ \text{mL}}{1,125\ \text{mL}} = 0.100\ \text{M}$$

as the final concentration.

Exercise 6.3.8

a. A nurse uses a syringe to inject 5.00 mL of 0.550 M heparin solution (heparin is an anticoagulant drug) into a 250 mL IV bag, for a final volume of 255 mL. What is the concentration of the resulting heparin solution?

b. A 0.885 M solution of KBr whose initial volume is 76.5 mL has more water added until its concentration is 0.500 M. What is the new volume of the solution?

Answer

a. 0.0108 M

b. 135.4 mL

Preparing IV Solutions

In a hospital emergency room, a physician orders an intravenous (IV) delivery of 100 mL of 0.5% KCl for a patient suffering from hypokalemia (low potassium levels). Does an aide run to a supply cabinet and take out an IV bag containing this concentration of KCl?

Not likely. It is more probable that the aide must make the proper solution from an IV bag of sterile solution and a more concentrated, sterile solution, called a *stock solution*, of KCl. The aide is expected to use a syringe to draw up some stock solution and inject it into the waiting IV bag and dilute it to the proper concentration. Thus the aide must perform a dilution calculation.



Figure 6.3.5:*Preparing IV Solution © Thinkstock. Medical personnel commonly must perform dilutions for IV solutions.*

If the stock solution is 10.0% KCl and the final volume and concentration need to be 100 mL and 0.50%, respectively, then it is an easy calculation to determine how much stock solution to use:

$$(10\%)V_1 = (0.50\%)(100\ \text{mL})$$

$$V_1 = 5\ \text{mL}$$

Of course, the addition of the stock solution affects the total volume of the diluted solution, but the final concentration is likely close enough even for medical purposes.

> Medical and pharmaceutical personnel are constantly dealing with dosages that require concentration measurements and dilutions. It is an important responsibility: calculating the *wrong* dose can be useless, harmful, or even fatal!

Key Takeaways

- Various concentration units are used to express the amounts of solute in a solution.
- Concentration units can be used as conversion factors in stoichiometry problems.
- New concentrations can be easily calculated if a solution is diluted.

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6.4: The Dissolution Process

Learning Objectives

- To describe the dissolution process at the molecular level

The Dissolution Process

What occurs at the molecular level to cause a solute to dissolve in a solvent? The answer depends in part on the solute, but there are some similarities common to all solutes.

Recall the rule that *like dissolves like*. This means that substances must have similar intermolecular forces to form solutions. When a soluble solute is introduced into a solvent, the particles of solute can interact with the particles of solvent. In the case of a solid or liquid solute, the interactions between the solute particles and the solvent particles are so strong that the individual solute particles separate from each other and, surrounded by solvent molecules, enter the solution. (Gaseous solutes already have their constituent particles separated, but the concept of being surrounded by solvent particles still applies.) This process is called **solvation** and is illustrated in Figure 6.4.1. When the solvent is water, the word **hydration**, rather than solvation, is used.

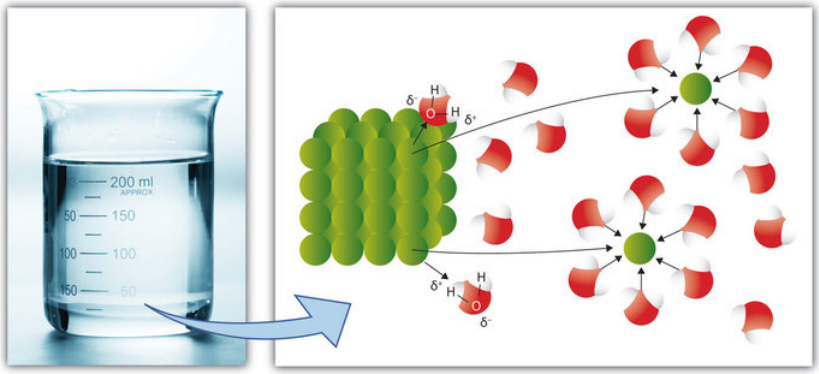


Figure 6.4.1: Solvation. When a solute dissolves, the individual particles of solute become surrounded by solvent particles. Eventually the particle detaches from the remaining solute, surrounded by solvent molecules in solution. Source: Photo © Thinkstock

Ionic Compounds and Covalent Compounds as Solutes

In the case of molecular solutes like glucose, the solute particles are individual molecules. However, if the solute is ionic, the individual ions separate from each other and become surrounded by solvent particles. That is, the cations and anions of an ionic solute separate when the solute dissolves. This process is referred to as **dissociation** (Figure 6.4.1).

The dissociation of soluble ionic compounds gives solutions of these compounds an interesting property: they conduct electricity. Because of this property, soluble ionic compounds are referred to as electrolytes. Many ionic compounds dissociate completely and are therefore called **strong electrolytes**. Sodium chloride is an example of a strong electrolyte. Some compounds dissolve but dissociate only partially, and solutions of such solutes may conduct electricity only weakly. These solutes are called **weak electrolytes**. Acetic acid (CH_3COOH), the compound in vinegar, is a weak electrolyte. Solutes that dissolve into individual neutral molecules without dissociation do not impart additional electrical conductivity to their solutions and are called nonelectrolytes. Table sugar ($C_{12}H_{22}O_{11}$) is an example of a nonelectrolyte.

> *The term electrolyte is used in medicine to mean any of the important ions that are dissolved in aqueous solution in the body. Important physiological electrolytes include* Na^+, K^+, Ca^{2+}, Mg^{2+}, *and* Cl^-.

Example 6.4.1

The following substances all dissolve to some extent in water. Classify each as an electrolyte or a nonelectrolyte.

1. potassium chloride (KCl)
2. fructose ($C_6H_{12}O_6$)
3. isopropyl alcohol [$CH_3CH(OH)CH_3$]
4. magnesium hydroxide [$Mg(OH)_2$]

Solution

Each substance can be classified as an ionic solute or a nonionic solute. Ionic solutes are electrolytes, and nonionic solutes are nonelectrolytes.

1. Potassium chloride is an ionic compound; therefore, when it dissolves, its ions separate, making it an electrolyte.
2. Fructose is a sugar similar to glucose. (In fact, it has the same molecular formula as glucose.) Because it is a molecular compound, we expect it to be a nonelectrolyte.
3. Isopropyl alcohol is an organic molecule containing the alcohol functional group. The bonding in the compound is all covalent, so when isopropyl alcohol dissolves, it separates into individual molecules but not ions. Thus, it is a nonelectrolyte
4. Magnesium hydroxide is an ionic compound, so when it dissolves it dissociates. Thus, magnesium hydroxide is an electrolyte.

Exercise 6.4.1

The following substances all dissolve to some extent in water. Classify each as an electrolyte or a nonelectrolyte.

a. acetone (CH_3COCH_3)
b. iron(III) nitrate [$Fe(NO_3)_3$]
c. elemental bromine (Br_2)
d. sodium hydroxide (NaOH)

Answer

a. nonelectrolyte

b. electrolyte

c. nonelectrolyte

d. electrolyte

Electrolytes in Body Fluids

Our body fluids are solutions of electrolytes and many other things. The combination of blood and the circulatory system is the *river of life*, because it coordinates all the life functions. When the heart stops pumping in a heart attack, the life ends quickly. Getting the heart restarted as soon as one can is crucial in order to maintain life.

The primary electrolytes required in the body fluid are cations (of calcium, potassium, sodium, and magnesium) and anions (of chloride, carbonates, aminoacetates, phosphates, and iodide). These are nutritionally called **macrominerals**.

Electrolyte balance is crucial to many body functions. Here's some extreme examples of what can happen with an imbalance of electrolytes: elevated potassium levels may result in cardiac arrhythmias; decreased extracellular potassium produces paralysis; excessive extracellular sodium causes fluid retention; and decreased plasma calcium and magnesium can produce muscle spasms of the extremities.

When a patient is dehydrated, a carefully prepared (commercially available) electrolyte solution is required to maintain health and well being. In terms of child health, oral electrolyte is given when a child is dehydrated due to diarrhea. The use of oral electrolyte maintenance solutions, which is responsible for saving millions of lives worldwide over the last 25 years, is one of the most

important medical advances in protecting the health of children in the century, explains Juilus G.K. Goepp, MD, assistant director of the Pediatric Emergency Department of the Children's Center at Johns Hopkins Hospital. If a parent provides an oral electrolyte maintenance solution at the very start of the illness, dehydration can be prevented. The functionality of electrolyte solutions is related to their properties, and interest in electrolyte solutions goes far beyond chemistry.

Sports drinks are designed to rehydrate the body after excessive fluid depletion. Electrolytes in particular promote normal rehydration to prevent fatigue during physical exertion. Are they a good choice for achieving the recommended fluid intake? Are they performance and endurance enhancers like they claim? Who should drink them?

Typically, eight ounces of a sports drink provides between fifty and eighty calories and 14 to 17 grams of carbohydrate, mostly in the form of simple sugars. Sodium and potassium are the most commonly included electrolytes in sports drinks, with the levels of these in sports drinks being highly variable. The American College of Sports Medicine says a sports drink should contain 125 milligrams of sodium per 8 ounces as it is helpful in replenishing some of the sodium lost in sweat and promotes fluid uptake in the small intestine, improving hydration.

Gatorade

In the summer of 1965, the assistant football coach of the University of Florida Gators requested scientists affiliated with the university study why the withering heat of Florida caused so many heat-related illnesses in football players and provide a solution to increase athletic performance and recovery post-training or game. The discovery was that inadequate replenishment of fluids, carbohydrates, and electrolytes was the reason for the “wilting” of their football players. Based on their research, the scientists concocted a drink for the football players containing water, carbohydrates, and electrolytes and called it “Gatorade.” In the next football season the Gators were nine and two and won the Orange Bowl. The Gators’ success launched the sports-drink industry, which is now a multibillion-dollar industry that is still dominated by Gatorade.



University of Florida football player Chip Hinton testing Gatorade in 1965, pictured next to the leader of its team of inventors, Robert Cade.

Key Takeaway

- When a solute dissolves, its individual particles are surrounded by solvent molecules and are separated from each other.

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CHAPTER OVERVIEW

7: Acids and Bases

7.1: Brønsted-Lowry Definition of Acids and Bases

7.2: Water - Both an Acid and a Base

7.3: The Strengths of Acids and Bases

7.4: Buffers

7.E: Acids and Bases (Exercises)

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7.1: Brønsted-Lowry Definition of Acids and Bases

Learning Objectives

1. Recognize a compound as a Brønsted-Lowry acid or a Brønsted-Lowry base.
2. Illustrate the proton transfer process that defines a Brønsted-Lowry acid-base reaction.

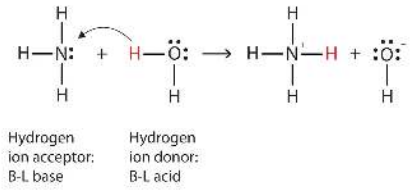
Ammonia (NH_3) increases the hydroxide ion concentration in aqueous solution by reacting with water rather than releasing hydroxide ions directly. In fact, the Arrhenius definitions of an acid and a base focus on hydrogen ions and hydroxide ions. Are there more fundamental definitions for acids and bases?

In 1923, the Danish scientist Johannes Brønsted and the English scientist Thomas Lowry independently proposed new definitions for acids and bases. Rather than considering both hydrogen and hydroxide ions, they focused on the hydrogen ion only. A Brønsted-Lowry acid is a compound that supplies a hydrogen ion in a reaction. A Brønsted-Lowry base, conversely, is a compound that accepts a hydrogen ion in a reaction. Thus, the Brønsted-Lowry definitions of an acid and a base focus on the movement of hydrogen ions in a reaction, rather than on the production of hydrogen ions and hydroxide ions in an aqueous solution.

Let us use the reaction of ammonia in water to demonstrate the Brønsted-Lowry definitions of an acid and a base. Ammonia and water molecules are reactants, while the ammonium ion and the hydroxide ion are products:

$$NH_3(aq) + H_2O(\ell) \rightarrow NH_4^+(aq) + OH^-(aq) \tag{7.1.1}$$

What has happened in this reaction is that the original water molecule has donated a hydrogen ion to the original ammonia molecule, which in turn has accepted the hydrogen ion. We can illustrate this as follows:



Because the water molecule donates a hydrogen ion to the ammonia, it is the Brønsted-Lowry acid, while the ammonia molecule—which accepts the hydrogen ion—is the Brønsted-Lowry base. Thus, ammonia acts as a base in both the Arrhenius sense and the Brønsted-Lowry sense.

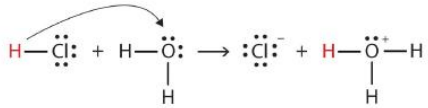
Is an Arrhenius acid like hydrochloric acid still an acid in the Brønsted-Lowry sense? Yes, but it requires us to understand what really happens when HCl is dissolved in water. Recall that the hydrogen *atom* is a single proton surrounded by a single electron. To make the hydrogen *ion*, we remove the electron, leaving a bare proton. Do we *really* have bare protons floating around in aqueous solution? No, we do not. What really happens is that the H^+ ion attaches itself to H_2O to make H_3O^+, which is called the *hydronium ion*. For most purposes, H^+ and H_3O^+ represent the same species, but writing H_3O^+ instead of H^+ shows that we understand that there are no bare protons floating around in solution. Rather, these protons are actually attached to solvent molecules.

> A proton in aqueous solution may be surrounded by more than one water molecule, leading to formulas like $H_5O_2^+$ or $H_9O_4^+$ rather than H_3O^+. It is simpler, however, to use H_3O^+.

With this in mind, how do we define HCl as an acid in the Brønsted-Lowry sense? Consider what happens when HCl is dissolved in H_2O:

$$HCl(g) + H_2O(\ell) \rightarrow H_3O^+(aq) + Cl^-(aq) \tag{7.1.2}$$

We can depict this process using Lewis electron dot diagrams:



Now we see that a hydrogen ion is transferred from the HCl molecule to the H_2O molecule to make chloride ions and hydronium ions. As the hydrogen ion donor, **HCl acts as a Brønsted-Lowry acid**; as a hydrogen ion acceptor, **H_2O is a Brønsted-Lowry base**. So HCl is an acid not just in the Arrhenius sense but also in the Brønsted-Lowry sense. Moreover, by the Brønsted-Lowry definitions, H_2O is a base in the formation of aqueous HCl. So the Brønsted-Lowry definitions of an acid and a base classify the dissolving of HCl in water as a reaction between an acid and a base—although the Arrhenius definition would not have labeled H_2O a base in this circumstance.

All Arrhenius acids and bases are Brønsted-Lowry acids and bases as well. However, not all Brønsted-Lowry acids and bases are Arrhenius acids and bases.

Example 7.1.1

Aniline ($C_6H_5NH_2$) is slightly soluble in water. It has a nitrogen atom that can accept a hydrogen ion from a water molecule just like the nitrogen atom in ammonia does. Write the chemical equation for this reaction and identify the Brønsted-Lowry acid and base.

Solution

$C_6H_5NH_2$ and H_2O are the reactants. When $C_6H_5NH_2$ accepts a proton from H_2O, it gains an extra H and a positive charge and leaves an OH^- ion behind. The reaction is as follows:

$$C_6H_5NH_2(aq) + H_2O(\ell) \rightarrow C_6H_5NH_3^+(aq) + OH^-(aq)$$

Because $C_6H_5NH_2$ accepts a proton, it is the Brønsted-Lowry base. The H_2O molecule, because it donates a proton, is the Brønsted-Lowry acid.

Exercise 7.1.1

Caffeine ($C_8H_{10}N_4O_2$) is a stimulant found in coffees and teas. When dissolved in water, it can accept a proton from a water molecule. Write the chemical equation for this process and identify the Brønsted-Lowry acid and base.

Answer

$C_8H_{10}N_4O_2(aq) + H_2O(\ell) \rightarrow C_8H_{11}N_4O_2^+(aq) + OH^-(aq)$

B-L base B-L acid

The Brønsted-Lowry definitions of an acid and a base can be applied to chemical reactions that occur in solvents other than water. The following example illustrates.

Example 7.1.2

Sodium amide ($NaNH_2$) dissolves in methanol (CH_3OH) and separates into sodium ions and amide ions (NH_2^-). The amide ions react with methanol to make ammonia and the methoxide ion (CH_3O^-). Write a balanced chemical equation for this process and identify the Brønsted-Lowry acid and base.

Solution

The equation for the reaction is between NH_2^- and CH_3OH to make NH_3 and CH_3O^- is as follows:

$$NH_2^-(solv) + CH_3OH(\ell) \rightarrow NH_3(solv) + CH_3O^-(solv)$$

The label *(solv)* indicates that the species are dissolved in some solvent, in contrast to *(aq)*, which specifies an aqueous (H_2O) solution. In this reaction, we see that the NH_2^- ion accepts a proton from a CH_3OH molecule to make an NH_3 molecule. Thus, as the proton acceptor, NH_2^- is the Brønsted-Lowry base. As the proton donor, CH_3OH is the Brønsted-Lowry acid.

? Exercise 7.1.2

Pyridinium chloride (C_5H_5NHCl) dissolves in ethanol (C_2H_5OH) and separates into pyridinium ions ($C_5H_5NH^+$) and chloride ions. The pyridinium ion can transfer a hydrogen ion to a solvent molecule. Write a balanced chemical equation for this process and identify the Brønsted-Lowry acid and base.

Answer

$C_5H_5NH^+(solv) + C_2H_5OH(\ell) \rightarrow C_5H_5N(solv) + C_2H_5OH_2^+(solv)$

B-L acid B-L base

Application in Everyday Life

Many people like to put lemon juice or vinegar, both of which are acids, on cooked fish (Figure 7.1.1). It turns out that fish have volatile amines (bases) in their systems, which are neutralized by the acids to yield involatile ammonium salts. This reduces the odor of the fish, and also adds a "sour" taste that we seem to enjoy.



$CH_3COOH + NH_2CH_2CH_2CH_2CH_2NH_2 \longrightarrow CH_3COO^- + NH_3^+CH_2CH_2CH_2CH_2NH_2$

Acetic acid + Putrescine → Acetate ion + Putrescinium ion

Figure 7.1.1: A neutralization reaction takes place between citric acid or acetic acid (proton donors) in lemons or vinegar and putrescine (proton acceptor) in the flesh of fish. (CC BY 4.0; OpenStax)

Pickling is a method used to preserve vegetables using a naturally produced acidic environment. The vegetable, such as a cucumber, is placed in a sealed jar submerged in a brine solution. The brine solution favors the growth of beneficial bacteria and suppresses the growth of harmful bacteria. The beneficial bacteria feed on starches in the cucumber and produce lactic acid as a waste product in a process called fermentation. The lactic acid eventually increases the acidity of the brine to a level that kills any harmful bacteria, which require a basic environment. Without the harmful bacteria consuming the cucumbers they are able to last much longer than if they were unprotected. A byproduct of the pickling process changes the flavor of the vegetables with the acid making them taste sour.

To Your Health: Brønsted-Lowry Acid-Base Reactions in Pharmaceuticals

There are many interesting applications of Brønsted-Lowry acid-base reactions in the pharmaceutical industry. For example, drugs often need to be water soluble for maximum effectiveness. However, many complex organic compounds are not soluble or are only slightly soluble in water. Fortunately, those drugs that contain proton-accepting nitrogen atoms (and there are a lot of them) can be

reacted with dilute hydrochloric acid [HCl(aq)]. The nitrogen atoms—acting as Brønsted-Lowry bases—accept the hydrogen ions from the acid to make an ion, which is usually much more soluble in water. The modified drug molecules can then be isolated as chloride salts:

\[\mathrm{RN(sl\: aq) + H^+(aq) \rightarrow RNH^+(aq) \xrightarrow{Cl^-(aq)} RNHCl(s)} \label{Eq3} \]

where RN represents some organic compound containing nitrogen. The label *(sl aq)* means "slightly aqueous," indicating that the compound RN is only slightly soluble. Drugs that are modified in this way are called *hydrochloride salts*. Examples include the powerful painkiller codeine, which is commonly administered as codeine hydrochloride. Acids other than hydrochloric acid are also used. Hydrobromic acid, for example, gives *hydrobromide salts*. Dextromethorphan, an ingredient in many cough medicines, is dispensed as dextromethorphan hydrobromide. The accompanying figure shows another medication (lidocaine) as a hydrochloride salt.



Figure used with permission from Wikipedia.

Conjugate Acid-Base Pairs

According to the Bronsted-Lowry theory of acids and bases, an acid is a proton donor and a base is a proton acceptor. Once an acid has given up a proton, the part that remains is called the acid's **conjugate base**. This species is a base because it can accept a proton (to re-form the acid). The conjugate base of HF (first example below) is fluoride ion, F^-.

$$\text{Acid} = H^+ + \text{Conjugate base of Acid}^-$$

$$HF \rightleftharpoons H^+ + F^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$NH_4^+ \rightleftharpoons H^+ + NH_3$$

Similarly, the part of the base that remains after a base accepts a proton is called the base's **conjugate acid**. This species is an acid because it can give up a proton (and thus re-form the base). The conjugate acid of fluoride ion, F^- (first example below) is HF.

$$H^+ + \text{Base} = \text{Conjugate acid of Base}^+$$

$$H^+ + F^- \rightleftharpoons HF$$

$$H^+ + OH^- \rightleftharpoons H_2O$$

$$H^+ + H_2O \rightleftharpoons H_3O^+$$

$$H^+ + NH_3 \rightleftharpoons NH_4^+$$

To summarize, the conjugate base of HF is fluoride ion, F^-, and the conjugate acid of fluoride ion, F^-, is HF. The HF/F- pair is referred to as a conjugate acid-base pair. The difference in the formulas of a conjugate acid-base pair (example: HF and F^-) is H^+. The table below lists conjugate acid-base pairs for your reference so that you can figure out the strategy of identifying them. For any given acid or base, you should be able to give its conjugate base or conjugate acid. The formula of an acid's conjugate base is generated by **removing a proton** (H^+) from the acid formula. The formula of the base's conjugate acid is formed by **adding a proton** (H^+) to the formula of the base.

Table 7.1.1. Conjugate acid-base pairs.

Conjugate Acid	Conjugate Base
H_3O^+	H_2O
H_2O	OH^-
H_2SO_4	HSO_4^-
HSO_4^-	SO_4^{2-}
NH_4^+	NH_3
NH_3	NH_2^-
CH_3COOH	CH_3COO^-
$CH_3NH_3^+$	CH_3NH_2

Example 7.1.3 : Conjugate Pairs

Write the formula of the conjugate base of (a) HCl and (b) HCO_3^-.

Write the formula of the conjugate acid of (c) $CH_3NH_2$and (d) OH^-.

Solution:

A conjugate base is formed by removing a proton (H^+). A conjugate acid is formed by accepting a proton (H^+).

a. After HCl donates a proton, a Cl^- ion is produced, and so Cl^- is the conjugate base.
b. After hydrogen carbonate ion, HCO_3^-, donates a proton, its conjugate base, CO_3^{2-} is produced.
c. After accepting a proton (H^+), CH_3NH_2 is converted to $CH_3NH_3^+$, its conjugate acid.
d. After accepting a proton (H^+), OH^- is converted to H_2O, its conjugate acid.

7.1.3Exercise : Conjugate Pairs

Write the formula of the conjugate base of (a) HNO_2 and (b) H_2CO_3.

Write the formula of the conjugate acid of (c) $C_6H5NH_2$and (d) HCO_3^-.

Answer

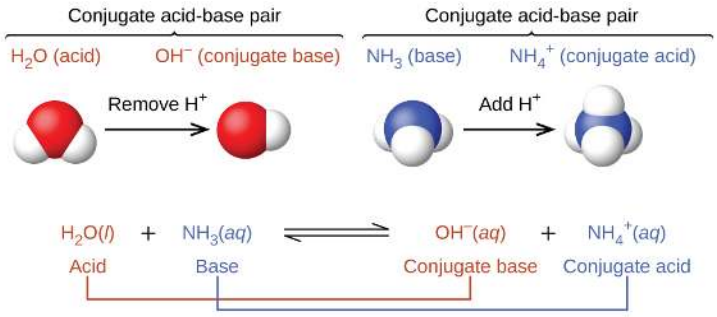
a. NO_2^- is the conjugate base of HNO_2.

b. HCO_3^- is the conjugate base of H_2CO_3

c. $C_6H5NH_3^+$ is the conjugate acid of C_6H5NH_2.

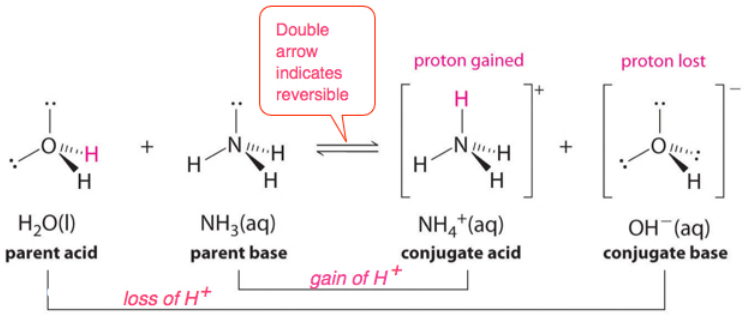
d. $H_2CO_3$is the conjugate acid ofHCO_3^-

In the reaction of ammonia with water to give ammonium ions and hydroxide ions, ammonia acts as a base by accepting a proton from a water molecule, which in this case means that water is acting as an acid. In the reverse reaction, an ammonium ion acts as an acid by donating a proton to a hydroxide ion, and the hydroxide ion acts as a base. The **conjugate acid–base pairs** for this reaction are NH_4^+/NH_3 and H_2O/OH^-. This means that the conjugate acid of the base NH_3 is NH_4^+ while the conjugate base of the acid NH_4^+ is NH_3. Similarly, the conjugate base of the acid H_2O is OH^-, and the conjugate acid of the base OH^- is H_2O.



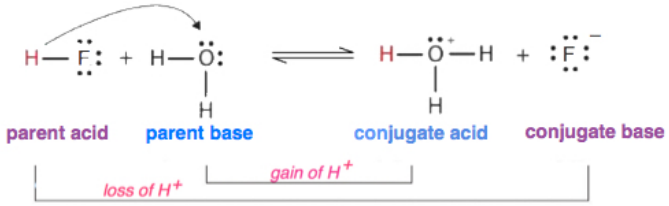
This figure has three parts in two rows. In the first row, two diagrams of acid-base pairs are shown. On the left, a space filling model of H subscript 2 O is shown with a red O atom at the center and two smaller white H atoms attached in a bent shape. Above this model is the label “H subscript 2 O (acid)” in purple. An arrow points right, which is labeled “Remove H superscript plus.” To the right is another space filling model with a single red O atom to which a single smaller white H atom is attached. The label in purple above this model reads, “O H superscript negative (conjugate base).” Above both of these red and white models is an upward pointing bracket that is labeled “Conjugate acid-base pair.” To the right is a space filling model with a central blue N atom to which three smaller white H atoms are attached in a triangular pyramid arrangement. A label in green above reads “N H subscript 3 (base).” An arrow labeled “Add H superscript plus” points right. To the right of the arrow is another space filling model with a blue central N atom and four smaller white H atoms in a tetrahedral arrangement. The green label above reads “N H subscript 3 superscript plus (conjugate acid).” Above both of these blue and white models is an upward pointing bracket that is labeled “Conjugate acid-base pair.” The second row of the figure shows the chemical reaction, H subscript 2 O (l) is shown in purple, and is labeled below in purple as “acid,” plus N H subscript 3 (a q) in green, labeled below in green as “base,” followed by a double sided arrow arrow and O H superscript negative (a q) in purple, labeled in purple as “conjugate base,” plus N H subscript 4 superscript plus (a q)” in green, which is labeled in green as “conjugate acid.” The acid on the left side of the equation is connected to the conjugate base on the right with a purple line. Similarly, the base on the left is connected to the conjugate acid on the right side.

In the **forward** reaction, the parent acid is H_2O and and the parent base is NH_3(shown in the illustration below). The acid H_2O loses a proton (H^+) to form its conjugate base OH^-. The base NH_3 gains a proton, to produce its conjugate acid NH_4^+. In the **reverse** reaction, the acid NH_4^+ loses a proton (H^+) to form its conjugate base NH_3. The base OH^- gains a proton, to produce its conjugate acid H_2O.



When hydrogen fluoride (HF) dissolves in water and ionizes, protons are transferred from hydrogen fluoride (parent acid) molecules to water (parent base) molecules, yielding hydronium ions (conjugate acid of water) and fluoride ions (conjugate base of HF):

$$HF + H_2O \rightleftharpoons H_3O^+ + F^-$$



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Example 7.1.3

Identify the conjugate acid-base pairs in this equilibrium.

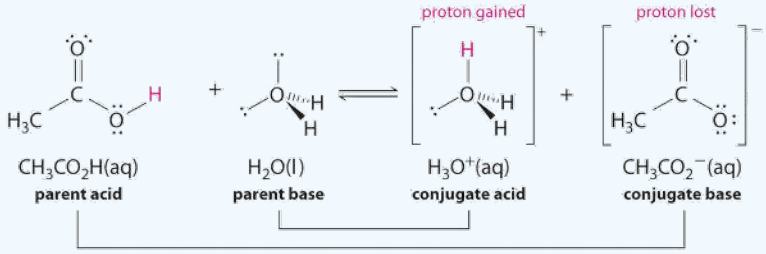
$$CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-$$

Solution

Similarly, in the reaction of acetic acid with water, acetic acid **donates** a proton to water, which acts as the base. In the reverse reaction, H_3O^+ is the acid that donates a proton to the acetate ion, which acts as the base.

Once again, we have two conjugate acid–base pairs:

- the parent acid and its conjugate base ($CH_3CO_2H/CH_3CO_2^-$) and
- the parent base and its conjugate acid (H_3O^+/H_2O).



Example 7.1.4

Identify the conjugate acid-base pairs in this equilibrium.

$$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$$

Solution

One pair is H_2O and OH^-, where H_2O has one more H^+ and is the conjugate acid, while OH^- has one less H^+ and is the conjugate base.

The other pair consists of $(CH_3)_3N$ and $(CH_3)_3NH^+$, where $(CH_3)_3NH^+$ is the conjugate acid (it has an additional proton) and $(CH_3)_3N$ is the conjugate base.

Exercise 7.1.4

Identify the conjugate acid-base pairs in this equilibrium.

$$NH_2^- + H_2O \rightleftharpoons NH_3 + OH^-$$

Answer:

H_2O (acid) and OH^- (base); NH_2^- (base) and NH_3 (acid)

The use of conjugate acid-base pairs allows us to make a very simple statement about relative strengths of acids and bases. *The stronger an acid, the weaker its conjugate base*, and, conversely, *the stronger a base, the weaker its conjugate acid.*

Key Takeaways

- A Brønsted-Lowry acid is a proton donor, and a Brønsted-Lowry base is a proton acceptor.
- Brønsted-Lowry acid-base reactions are essentially proton transfer reactions.

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7.2: Water - Both an Acid and a Base

Learning Objectives

- To write chemical equations for water acting as an acid and as a base.

Water (H_2O) is an interesting compound in many respects. Here, we will consider its ability to behave as an acid or a base.

In some circumstances, a water molecule will accept a proton and thus act as a **Brønsted-Lowry base**. We saw an example in the dissolving of HCl in H_2O:

$$\mathrm{HCl} + \mathrm{H_2O}(\ell) \rightarrow \mathrm{H_3O^+(aq)} + \mathrm{Cl^-(aq)} \tag{7.2.1}$$

In other circumstances, a water molecule can donate a proton and thus act as a **Brønsted-Lowry acid**. For example, in the presence of the amide ion (see Example 4 in Section 10.2), a water molecule donates a proton, making ammonia as a product:

$$H_2O(\ell) + NH_2^-(aq) \rightarrow OH^-(aq) + NH_3(aq) \tag{7.2.2}$$

In this case, NH_2^- is a Brønsted-Lowry base (the proton acceptor).

So, depending on the circumstances, H_2O can act as either a Brønsted-Lowry acid or a Brønsted-Lowry base. Water is not the only substance that can react as an acid in some cases or a base in others, but it is certainly the most common example—and the most important one. A substance that can either donate or accept a proton, depending on the circumstances, is called an **amphiprotic** compound.

A water molecule can act as an acid or a base even in a sample of pure water. About 6 in every 100 million (6 in 10^8) water molecules undergo the following reaction:

$$H_2O(\ell) + H_2O(\ell) \rightarrow H_3O^+(aq) + OH^-(aq) \tag{7.2.3}$$

This process is called the **autoionization of water** (Figure 7.2.1) and occurs in every sample of water, whether it is pure or part of a solution. Autoionization occurs to some extent in any amphiprotic liquid. (For comparison, liquid ammonia undergoes autoionization as well, but only about 1 molecule in a million billion (1 in 10^{15}) reacts with another ammonia molecule.)

Note

It is rare to truly have pure water. Water exposed to air will usually be slightly acidic because dissolved carbon dioxide gas, or carbonic acid, decreases the pH slightly below 7. Alternatively, dissolved minerals, like calcium carbonate (limestone), can make water slightly basic.

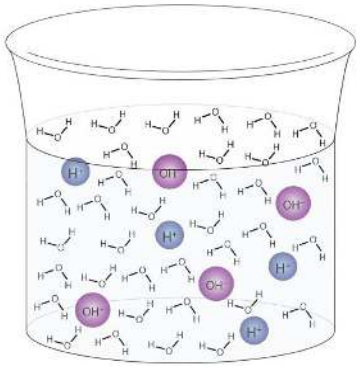


Figure 7.2.1 Autoionization. A small fraction of water molecules—approximately 6 in 100 million—ionize spontaneously into hydronium ions and hydroxide ions. This picture necessarily overrepresents the amount of autoionization that really occurs in pure water.

Example 7.2.1

Identify water as either a Brønsted-Lowry acid or a Brønsted-Lowry base.

1. $H_2O(\ell) + NO_2^-(aq) \rightarrow HNO_2(aq) + OH^-(aq)$
2. $HC_2H_3O_2(aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + C_2H_3O_2^-(aq)$

Solution

1. In this reaction, the water molecule donates a proton to the NO_2^- ion, making $OH^-(aq)$. As the proton donor, H_2O acts as a Brønsted-Lowry acid.
2. In this reaction, the water molecule accepts a proton from $HC_2H_3O_2$, becoming $H_3O^+(aq)$. As the proton acceptor, H_2O is a Brønsted-Lowry base.

Exercise 7.2.2

Identify water as either a Brønsted-Lowry acid or a Brønsted-Lowry base.

1. $HCOOH(aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + HCOO^-(aq)$
2. $H_2O(\ell) + PO_4^{3-}(aq) \rightarrow OH^-(aq) + HPO_4^{2-}(aq)$

Answer

1. H_2O acts as the proton acceptor (Brønsted-Lowry base)
2. H_2O acts as the proton donor (Brønsted-Lowry acid)

Key Takeaway

- Water molecules can act as both an acid and a base, depending on the conditions.

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7.3: The Strengths of Acids and Bases

Learning Objectives

- Describe the difference between strong and weak acids and bases.
- Describe how a chemical reaction reaches chemical equilibrium.
- Define the pH scale and use it to describe acids and bases.

Acids and bases do not all demonstrate the same degree of chemical activity in solution. Different acids and bases have different strengths.

Strong and Weak Acids

Let us consider the strengths of acids first. A small number of acids ionize completely in aqueous solution. For example, when HCl dissolves in water, every molecule of HCl separates into a hydronium ion and a chloride ion:

$$\mathrm{HCl\,(g) + H_2O\,(l) \xrightarrow{\sim 100\ \%} H_3O^+\,(aq) + Cl^-\,(aq)} \tag{7.3.1}$$

HCl(aq) is one example of a **strong acid**, which is a compound that is essentially **100% ionized** in aqueous solution. There are very few strong acids. The important ones are listed in Table 7.3.1.

Table 7.3.1: Strong Acids and Bases (All in Aqueous Solution)

Acids	Bases
HCl	LiOH
HBr	NaOH
HI	KOH
HNO_3	$Mg(OH)_2$
H_2SO_4	$Ca(OH)_2$
$HClO_4$	

By analogy, a strong base is a compound that is essentially 100% ionized in aqueous solution. As with acids, there are only a few strong bases, which are also listed in Table 7.3.1.

If an acid is **not listed** in Table 7.3.1, it is likely a **weak acid**, which is a compound that is not 100% ionized in aqueous solution. Similarly, a weak base is a compound that is not 100% ionized in aqueous solution. For example, acetic acid ($HC_2H_3O_2$) is a weak acid. The ionization reaction for acetic acid is as follows:

$$\mathrm{HC_2H_3O_2\,(aq) + H_2O(\ell) \rightarrow H_3O^+\,(aq) + C_2H_3O_2^-\,(aq)} \tag{7.3.2}$$

Depending on the concentration of $HC_2H_3O_2$, the ionization reaction may occur only for 1%–5% of the acetic acid molecules.

Looking Closer: Household Acids and Bases

Many household products are acids or bases. For example, the owner of a swimming pool may use muriatic acid to clean the pool. Muriatic acid is another name for hydrochloric acid [$\mathrm{HCl\,(aq)}$]. Vinegar has already been mentioned as a dilute solution of acetic acid [$\mathrm{HC_2H_3O_2\,(aq)}$]. In a medicine chest, one may find a bottle of vitamin C tablets; the chemical name of vitamin C is ascorbic acid ($\mathrm{HC_6H_7O_6}$).

One of the more familiar household bases is ammonia (NH_3), which is found in numerous cleaning products. As we mentioned previously, ammonia is a base because it increases the hydroxide ion concentration by reacting with water:

$$\mathrm{NH_3\,(aq) + H_2O(\ell) \rightarrow NH_4^+\,(aq) + OH^-\,(aq)} \tag{7.3.3}$$

Many soaps are also slightly basic because they contain compounds that act as Brønsted-Lowry bases, accepting protons from water and forming excess hydroxide ions. This is one reason that soap solutions are slippery.



Figure 7.3.1: (left) Bottles of alkaline drain cleaners containing sodium hydroxide can dissolve greases and hair. (right) Chemical burns caused by sodium hydroxide solution photographed 44 hours after exposure. Figures used with permission from Wikipedia.

Perhaps the most dangerous household chemical is the lye-based drain cleaner. Lye is a common name for sodium hydroxide, although it is also used as a synonym for potassium hydroxide. Lye is an extremely caustic chemical that can react with grease, hair, food particles, and other substances that may build up and form a clog in a pipe. Unfortunately, lye can also attack tissues and other substances in our bodies. Thus, when we use lye-based drain cleaners, we must be very careful not to touch any of the solid drain cleaner or spill the water it was poured into. Safer, nonlye drain cleaners use peroxide compounds to react on the materials in the clog and clear the drain.

Chemical Equilibrium in Weak Acids and Bases

The behavior of **weak acids and bases** illustrates a key concept in chemistry. Does the chemical reaction describing the ionization of a weak acid or base just stop when the acid or base is done ionizing? Actually, no. Rather, the reverse process—the reformation of the molecular form of the acid or base—occurs, ultimately at the same rate as the ionization process. For example, the ionization of the weak acid $HC_2H_3O_2\,(aq)$ is as follows:

$$HC_2H_3O_2\,(aq) + H_2O(\ell) \rightarrow H_3O^+\,(aq) + C_2H_3O_2^-\,(aq) \tag{7.3.4}$$

The reverse process also begins to occur:

$$H_3O^+\,(aq) + C_2H_3O_2^-\,(aq) \rightarrow HC_2H_3O_2\,(aq) + H_2O(\ell) \tag{7.3.5}$$

Eventually, there is a balance between the two opposing processes, and no additional change occurs. The chemical reaction is better represented at this point with a double arrow:

$$HC_2H_3O_2\,(aq) + H_2O(\ell) \rightleftharpoons H_3O^+\,(aq) + C_2H_3O_2^-\,(aq) \tag{7.3.6}$$

The $\rightleftharpoons$ implies that **both the forward and reverse reactions** are occurring, and their effects cancel each other out. A process at this point is considered to be at **chemical equilibrium** (or equilibrium). It is important to note that the processes do not stop. They balance out each other so that there is no further net change; that is, chemical equilibrium is a *dynamic equilibrium*.

Example 7.3.1: Partial Ionization

Write the equilibrium chemical equation for the partial ionization of each weak acid or base.

a. HNO_2(aq)
b. C_5H_5N(aq)

Solution

a. $HNO_2(aq) + H_2O(\ell) \leftrightarrows NO_2^-(aq) + H_3O^+(aq)$
b. $C_5H_5N(aq) + H_2O(\ell) \leftrightarrows C_5H_5NH^+(aq) + OH^-(aq)$

? Exercise 7.3.1

Write the equilibrium chemical equation for the partial ionization of each weak acid or base.

a. $HF_{(aq)}$
b. $AgOH_{(aq)}$
c. $CH_3NH_2(aq)$

Answer

a. $HF(aq) + H_2O(\ell) \leftrightarrows F^-(aq) + H_3O^+(aq)$

b. $AgOH(aq) \leftrightarrows Ag^+(aq) + OH^-(aq)$

c. $CH_3NH_2(aq) + H_2O(\ell) \leftrightarrows CH_3NH_3^+(aq) + OH^-(aq)$

Acid Ionization Constant, K_a

The ionization for a general weak acid, HA, can be written as follows:

$$\mathrm{HA}\,(aq) \rightleftharpoons \mathrm{H^+}\,(aq) + \mathrm{A^-}\,(aq)$$

Because the acid is weak, an equilibrium expression can be written. An **acid ionization constant** (K_a) is the equilibrium constant for the ionization of an acid.

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

The acid ionization represents the fraction of the original acid that has been ionized in solution. Therefore, the numerical value of K_a is a reflection of the strength of the acid. Weak acids with relatively higher K_a values are stronger than acids with relatively lower K_a values. Because strong acids are essentially 100% ionized, the concentration of the acid in the denominator is nearly zero and the K_a value approaches infinity. For this reason, K_a values are generally reported for weak acids only.

The table below is a listing of acid ionization constants for several acids. Note that polyprotic acids have a distinct ionization constant for each ionization step, with each successive ionization constant being smaller than the previous one.

Table 7.3.2: Acid Ionization Constants at $25^\circ C$

Name of Acid	Ionization Equation	K_a
Sulfuric acid	$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$ $HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$	very large 1.3×10^{-2}
Hydrofluoric acid	$HF \rightleftharpoons H^+ + F^-$	7.1×10^{-4}
Nitrous acid	$HNO_2 \rightleftharpoons H^+ + NO_2^-$	4.5×10^{-4}
Benzoic acid	$C_6H_5COOH \rightleftharpoons H^+ + C_6H_5COO^-$	6.5×10^{-5}
Acetic acid	$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$	1.8×10^{-5}
Carbonic acid	$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$ $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	4.2×10^{-7} 4.8×10^{-11}

Hydrofluoric acid $HF_{(aq)}$ reacts directly with glass (very few chemicals react with glass). Hydrofluoric acid is used in glass etching.

Strong and Weak Bases and Base Ionization Constant, K_b

As with acids, bases can either be strong or weak, depending on their extent of ionization. A **strong base** is a base, which ionizes completely in an aqueous solution. The most common strong bases are soluble metal hydroxide compounds such as potassium

hydroxide. Some metal hydroxides are not as strong simply because they are not as soluble. Calcium hydroxide is only slightly soluble in water, but the portion that does dissolve also dissociates into ions.

A **weak base** is a base that ionizes only slightly in an aqueous solution. Recall that a base can be defined as a substance, which accepts a hydrogen ion from another substance. When a weak base such as ammonia is dissolved in water, it accepts an H^+ ion from water, forming the hydroxide ion and the conjugate acid of the base, the ammonium ion.

$$NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4{}^+\,(aq) + OH^-\,(aq)$$

The equilibrium greatly favors the reactants and the extent of ionization of the ammonia molecule is very small.

An equilibrium expression can be written for the reactions of weak bases with water. Because the concentration of water is extremely large and virtually constant, the water is not included in the expression. A **base ionization constant** (K_b) is the equilibrium constant for the ionization of a base. For ammonia the expression is:

$$K_b = \frac{[NH_4{}^+]\,[OH^-]}{[NH_3]}$$

The numerical value of K_b is a reflection of the strength of the base. Weak bases with relatively higher K_b values are stronger than bases with relatively lower K_b values. Table 7.3.3 is a listing of base ionization constants for several weak bases.

Table 7.3.3: Base Ionization Constants at 25°C

Name of Base	Ionization Equation	K_b
Methylamine	$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3{}^+ + OH^-$	5.6×10^{-4}
Ammonia	$NH_3 + H_2O \rightleftharpoons NH_4{}^+ + OH^-$	1.8×10^{-5}
Pyridine	$C_5H_5N + H_2O \rightleftharpoons C_5H_5NH^+ + OH^-$	1.7×10^{-9}
Acetate ion	$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$	5.6×10^{-10}
Fluoride ion	$F^- + H_2O \rightleftharpoons HF + OH^-$	1.4×10^{-11}
Urea	$H_2NCONH_2 + H_2O \rightleftharpoons H_2NCONH_3{}^+ + OH^-$	1.5×10^{-14}

The Ion-Product of Water

As we have already seen, H_2O can act as an acid or a base. Within any given sample of water, some H_2O molecules are acting as acids, and other H_2O molecules are acting as bases. The chemical equation is as follows:

$$\underbrace{H_2O}_{\text{acid}} + \underbrace{H_2O}_{\text{base}} \rightleftharpoons H_3O^+ + OH^- \tag{7.3.7}$$

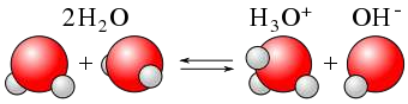


Figure 7.3.2: Autoionization of water, giving hydroxide and hydronium ions.

Similar to a weak acid, the autoionization of water is an equilibrium process, and is more properly written as follows:

$$H_2O(\ell) + H_2O(\ell) \rightleftharpoons H_3O^+\,(aq) + OH^-\,(aq) \tag{7.3.8}$$

We often use the simplified form of the reaction:

$$H_2O\,(l) \rightleftharpoons H^+\,(aq) + OH^-\,(aq)$$

The equilibrium constant for the autoionization of water is referred to as the ion-product for water and is given the symbol Kw.

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

The **ion-product of water (*Kw*)** is the mathematical product of the concentration of hydrogen ions and hydroxide ions. Note that H_2O is not included in the ion-product expression because it is a pure liquid. The value of Kw is very small, in accordance with a reaction that favors the reactants. At 25°C, the experimentally determined value of K_w in pure water is $1.0{\times}10^{-14}$.

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$$

In a sample of 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 Kw is taken.

$$[H^+] = [OH^-] = 1.0\times10^{-7}$$

The product of these two concentrations is 1.0×10^{-14}

$$[H^+]\times[OH^-] = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$$

- For acids, the concentration of H^+ or $[H^+]$) is greater than 1.0×10^{-7} M
- For bases, the concentration of OH^- or $[OH^-]$ is greater than 1.0×10^{-7} M.

Aqueous HCl is an example of acidic solution. Hydrogen chloride (HCl) ionizes to produce H^+ and Cl^- ions upon dissolving in water. This **increases the concentration of H^+ ions** in the solution. According to **Le Chatelier's principle**, the equilibrium represented by

$$H_2O\,(l) \rightleftharpoons H^+\,(aq) + OH^-\,(aq)$$

$$HCl\,(g) \longrightarrow H^+\,(aq) + Cl^-\,(aq)$$

is **forced to the left**, towards the reactant. As a result, the **concentration of the hydroxide ion decreases**.

Now, consider KOH (aq), a **basic solution**. Solid potassium hydroxide (KOH) dissociates in water to yield potassium ions and hydroxide ions.

$$KOH(s) \rightarrow K^+(aq) + OH^-(aq)$$

The **increase in concentration of the OH^- ions** will cause a decrease in the concentration of the H^+ ions.

No matter whether the aqueous solution is an acid, a base, or neutral:and the ion-product of $[H^+][OH^-]$ remains constant.

- For acidic solutions, $[H^+]$) is greater than $[OH^-]$.
- For basic solutions, [OH−] is greater than $[H^+]$.
- For neutral solutions, $[H_3O^+] = [OH-] = 1.0\times10^{-7}$M

This means that if you know $[H^+]$ for a solution, you can calculate what $[OH^-]$) has to be for the product to equal 1.0×10^{-14}, or if you know $[OH^-]$), you can calculate $[H^+]$. This also implies that as one concentration goes up, the other must go down to compensate so that their product always equals the value of K_w.

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \tag{7.3.9}$$

Example 7.3.2

Hydrochloric acid (HCl) is a strong acid, meaning it is 100% ionized in solution. What is the $[H^+]$ and the $[OH^-]$ in a solution of 2.0×10^{-3} M HCl?

Solution

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

Known

- $[HCl] = 2.0\times10^{-3}$ M
- $Kw = 1.0\times10^{-14}$

Unknown

- $[H^+]$=?M
- $[OH^-]$=?M

Because HCl is 100% ionized, the concentration of H+ ions in solution will be equal to the original concentration of HCl. Each HCl molecule that was originally present ionizes into one H+ ion and one Cl− ion. The concentration of OH− can then be determined from the [H+] and Kw.

Step 2: Solve.

$$[H^+]=2.0\times10^{-3}\,M$$

$$Kw = [H^+][OH^-] = 1.0\times10^{-14}$$

$$[OH^-] = Kw/[H^+] = 1.0\times10^{-14}/2.0\times10^{-3} = 5.0\times10^{-12}\,M$$

Step 3: Think about your result.

The $[H^+]$ is much higher than the $[OH^-]$ because the solution is acidic. As with other equilibrium constants, the unit for Kw is customarily omitted.

7.3.2 Exercise

Sodium hydroxide (NaOH) is a strong base. What is the $[H^+]$ and the $[OH^-]$ in a 0.001 M NaOH solution at 25 °C?

Answer

$[OH^-]$ = 0.001M or 1 x 10^{-3}M; $[H^+]=1\times10^{-11}$M.

The pH Scale

One qualitative measure of the strength of an acid or a base solution is the pH scale, which is based on the concentration of the hydronium (or hydrogen) ion in aqueous solution.

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

or

$$pH = -\log[H_3O^+]$$

Figure 7.3.3 illustrates this relationship, along with some examples of various solutions. Because hydrogen ion concentrations are generally less than one (for example $1.3 \times 10^{-3}\ M$), the log of the number will be a negative number. To make pH even easier to work with, pH is defined as the ***negative*** **log of** $[H_3O^+]$, which will give a positive value for pH.

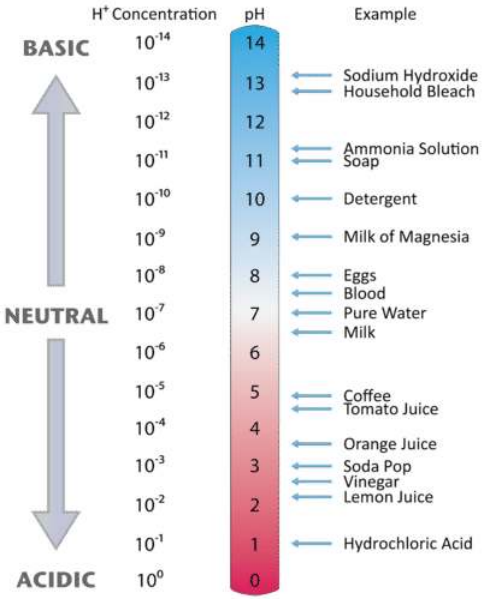


Figure 7.3.3: The relationship between $[H^+]$ and pH *values for several common materials.*

A neutral (neither acidic nor basic) solution has a pH of 7. A pH below 7 means that a solution is acidic, with lower values of pH corresponding to increasingly acidic solutions. A pH greater than 7 indicates a basic solution, with higher values of pH corresponding to increasingly basic solutions. Thus, given the pH of several solutions, you can state which ones are acidic, which ones are basic, and which are more acidic or basic than others. These are summarized in Table \(\PageIndex{4}.

Table 7.3.4: Acidic, Basic and Neutral pH Values

Acidic, Basic and Neutral pH Values

Classification	Relative Ion Concentrations	pH at 25 °C
acidic	$[H^+] > [OH^-]$	pH < 7
neutral	$[H^+] = [OH^-]$	pH = 7
basic	$[H^+] < [OH^-]$	pH > 7

Example 7.3.3

Find the pH, given the $[H^+]$ of the following:

a. 1×10^{-3} M
b. 2.5×10^{-11} M
c. 4.7×10^{-9} M

Solution

pH = - log $[H_3O^+]$

Substitute the known quantity into the equation and solve. Use a scientific calculator for b and c.

a. pH = - log $[1 \times 10^{-3}]$ = 3.0 (1 decimal place since 1 has 1 significant figure)
b. pH = - log $[2.5 \times 10^{-11}]$ = 10.60 (2 decimal places since 2.5 has 2 significant figures)
c. pH = - log $[4.7 \times 10^{-9}]$ = 8.33 (2 decimal places since 4.7 has 2 significant figures)

Note on significant figures:

Because the number(s) before the decimal point in the pH value relate to the power on 10, the number of digits *after* the decimal point (underlined) is what determines the number of significant figures in the final answer.

7.3.3 Exercise

Find the pH, given $[H^+]$ of the following:

a. 5.8×10^{-4} M
b. 1.0×10^{-7} M

Answer

a. 3.24

b. 7.00

Table 7.3.5 lists the pH of several common solutions. The most acidic among the listed solutions is battery acid with the lowest pH value (0.3). The most basic is 1M NaOH solution with the highest pH value of 14.0. Notice that some biological fluids (stomach acid and urine) are nowhere near neutral. You may also notice that many food products are slightly acidic. They are acidic because they contain solutions of weak acids. If the acid components of these foods were strong acids, the food would likely be inedible.

Table 7.3.5: The pH Values of Some Common Solutions

Solution	pH
battery acid	0.3
stomach acid	1–2
lemon or lime juice	2.1
vinegar	2.8–3.0
Coca-Cola	3
wine	2.8–3.8
beer	4–5
coffee	5
milk	6
urine	6
pure H_2O	7
(human) blood	7.3–7.5
sea water	8
antacid (milk of magnesia)	10.5
NH_3 (1 M)	11.6
bleach	12.6
NaOH (1 M)	14.0

Example 7.3.4

Label each solution as acidic, basic, or neutral based only on the stated pH.

a. milk of magnesia, pH = 10.5
b. pure water, pH = 7
c. wine, pH = 3.0

Solution

a. With a pH greater than 7, milk of magnesia is basic. (Milk of magnesia is largely $Mg(OH)_2$.)
b. Pure water, with a pH of 7, is neutral.
c. With a pH of less than 7, wine is acidic.

7.3.4 Exercise

Identify each substance as acidic, basic, or neutral based only on the stated pH.

a. human blood with pH = 7.4
b. household ammonia with pH = 11.0
c. cherries with pH = 3.6

Answer

a. slightly basic

b. basic

c. acidic

Acid Rain

Normal rainwater has a pH between 5 and 6 due to the presence of dissolved CO_2 which forms carbonic acid:

$$H_2O\,(l) + CO_2\,(g) \longrightarrow H_2CO_3\,(aq) \tag{7.3.10}$$

$$H_2CO_3\,(aq) \rightleftharpoons H^+\,(aq) + HCO_3{}^-\,(aq) \tag{7.3.11}$$

Acid rain is rainwater that has a pH of less than 5, due to a variety of nonmetal oxides, including CO_2, SO_2, SO_3, NO, and NO_2 being dissolved in the water and reacting with it to form not only carbonic acid, but sulfuric acid and nitric acid. The formation and subsequent ionization of sulfuric acid are shown here:

$$H_2O\,(l) + SO_3\,(g) \longrightarrow H_2SO_4\,(aq) \tag{7.3.12}$$

$$H_2SO_4\,(aq) \longrightarrow H^+\,(aq) + HSO_4{}^-\,(aq) \tag{7.3.13}$$

Carbon dioxide is naturally present in the atmosphere because we and most other organisms produce it as a waste product of metabolism. Carbon dioxide is also formed when fires release carbon stored in vegetation or when we burn wood or fossil fuels. Sulfur trioxide in the atmosphere is naturally produced by volcanic activity, but it also stems from burning fossil fuels, which have traces of sulfur, and from the process of "roasting" ores of metal sulfides in metal-refining processes. Oxides of nitrogen are formed in internal combustion engines where the high temperatures make it possible for the nitrogen and oxygen in air to chemically combine.

Acid rain is a particular problem in industrial areas where the products of combustion and smelting are released into the air without being stripped of sulfur and nitrogen oxides. In North America and Europe until the 1980s, it was responsible for the destruction of forests and freshwater lakes, when the acidity of the rain actually killed trees, damaged soil, and made lakes uninhabitable for all but the most acid-tolerant species. Acid rain also corrodes statuary and building facades that are made of marble and limestone (Figure 7.3.4). Regulations limiting the amount of sulfur and nitrogen oxides that can be released into the atmosphere by industry and automobiles have reduced the severity of acid damage to both natural and manmade environments in North America and Europe. It is now a growing problem in industrial areas of China and India.


(a)


(b)

Figure 7.3.4: (a) Acid rain makes trees more susceptible to drought and insect infestation, and depletes nutrients in the soil. (b) It also is corrodes statues that are carved from marble or limestone. (credit a: modification of work by Chris M Morris; credit b: modification of work by "Eden, Janine and Jim"/Flickr) Two photos are shown. Photograph a on the left shows the upper portion of trees against a bright blue sky. The tops of several trees at the center of the photograph have bare branches and appear to be dead. Image b shows a statue of a man that appears to from the revolutionary war era in either marble or limestone.

Key Takeaways

- Acids and bases can be strong or weak depending on the extent of ionization in solution.
- Most chemical reactions reach equilibrium at which point there is no net change.
- The ion-product of $[H^+][OH^-]$ in an aqueous solution remains constant.
- A ***p*H** value is simply the *negative* of the logarithm of the H^+ ion concentration ($-\log[H^+]$).
- The pH scale is used to succinctly communicate the acidity or basicity of a solution.
- A solution is **acidic** if *p*H < 7.
- A solution is **basic** if *p*H > 7.
- A solution is **neutral** if *p*H = 7.

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7.4: Buffers

Learning Objectives

- To define *buffer* and describe how it reacts with an acid or a base.

Weak acids are relatively common, even in the foods we eat. But we occasionally come across a strong acid or base, such as stomach acid, that has a strongly acidic pH of 1–2. By definition, strong acids and bases can produce a relatively large amount of hydrogen or hydroxide ions and, as a consequence, have a marked chemical activity. In addition, very small amounts of strong acids and bases can change the pH of a solution very quickly. If 1 mL of stomach acid [which we will approximate as 0.05 M HCl(aq)] is added to the bloodstream, and if no correcting mechanism is present, the pH of the blood would go from about 7.4 to about 4.9—a pH that is not conducive to continued living. Fortunately, the body has a mechanism for minimizing such dramatic pH changes.

The mechanism involves a **buffer**, a solution that resists dramatic changes in pH. A *buffer* (or *buffered*) solution is one that resists a change in its pH when H^+ or OH^- ions are added or removed owing to some other reaction taking place in the same solution. Buffers do so by being composed of certain pairs of solutes: either a **weak acid plus its conjugate base** or a **weak base plus its conjugate acid**.

For example, a buffer can be composed of dissolved **acetic acid ($HC_2H_3O_2$, a weak acid) and sodium acetate** ($NaC_2H_3O_2$). Sodium acetate is a salt that dissociates into sodium ions and acetate ions in solution. For as long as acetic acid and acetate ions are present in significant amounts a solution, this can resist dramatic pH changes. Another example of a buffer is a solution containing **ammonia (NH_3, a weak base) and ammonium chloride** (NH_4Cl). Ammonium acetate is also a salt that dissociates into ammonium ions and chloride ions in solution. The presence of ammonium ions with ammonia molecules satisfies the requisite condition for a buffer solution.

How Buffers Work

The essential component of a buffer system is a **conjugate acid-base pair** whose concentration is fairly high in relation to the concentrations of added H^+ or OH^- it is expected to buffer against. Let us use an acetic acid–sodium acetate buffer to demonstrate how buffers work. If a strong base—a source of OH^-(aq) ions—is added to the buffer solution, those hydroxide ions will react with the acetic acid in an acid-base reaction:

$$HC_2H_3O_2\,(aq) + OH^-\,(aq) \longrightarrow H_2O(\ell) + C_2H_3O_2^-\,(aq) \tag{7.4.1}$$

Rather than changing the pH dramatically by making the solution basic, the added hydroxide ions react to make water, and the pH does not change much.

> Many people are aware of the concept of buffers from *buffered aspirin*, which is aspirin that also has magnesium carbonate, calcium carbonate, magnesium oxide, or some other salt. The salt acts like a base, while aspirin is itself a weak acid.

If a strong acid—a source of H^+ ions—is added to the buffer solution, the H^+ ions will react with the anion from the salt. Because $HC_2H_3O_2$ is a weak acid, it is not ionized much. This means that if lots of hydrogen ions and acetate ions (from sodium acetate) are present in the same solution, they will come together to make acetic acid:

$$H^+\,(aq) + C_2H_3O_2^-\,(aq) \longrightarrow HC_2H_3O_2\,(aq) \tag{7.4.2}$$

Rather than changing the pH dramatically and making the solution acidic, the added hydrogen ions react to make molecules of a weak acid. Figure 7.4.1 illustrates both actions of a buffer.

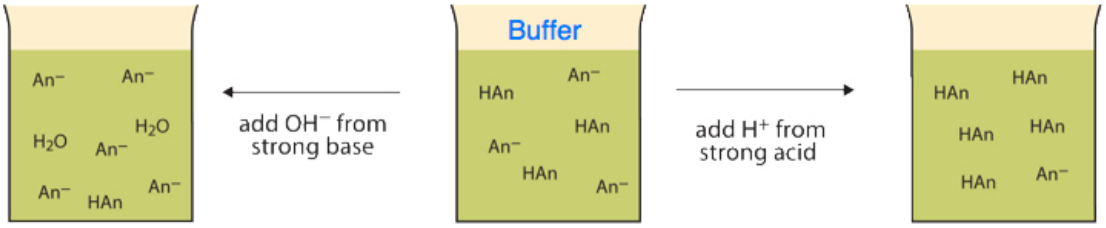


Figure 7.4.1: The Action of Buffers. Buffers can react with both strong acids (top) and strong bases (bottom) to minimize large changes in pH.

A simple buffer system might be a 0.2 *M* solution of sodium acetate; the conjugate pair here is acetic acid HAc and its conjugate base, the acetate ion Ac^-. The idea is that this conjugate pair "pool" will be available to gobble up any small ($\leq 10^{-3}$ *M*) addition of H+ or OH^- that may result from other processes going on in the solution.

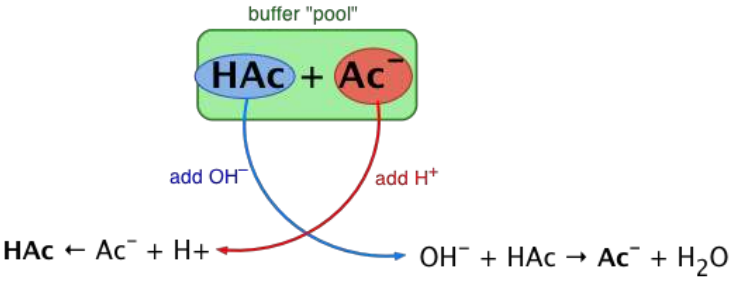


Figure 7.4.2: How HAc/Ac buffer works

Buffers work well only for limited amounts of added strong acid or base. Once either solute is all reacted, the solution is no longer a buffer, and rapid changes in pH may occur. We say that a buffer has a certain capacity. Buffers that have more solute dissolved in them to start with have larger capacities, as might be expected.

Buffers made from weak bases and salts of weak bases act similarly. For example, in a buffer containing NH_3 and NH_4Cl, ammonia molecules can react with any excess hydrogen ions introduced by strong acids:

$$NH_{3(aq)} + H^+_{(aq)} \rightarrow NH^+_{4(aq)} \tag{7.4.3}$$

while the ammonium ion [NH_4^+(aq)] can react with any hydroxide ions introduced by strong bases:

$$NH^+_{4(aq)} + OH^-_{(aq)} \rightarrow NH_{3(aq)} + H_2O_{(\ell)} \tag{7.4.4}$$

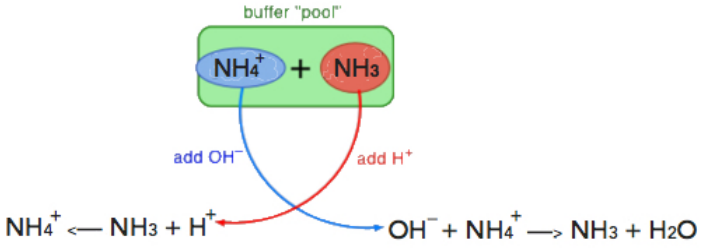


Figure 7.4.3: How NH_4^+/NH_3 buffer works

Example 7.4.1

Which solute combinations can make a buffer solution? Assume all are aqueous solutions.

a. $HCHO_2$ and $NaCHO_2$
b. HCl and NaCl
c. CH_3NH_2 and CH_3NH_3Cl
d. NH_3 and NaOH

Solution

a. Formic acid ($HCHO_2$) is a weak acid, while $NaCHO_2$ is a salt supplying —formate ion (CHO_2^-), the conjugate base of $HCHO_2$. The combination of these two solutes would make a buffer solution.
b. Hydrochloric acid (HCl) is a strong acid, not a weak acid, so the combination of these two solutes would not make a buffer solution.
c. Methylamine (CH_3NH_2) is like ammonia, a weak base. The compound CH_3NH_3Cl is a salt supplying $CH_3NH_3^+$, the conjugate acid of CH_3NH_2. The combination of these two solutes would make a buffer solution.
d. Ammonia (NH_3) is a weak base, but NaOH is a strong base. The combination of these two solutes would not make a buffer solution.

? Exercise 7.4.1

Which solute combinations can make a buffer solution? Assume all are aqueous solutions.

a. $NaHCO_3$ and NaCl
b. H_3PO_4 and NaH_2PO_4
c. NH_3 and $(NH_4)_3PO_4$
d. NaOH and NaCl

Answer

b. H_3PO_4 (weak acid) and $H_2PO_4^-$(conjugate base of H_3PO_4) make a buffer.

c. NH_3(weak base) and NH_4^+ (conjugate acid of NH_3) make a buffer

✔ Food and Drink App: The Acid That Eases Pain

Although medicines are not exactly "food and drink," we do ingest them, so let's take a look at an acid that is probably the most common medicine: acetylsalicylic acid, also known as aspirin. Aspirin is well known as a pain reliever and antipyretic (fever reducer).

The structure of aspirin is shown in the accompanying figure. The acid part is circled; it is the H atom in that part that can be donated as aspirin acts as a Brønsted-Lowry acid. Because it is not given in Table 10.5.1, acetylsalicylic acid is a weak acid. However, it is still an acid, and given that some people consume relatively large amounts of aspirin daily, its acidic nature can cause problems in the stomach lining, despite the stomach's defenses against its own stomach acid.

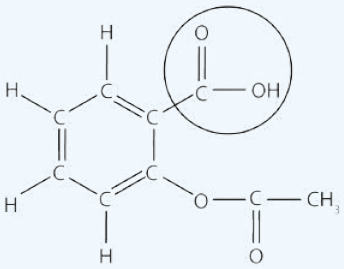


Figure 7.4.4 The Molecular Structure of Aspirin. The circled atoms are the acid part of the molecule.

Because the acid properties of aspirin may be problematic, many aspirin brands offer a "buffered aspirin" form of the medicine. In these cases, the aspirin also contains a buffering agent-usually MgO-that regulates the acidity of the aspirin to minimize its acidic side effects.

As useful and common as aspirin is, it was formally marketed as a drug starting in 1899. The US Food and Drug Administration (FDA), the governmental agency charged with overseeing and approving drugs in the United States, wasn't formed until 1906. Some have argued that if the FDA had been formed before aspirin was introduced, aspirin may never have gotten approval due to its potential for side effects-gastrointestinal bleeding, ringing in the ears, Reye's syndrome (a liver

problem), and some allergic reactions. However, recently aspirin has been touted for its effects in lessening heart attacks and strokes, so it is likely that aspirin is here to stay.

Buffer solutions are essential components of all living organisms.

- Our blood is buffered to maintain a pH of 7.4 that must remain unchanged as metabolically-generated CO_2 (carbonic acid) is added and then removed by our lungs.
- Buffers in the oceans, in natural waters such as lakes and streams, and within soils help maintain their environmental stability against acid rain and increases in atmospheric CO_2.
- Many industrial processes, such as brewing, require buffer control, as do research studies in biochemistry and physiology that involve enzymes, are active only within certain pH ranges.

The pH in living systems (Figure \(\PageIndex{1}\)) is maintained by buffer systems.

Table 7.3.2: pH in Living Systems

Compartment	pH
Gastric Acid	1
Lysosomes	4.5
Granules of Chromaffin Cells	5.5
Human Skin	5.5
Urine	6
Neutral H_2O at 37 °C	6.81
Cytosol	7.2
Cerebrospinal Fluid	7.3
Blood	7.43-7.45
Mitochondrial Matrix	7.5
Pancreas Secretions	8.1

Human blood has a buffering system to minimize extreme changes in pH. One buffer in blood is based on the presence of HCO_3^- and H_2CO_3 [H_2CO_3 is another way to write CO_2(aq)]. With this buffer present, even if some stomach acid were to find its way directly into the bloodstream, the change in the pH of blood would be minimal. Inside many of the body's cells, there is a buffering system based on phosphate ions.

Medicine: The Buffer System in Blood

The normal pH of human blood is about 7.4. The carbonate buffer system in the blood uses the following equilibrium reaction:

$$\mathrm{CO_2}(g) + 2\,\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2CO_3}(aq) \rightleftharpoons \mathrm{HCO_3}^-(aq) + \mathrm{H_3O}^+(aq)$$

The concentration of carbonic acid, H_2CO_3 is approximately 0.0012 *M*, and the concentration of the hydrogen carbonate ion, HCO_3^-, is around 0.024 *M*. Using the Henderson-Hasselbalch equation and the pK_a of carbonic acid at body temperature, we can calculate the pH of blood:

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{base}]}{[\mathrm{acid}]} = 6.1 + \log\frac{0.024}{0.0012} = 7.4$$

The fact that the H_2CO_3 concentration is significantly lower than that of the HCO_3^- ion may seem unusual, but this imbalance is due to the fact that most of the by-products of our metabolism that enter our bloodstream are acidic. Therefore, there must be a larger proportion of base than acid, so that the capacity of the buffer will not be exceeded.

Lactic acid is produced in our muscles when we exercise. As the lactic acid enters the bloodstream, it is neutralized by the HCO_3^- ion, producing H_2CO_3. An enzyme then accelerates the breakdown of the excess carbonic acid to carbon dioxide and water, which can be eliminated by breathing. In fact, in addition to the regulating effects of the carbonate buffering system on the pH of blood, the body uses breathing to regulate blood pH. If the pH of the blood decreases too far, an increase in breathing removes CO_2 from the blood through the lungs driving the equilibrium reaction such that $[H_3O^+]$ is lowered. If the blood is too alkaline, a lower breath rate increases CO_2 concentration in the blood, driving the equilibrium reaction the other way, increasing $[H^+]$ and restoring an appropriate pH.

Career Focus: Blood Bank Technology Specialist

At this point in this text, you should have the idea that the chemistry of blood is fairly complex. Because of this, people who work with blood must be specially trained to work with it properly.

A blood bank technology specialist is trained to perform routine and special tests on blood samples from blood banks or transfusion centers. This specialist measures the pH of blood, types it (according to the blood's ABO+/− type, Rh factors, and other typing schemes), tests it for the presence or absence of various diseases, and uses the blood to determine if a patient has any of several medical problems, such as anemia. A blood bank technology specialist may also interview and prepare donors to give blood and may actually collect the blood donation.

Blood bank technology specialists are well trained. Typically, they require a college degree with at least a year of special training in blood biology and chemistry. In the United States, training must conform to standards established by the American Association of Blood Banks.

Key Takeaway

- A buffer is a solution that resists sudden changes in pH.

Concept Review Exercise

1. Explain how a buffer prevents large changes in pH.

Answer

1. A buffer has components that react with both strong acids and strong bases to resist sudden changes in pH.

Exercises

1. Describe a buffer. What two related chemical components are required to make a buffer?
2. Can a buffer be made by combining a strong acid with a strong base? Why or why not?
3. Which solute combinations can make a buffer? Assume all are aqueous solutions.
    1. HCl and NaCl
    2. HNO_2 and $NaNO_2$
    3. NH_4NO_3 and HNO_3
    4. NH_4NO_3 and NH_3
4. Which solute combinations can make a buffer? Assume all are aqueous solutions.
    1. H_3PO_4 and Na_3PO_4
    2. $NaHCO_3$ and Na_2CO_3
    3. $NaNO_3$ and $Ca(NO_3)_2$
    4. HN_3 and NH_3
5. For each combination in Exercise 3 that is a buffer, write the chemical equations for the reactions of the buffer components when a strong acid and a strong base is added.
6. For each combination in Exercise 4 that is a buffer, write the chemical equations for the reaction of the buffer components when a strong acid and a strong base is added.
7. The complete phosphate buffer system is based on four substances: H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}. What different buffer solutions can be made from these substances?

8. Explain why NaBr cannot be a component in either an acidic or a basic buffer.
9. Explain why $Mg(NO_3)_2$ cannot be a component in either an acidic or a basic buffer.

Answers

1. A buffer resists sudden changes in pH. It has a weak acid or base and a salt of that weak acid or base.
2. No. Combining a strong acid and a strong base will produce salt and water. Excess strong acid or strong base will not act as a buffer.
3. 1. not a buffer
   2. buffer
   3. not a buffer
   4. buffer

4. 1. not a buffer

2. buffer

3. not a buffer

4. not buffer

5. 3b: strong acid: $H^+ + NO_2^- \rightarrow HNO_2$; strong base: $OH^- + HNO_2 \rightarrow H_2O + NO_2^-$; 3d: strong acid: $H^+ + NH_3 \rightarrow NH_4^+$; strong base: $OH^- + NH_4^+ \rightarrow H_2O + NH_3$
6. 4b: strong acid: $H^+ + CO_3^{2-} \rightarrow HCO3^-$; strong base: $OH^- + HCO_3^- \rightarrow H_2O + CO_3^{2-}$;
7. Buffers can be made by combining H_3PO_4 and $H_2PO_4^-$, $H_2PO_4^-$ and HPO_4^{2-}, and HPO_4^{2-} and PO_4^{3-}.
8. NaBr splits up into two ions in solution, Na^+ and Br^-. Na^+ will not react with any added base knowing that NaOH is a strong base. Br- will not react with any added acid knowing that HBr is a strong acid. Because NaBr will not react with any added base or acid, it does not resist change in pH and is not a buffer.
9. $Mg(NO_3)_2$ includes two types of ions, Mg^{2+} and NO_3^-. $Mg(OH)_2$ is strong base and completely dissociates (100% falls apart), so Mg^{2+} will not react with any added base (0% combines with OH^-). $HNO_3$is strong acid and completely dissociates (100% falls apart), so NO_3^- will not react with any added acid (0% combines with H^+). Because $Mg(NO_3)_2$ will not react with any added base or acid, it does not resist change in pH and is not a buffer.

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7.E: Acids and Bases (Exercises)

10.1: Arrhenius Definition of Acids and Bases

Concept Review Exercises

1. Give the Arrhenius definitions of an acid and a base.
2. What is neutralization?

Answers

1. Arrhenius acid: a compound that increases the concentration of hydrogen ion (H^+) in aqueous solution; Arrhenius base: a compound that increases the concentration of hydroxide ion (OH^-) in aqueous solution.
2. the reaction of an acid and a base

Exercises

1. Give two examples of Arrhenius acids.
2. Give two examples of Arrhenius bases.
3. List the general properties of acids.
4. List the general properties of bases.
5. Name each compound. (For acids, look up the name in Table 10.1.1. For bases, use the rules for naming ionic compounds from Chapter 3.)

    a. HBr(aq)

    b. $Ca(OH)_2$(aq)

    c. HNO_3(aq)

    d. $Fe(OH)_3$(aq)

6. Name each compound.

    a. HI(aq)

    b. $Cu(OH)_2$(aq)

    c. H_3PO_4(aq)

    d. CsOH(aq)

7. Write a balanced chemical equation for the neutralization of $Ba(OH)_2$(aq) with HNO_3(aq).

8. Write a balanced chemical equation for the neutralization of H_2SO_4(aq) with $Cr(OH)_3$(aq).

9. Gastric juice, the digestive fluid produced in the stomach, contains hydrochloric acid, HCl. Milk of Magnesia, a suspension of solid $Mg(OH)_2$ in an aqueous medium, is sometimes used to neutralize excess stomach acid. Write a complete balanced equation for the neutralization reaction.

10. Identify the salt produced in each acid-base reaction below. Then, balance the equation.

    a. $2HCl + Sr(OH)_2 \rightarrow 2H_2O$ + ??

    b. KNO_3; $HNO_3 + KOH \rightarrow$?? + H_2O

    c. $HF + Ca(OH)_2$ ---> ?? + H_2O

11. How many moles of sodium hydroxide (NaOH) are needed to neutralize 0.844 mol of acetic acid ($HC_2H_3O_2$)? (Hint: begin by writing a balanced chemical equation for the process.)

12. How many moles of perchloric acid ($HClO_4$) are needed to neutralize 0.052 mol of calcium hydroxide [$Ca(OH)_2$]? (Hint: begin by writing a balanced chemical equation for the process

13. Hydrazoic acid (HN_3) can be neutralized by a base.

a. Write the balanced chemical equation for the reaction between hydrazoic acid and calcium hydroxide.

b. How many milliliters of 0.0245 M $Ca(OH)_2$ are needed to neutralize 0.564 g of HN_3?

14. Citric acid ($H_3C_6H_5O_7$) has three hydrogen atoms that can form hydrogen ions in solution.

a. Write the balanced chemical equation for the reaction between citric acid and sodium hydroxide.

b. If an orange contains 0.0675 g of $H_3C_6H_5O_7$, how many milliliters of 0.00332 M NaOH solution are needed to neutralize the acid?

15. Magnesium hydroxide [$Mg(OH)_2$] is an ingredient in some antacids. How many grams of $Mg(OH)_2$ are needed to neutralize the acid in 158 mL of 0.106 M HCl(aq)? It might help to write the balanced chemical equation first.

16. Aluminum hydroxide [$Al(OH)_3$] is an ingredient in some antacids. How many grams of $Al(OH)_3$ are needed to neutralize the acid in 96.5 mL of 0.556 M H_2SO_4(aq)? It might help to write the balanced chemical equation first.

17. Write the balanced chemical equation for the reaction between HBr and $Ca(OH)_2$. What volume of 0.010 M HBr solution is be required to neutralize 25 mL of a 0.0100*M* $Ca(OH)_2$ solution?

18. Write the balanced chemical equation for the reaction between HNO_3 and KOH. What volume of 0.5M HNO_3 is required to neutralize 60 mL of 0.4M KOH solution?

Answers

1. HCl and HNO_3 (answers will vary)
2. NaOH and $Ca(OH)_2$ (answers will vary)
3. sour taste, react with metals, react with bases, and turn litmus red
4. bitter taste, feels slippery, react with acids and turn litmus blue
5. a. hydrobromic acid

b. calcium hydroxide

c. nitric acid

d. iron(III) hydroxide

6. a. hydroiodic acid

b. cupric hydroxide

c. phosphoric acid

d. cesium hydroxide

7. $2HNO_3(aq) + Ba(OH)_2(aq) \rightarrow Ba(NO_3)_2(aq) + 2H_2O$

8. $3H_2SO_4(aq) + 2Cr(OH)_3(aq) \rightarrow Cr_2(SO_4)_3(aq) + 6H_2O$

9. $Mg(OH)_2 + 2HCl$ --> $MgCl_2 + 2H_2O$

10. a. $SrCl_2$; $2HCl + Sr(OH)_2 \rightarrow 2H_2O + SrCl_2$

b. KNO_3; $HNO_3 + KOH \rightarrow KNO_3 + H_2O$

c. CaF_2; $2HF + Ca(OH)_2 \rightarrow CaF_2 + 2H_2O$

11. 0.844 mol

12. 0.104 mol

13. Part 1: $2HN_3(aq) + Ca(OH)_2 \rightarrow Ca(N_3)_2 + 2H_2O$

Part 2: 268 mL

14. Part 1: $H_3C_6H_5O_7(aq) + 3NaOH(aq) \rightarrow Na_3C_6H_5O_7(aq) + 3H_2O$

Part 2: 317.5 mL

15. 0.488 g

16. 2.79 g

17. $2HBr + Ca(OH)_2 \rightarrow CaBr_2 + 2H_2O$; 50 mL HBr

18. $HNO_3 + KOH \rightarrow KNO_3 + H_2O$; 48 mL HNO_3

10.2: Brønsted-Lowry Definition of Acids and Bases

Concept Review Exercise

1. Give the definitions of a Brønsted-Lowry acid and a Brønsted-Lowry base.

Answer

1. A Brønsted-Lowry acid is a proton donor, while a Brønsted-Lowry base is a proton acceptor.

Exercises

1. Label each reactant as a Brønsted-Lowry acid or a Brønsted-Lowry base.

   $HCl(aq) + NH_3(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$

2. Label each reactant as a Brønsted-Lowry acid or a Brønsted-Lowry base.

   $H_2O(\ell) + N_2H_4(aq) \rightarrow N_2H_5^+(aq) + OH^-(aq)$

3. Explain why a Brønsted-Lowry acid can be called a proton donor.
4. Explain why a Brønsted-Lowry base can be called a proton acceptor.
5. Write the chemical equation of the reaction of ammonia in water and label the Brønsted-Lowry acid and base.
6. Write the chemical equation of the reaction of methylamine (CH_3NH_2) in water and label the Brønsted-Lowry acid and base.
7. Demonstrate that the dissolution of HNO_3 in water is actually a Brønsted-Lowry acid-base reaction by describing it with a chemical equation and labeling the Brønsted-Lowry acid and base.
8. Identify the Brønsted-Lowry acid and base in the following chemical equation:

   $C_3H_7NH_2(aq) + H_3O^+(aq) \rightarrow C_3H_7NH_3^+(aq) + H_2O(\ell)$

9. Identify the Brønsted-Lowry acid and the Brønsted-Lowry base in each of the following equations

   1. $NO_2^- + H_2O \longrightarrow HNO_2 + OH^-$
   2. $HBr + H_2O \longrightarrow H_3O^+ + Br^-$
   3. $HS^- + H_2O \longrightarrow H_2S + OH^-$
   4. $H_2PO_4^- + OH^- \longrightarrow HPO_4^{2-} + H_2O$
   5. $H_2PO_4^- + HCl \longrightarrow H_3PO_4 + Cl^-$

10. Write the chemical equation for the reaction that occurs when cocaine hydrochloride ($C_{17}H_{22}ClNO_4$) dissolves in water and donates a proton to a water molecule. (When hydrochlorides dissolve in water, they separate into chloride ions and the appropriate cation.)

11. If codeine hydrobromide has the formula $C_{18}H_{22}BrNO_3$, what is the formula of the parent compound codeine?

Answers

1. HCl: Brønsted-Lowry acid; NH_3: Brønsted-Lowry base
2. H_2O: Brønsted-Lowry acid; N_2H_4: Brønsted-Lowry base
3. A Brønsted-Lowry acid gives away an H^+ ion—nominally, a proton—in an acid-base reaction.
4. A Brønsted-Lowry base accepts an H^+ ion (a proton) in an acid-base reaction.
5. $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$ (here NH_3= Brønsted-Lowry base; H_2O = Brønsted-Lowry acid)
6. $CH_3NH_2 + H_2O \rightarrow CH_3NH_3^+ + OH^-$ (here CH_3NH_2= Brønsted-Lowry base; H_2O = Brønsted-Lowry acid)
7. $HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$ (here HNO_3 = Brønsted-Lowry acid; H_2O = Brønsted-Lowry base)

8. $C_3H_7NH_2(aq) + H_3O^+(aq) \rightarrow C_3H_7NH_3^+(aq) + H_2O(\ell)$ (here H_3O^+ = Brønsted-Lowry acid; $C_3H_7NH_2$ = Brønsted-Lowry base)

10.3: Water - Both an Acid and a Base

Concept Review Exercises

1. Explain how water can act as an acid.
2. Explain how water can act as a base.

Answers

1. Under the right conditions, H_2O can donate a proton, making it a Brønsted-Lowry acid.
2. Under the right conditions, H_2O can accept a proton, making it a Brønsted-Lowry base.

Exercises

1. Is $H_2O(\ell)$ acting as an acid or a base?

   $H_2O(\ell) + NH_4^+(aq) \rightarrow H_3O^+(aq) + NH_3(aq)$

2. Is $H_2O(\ell)$ acting as an acid or a base?

   $CH_3^-(aq) + H_2O(\ell) \rightarrow CH_4(aq) + OH^-(aq)$

3. In the aqueous solutions of some salts, one of the ions from the salt can react with water molecules. In some $C_2H_3O_2^-$ solutions, the following reaction can occur:

   $C_2H_3O_2^-(aq) + H_2O(\ell) \rightarrow HC_2H_3O_2(aq) + OH^-(aq)$

   Is H_2O acting as an acid or a base in this reaction?

4. In the aqueous solutions of some salts, one of the ions from the salt can react with water molecules. In some NH_4^+ solutions, the following reaction can occur:

   $NH_4^+(aq) + H_2O \rightarrow NH_3(aq) + H_3O^+(aq)$

   Is H_2O acting as an acid or a base in this reaction?

5. Why is pure water considered neutral?

Answers

1. base
2. acid
3. acid
4. base

5. When water ionizes, equal amounts of H^+ (acid) and OH^- (base) are formed, so the solution is neither acidic nor basic: $H_2O(\ell) \rightarrow H^+(aq) + OH^-(aq)$

10.4: The Strengths of Acids and Bases

Concept Review Exercises

1. Explain the difference between a strong acid or base and a weak acid or base.
2. Explain what is occurring when a chemical reaction reaches equilibrium.
3. Define *pH*.

AnswerS

1. A strong acid or base is 100% ionized in aqueous solution; a weak acid or base is less than 100% ionized.
2. The overall reaction progress stops because the reverse process balances out the forward process.
3. pH is a measure of the hydrogen ion concentration.

Exercises

1. Name a strong acid and a weak acid. (Hint: use Table 10.4.1.)
2. Name a strong base and a weak base. (Hint: use Table 10.4.1.)
3. Is each compound a strong acid or a weak acid? Assume all are in aqueous solution. (Hint: use Table 10.4.1.)
    1. HF
    2. $HC_2H_3O_2$
    3. HCl
    4. $HClO_4$
4. Is each compound a strong acid or a weak acid? Assume all are in aqueous solution. (Hint: use Table 10.4.1.)
    1. H_2SO_4
    2. HSO_4^-
    3. HPO_4^{2-}
    4. HNO_3
5. Is each compound a strong base or a weak base? Assume all are in aqueous solution. (Hint: use Table 10.4.1.)
    1. NH_3
    2. NaOH
    3. $Mg(OH)_2$
    4. $Cu(OH)_2$
6. Is each compound a strong base or a weak base? Assume all are in aqueous solution. (Hint: use Table 10.4.1.)
    1. KOH
    2. H_2O
    3. $Fe(OH)_2$
    4. $Fe(OH)_3$
7. Write the chemical equation for the equilibrium process for each weak acid in Exercise 3.
8. Write the chemical equation for the equilibrium process for each weak acid in Exercise 4.
9. Write the chemical equation for the equilibrium process for each weak base in Exercise 5.
10. Write the chemical equation for the equilibrium process for each weak base in Exercise 6.
11. Which is the stronger acid—HCl(aq) or HF(aq)?
12. Which is the stronger base—KOH(aq) or $Ni(OH)_2$(aq)?
13. Consider the two acids in Exercise 11. For solutions that have the same concentration, which one would you expect to have a lower pH?
14. Consider the two bases in Exercise 12. For solutions that have the same concentration, which one would you expect to have a higher pH?
15. Consider the list of substances in Table \PageIndex3\PageIndex3.2"The pH Values of Some Common Solutions". What is the most acidic substance on the list that you have encountered recently?
16. Consider the list of substances in Table \PageIndex3\PageIndex3.2"The pH Values of Some Common Solutions". What is the most basic substance on the list that you have encountered recently?
17. Indicate whether solutions with the following pH values are acidic, basic, or neutral:
    1. pH = 9.4
    2. pH = 7.0
    3. pH = 1.2
    4. pH = 6.5

Answers

1. strong acid: HCl; weak acid: $HC_2H_3O_2$ (answers will vary)
2. strong base: NaOH; weak base: NH_3 (answers will vary)
3. 1. weak
    2. weak

3. strong
4. strong

4. 1. strong
2. weak
3. weak
4. strong

5. 1. weak
2. strong
3. strong
4. weak

6. 1. strong
2. weak
3. weak
4. weak

7. 3a: $HF(aq) \leftrightarrows H^+(aq) + F^-(aq)$; 3b: $HC_2H_3O_2(aq) \leftrightarrows H^+(aq) + C_2H_3O_2^-(aq)$

8. 4b: $HSO_4^-(aq) \leftrightarrows H^+(aq) + SO_4^{2-}(aq)$; 4c: $HPO_4^{2-}(aq) \leftrightarrows H^+(aq) + PO_4^{3-}(aq)$

9. 5a: $NH_3(aq) + H_2O \leftrightarrows NH_4^+(aq) + OH^-(aq)$; 5d: $Cu(OH)_2(aq) \leftrightarrows Cu^{2+}(aq) + 2OH^-(aq)$

10. 6b: $H_2O + H_2O \leftrightarrows H_3O^+(aq) + OH^-(aq)$; 6c: $Fe(OH)_2(aq) \leftrightarrows Fe^{2+}(aq) + 2OH^-(aq)$; 6d: $Fe(OH)3(aq) \leftrightarrows Fe^{3+}(aq) + 3OH^-(aq)$

11. HCl(aq)

12. KOH(aq)

13. HCl(aq)

14. KOH(aq)

15. (answers will vary)

16. (answers will vary)

17. 1. basic

2. neutral

3. acidic (strongly)

4. acidic (mildly)

10.5: Buffers

Concept Review Exercise

1. Explain how a buffer prevents large changes in pH.

Answer

1. A buffer has components that react with both strong acids and strong bases to resist sudden changes in pH.

Exercises

1. Describe a buffer. What two related chemical components are required to make a buffer?
2. Can a buffer be made by combining a strong acid with a strong base? Why or why not?
3. Which solute combinations can make a buffer? Assume all are aqueous solutions.
    1. HCl and NaCl
    2. HNO_2 and $NaNO_2$
    3. NH_4NO_3 and HNO_3

4. NH_4NO_3 and NH_3

4. Which solute combinations can make a buffer? Assume all are aqueous solutions.
    1. H_3PO_4 and Na_3PO_4
    2. $NaHCO_3$ and Na_2CO_3
    3. $NaNO_3$ and $Ca(NO_3)_2$
    4. HN_3 and NH_3
5. For each combination in Exercise 3 that is a buffer, write the chemical equations for the reactions of the buffer components when a strong acid and a strong base is added.
6. For each combination in Exercise 4 that is a buffer, write the chemical equations for the reaction of the buffer components when a strong acid and a strong base is added.
7. The complete phosphate buffer system is based on four substances: H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}. What different buffer solutions can be made from these substances?
8. Explain why NaBr cannot be a component in either an acidic or a basic buffer.
9. Explain why $Mg(NO_3)_2$ cannot be a component in either an acidic or a basic buffer.

Answers

1. A buffer resists sudden changes in pH. It has a weak acid or base and a salt of that weak acid or base.
2. No. Combining a strong acid and a strong base will produce salt and water. Excess strong acid or strong base will not act as a buffer.
3. 1. not a buffer
    2. buffer
    3. not a buffer
    4. buffer

4. 1. not a buffer

2. buffer

3. not a buffer

4. not buffer

5. 3b: strong acid: $H^+ + NO_2^- \rightarrow HNO_2$; strong base: $OH^- + HNO_2 \rightarrow H_2O + NO_2^-$; 3d: strong acid: $H^+ + NH_3 \rightarrow NH_4^+$; strong base: $OH^- + NH_4^+ \rightarrow H_2O + NH_3$
6. 4b: strong acid: $H^+ + CO_3^{2-} \rightarrow HCO3^-$; strong base: $OH^- + HCO_3^- \rightarrow H_2O + CO_3^{2-}$;
7. Buffers can be made by combining H_3PO_4 and $H_2PO_4^-$, $H_2PO_4^-$ and HPO_4^{2-}, and HPO_4^{2-} and PO_4^{3-}.
8. NaBr splits up into two ions in solution, Na^+ and Br^-. Na^+ will not react with any added base knowing that NaOH is a strong base. Br- will not react with any added acid knowing that HBr is a strong acid. Because NaBr will not react with any added base or acid, it does not resist change in pH and is not a buffer.
9. $Mg(NO_3)_2$ includes two types of ions, Mg^{2+} and NO_3^-. $Mg(OH)_2$ is strong base and completely dissociates (100% falls apart), so Mg^{2+} will not react with any added base (0% combines with OH^-). $HNO_3$is strong acid and completely dissociates (100% falls apart), so NO_3^- will not react with any added acid (0% combines with H^+). Because $Mg(NO_3)_2$ will not react with any added base or acid, it does not resist change in pH and is not a buffer.

Additional Exercises

1. The properties of a 1.0 M HCl solution and a 1.0 M $HC_2H_3O_2$ solution are compared. Measurements show that the hydrochloric acid solution has a higher osmotic pressure than the acetic acid solution. Explain why.
2. Of a 0.50 M HNO_3 solution and a 0.50 M $HC_2H_3O_2$ solution, which should have the higher boiling point? Explain why.
3. The reaction of sulfuric acid [$H_2SO_4(aq)$] with sodium hydroxide [NaOH(aq)] can be represented by two separate steps, with only one hydrogen ion reacting in each step. Write the chemical equation for each step.
4. The reaction of aluminum hydroxide [$Al(OH)_3(aq)$] with hydrochloric acid [HCl(aq)] can be represented by three separate steps, with only one hydroxide ion reacting in each step. Write the chemical equation for each step.

5. A friend brings you a small sample of an unknown chemical. Assuming that the chemical is soluble in water, how would you determine if the chemical is an acid or a base?
6. A neutral solution has a hydrogen ion concentration of about 1×10^{-7} M. What is the concentration of the hydroxide ion in a neutral solution?
7. The Lewis definitions of an acid and a base are based on electron pairs, not protons. A Lewis acid is an electron pair acceptor, while a Lewis base is an electron pair donor. Use Lewis diagrams to show that

   $H^+(aq) + OH^-(aq) \rightarrow H_2O(\ell)$

   is an acid-base reaction in the Lewis sense as well as in the Arrhenius and Brønsted-Lowry senses.

8. Given the chemical reaction

   $NH_3(g) + BF_3(g) \rightarrow NH_3—BF_3(s)$

   show that the reaction illustrated by this equation is an acid-base reaction if we use the Lewis definitions of an acid and a base (see Exercise 7). The product contains a bond between the N and B atoms.

Answers

1. HCl is a strong acid and yields more ions in solution. $HC_2H_3O_2$ is a weak acid and undergoes partial ionization in solution.
2. HNO_3 is a strong acid while $HC_2H_3O_2$ is a weak acid. HNO_3 dissociates 100% and its solution contains more ions. The more ions the solution contains the lower is its vapor pressure; the higher temperature is required for it to boil.
3. $H_2SO_4 + NaOH \rightarrow NaHSO_4 + H_2O$; $NaHSO_4 + NaOH \rightarrow Na_2SO_4 + H_2O$
4. $Al(OH)_3 + HCl \rightarrow Al(OH)_2Cl + H_2O$; $Al(OH)_2Cl + HCl \rightarrow Al(OH)Cl_2 + H_2O$; $Al(OH)Cl_2 + HCl \rightarrow AlCl3 + H_2O$
5. One way is to add it to $NaHCO_3$; if it bubbles, it is an acid. Alternatively, add the sample to litmus and look for a characteristic color change (red for acid, blue for base).
6. In a neutral solution, $[OH^-] = [H^+] = 1.0 \times 10^{-7}$ M
7. The O atom is donating an electron pair to the H^+ ion, making the base an electron pair donor and the acid an electron pair acceptor.
8. The N atom is donating a lone pair to B in BF_3, Hence NH_3 is the Lewis base and BF_3 is the Lewis acid.

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CHAPTER OVERVIEW

8: Biological Molecules

8.1: Introduction to Structure and Function

8.2: Building Blocks

8.3: Proteins

8.4: Nucleic Acids

8.5: Carbohydrates

8.6: Lipids and Membranes

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8.1: Introduction to Structure and Function

If we hope to understand function in biological systems, we must first understand structure. At a simple level, we can divide molecules up according to their affinities for water – hydrophobic (limited solubility in water), hydrophilic (soluble in water) and amphiphilic (have characteristics of both hydrophobicity and hydrophilicity). Hydrophobicity in biological molecules arises largely because carbon-hydrogen bonds have electrons that are fairly evenly shared (not unlike carbon-carbon bonds). By contrast, the electrons between the oxygen and hydrogen of water are not equally shared. Oxygen has a greater electronegativity, so it holds them closer than hydrogen does. As a consequence, oxygen has what we call a partial negative charge and hydrogen has a partial positive charge.

Virtually all of life on Earth is built upon the biochemistry that arises from the molecular properties described in the preceding paragraph. The biomolecules referred to as lipids are largely water insoluble because they have predominantly carbon-hydrogen bonds with few ionic or hydrogen bond characteristics.

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8.2: Building Blocks

Biological macromolecules are all polymers of a sort, even fats, in which the fatty acids can be thought of as polymers of carbon. (We will consider fatty compounds - fats, glycerophospholipids, sphingolipids, isoprenoids/terpenoids separately). The remaining categories of biological macromolecules include proteins, nucleic acids, and polysaccharides. The building blocks of these, respectively, are amino acids, nucleotides, and monosaccharides (sugars). Of these, the most diverse collection of chemical properties is found among the amino acids.

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8.3: Proteins

Whereas nucleotides all are water soluble and have the same basic composition (sugar, base, phosphate) and the sugars also are water soluble and mostly contain 5 or 6 carbons (a few exceptions), the amino acids (general structure below) are structurally and chemically diverse.

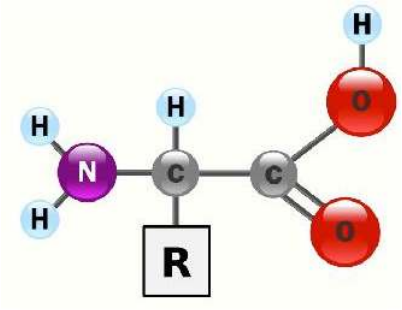


Figure 8.3.1: Amino Acid Schematic

Though all of the amino acids are, in fact, soluble in water, the interactions of their side chains with water differ significantly. This is important, because it is only in the side chains (R-groups) that amino acids differ from each other. Based on side chains, we can group the 20 amino acids found in proteins as follows:

- Aromatic (phenylalanine, tyrosine, tryptophan)
- Aliphatic (leucine, isoleucine, alanine, methionine, valine)
- Hydroxyl/Sulfhydryl (threonine, serine, tyrosine, cysteine)
- Carboxyamide (glutamine, asparagine)
- R-Acids (glutamic acid, aspartic acid)
- R-Amines (lysine, histidine, arginine)
- Odd (glycine, proline)

Note that tyrosine has a hydroxyl group and fits into two categories. Note also that biochemistry books vary in how they organize amino acids into categories. Amino acids are joined to each other by peptide bonds. This introduces a slight simplifying aspect to the structure of proteins – one need only consider the positioning of the R-groups around each peptide bond when determining protein structure schematically. Proteins that are in aqueous environments, such as the cytoplasm of the cell, have their amino acids arranged so that those with hydrophilic side chains (such as threonine or lysine) predominate on the exterior of the protein so as to interact with water. The hydrophobic amino acids in these proteins are found predominantly on the interior. When one examines the structure of proteins in non-aqueous environments, such as the interior of a lipid bilayer, the arrangement is flipped – hydrophobics predominate on the outside where they can interact with the hydrophobic side chains of membrane fatty acids and the hydrophilic amino acids are arranged anyplace where they can contact water. For a protein like porin, which provides an interior channel through which water can pass, this is where the hydrophilics are found. For transmembrane proteins, which project through both sides of the membrane, the hydrophilics are found at each point where the polypeptide chain emerges from the membrane.

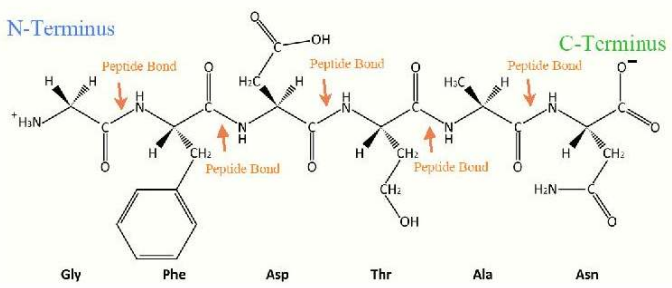


Figure 8.3.2: An image of the primary structure of a protein.

Primary Structure

How do proteins obtain such arrangements of amino acids? As we shall see, the structures of all proteins ultimately arise from their amino acid sequences. The amino acid sequence is referred to as the primary structure and changes in it can affect every other level of structure as well as the properties of a protein. The primary structure of a protein arrived at its current state as a result of mutation and selection over evolutionary time. On a more immediate time scale, 3D protein structure arises as a result of a phenomenon called folding. Protein folding results from three different structural elements beyond primary structure. They are referred to as secondary, tertiary, and quaternary structures, each arising from interactions between progressively more distant amino acids in the primary structure.

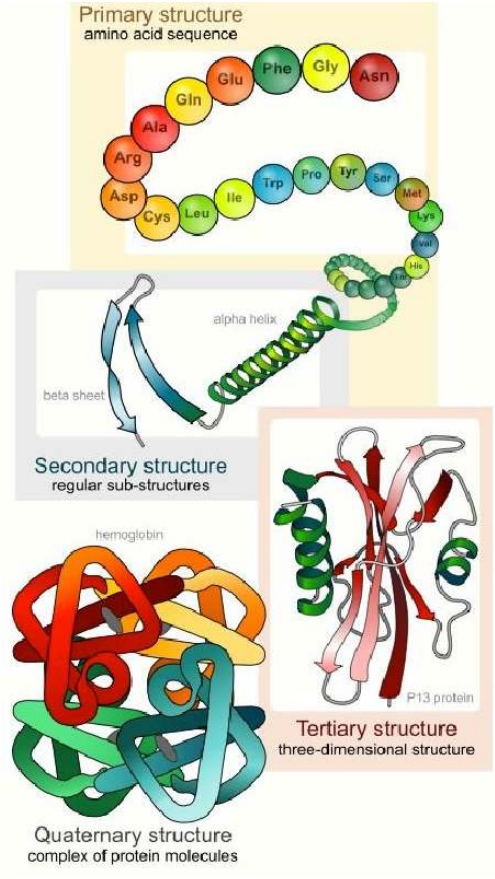


Figure 8.3.3: *Schematic of a protein.*

Secondary Structure

Interactions between amino acids within about ten units of each other give rise to regular repeating structures. These secondary structures include the well known alpha-helix and beta strands. Both were predicted by Linus Pauling, Robert Corey, and Herman Branson in 1951. Each structure has unique features. We use the terms rise, repeat, and pitch to describe the parameters of a helix. The repeat is the number of residues in a helix before it begins to repeat itself. The rise is the distance the helix elevates with addition of each residue. The pitch is the distance between the turns of the helix.

Alpha Helix

The alpha helix (Figure 8.3.3) forms as the result of interactions between amino acids separated by four residues. Interestingly, the side chains of the amino acids in an alpha helix are all pointed outwards from the axis of the helix. Alpha helices have a repeat of 3.6 amino acid residues per turn of the helix, meaning that four turns of the helix have approximately 14 amino acid residues. Hydrogen bonds occur between the C=O of one amino acid and the N-H of another amino acid four residues distant and these help to stabilize the structure (note that the C=O and N-H involved are part of the polypeptide backbone, not the R-groups). Some amino

acids have high helix forming tendencies. They include methionine, alanine, leucine, uncharged glutamate, and lysine. Others, such as proline, glycine, and negatively charged aspartate, disfavor its formation.

Beta Strands

Beta strands are the most fundamental helix, having essentially a 2D backbone of 'fold' like those of the pleats of a curtain. Indeed, beta strands can be arranged together to form what are called beta sheets. Other regular structures are also known. What determines whether a given stretch of a protein is in a helical or other structure? Here is where the shape and chemistry of the side chains play a role.

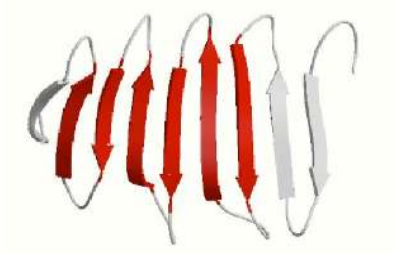


Figure 8.3.4: *A beta sheet.*

Fibrous Proteins

Not all proteins have significant amounts of tertiary or quaternary structure. (As we shall see, these last two levels of structure arise from 'bends' in polypeptide chains and interactions between separate polypeptide chains, respectively.)

Alpha keratin, for example, is what we refer to as a fibrous protein (also called scleroprotein). Alpha keratin has primary structure and secondary structure, but little tertiary or quaternary structure.

Consequently, alpha keratin exists mostly as long fibers, such as are found in hair. Beta-keratin is a harder fibrous protein found in nails, scales, and claws. It is made up mostly of beta sheets. Proline, which is the least flexible amino acid, due to attachment of the side chain to the alpha-amino grip, is less likely to be found in alpha helices, but curiously it is found abundantly in the fibrous protein known as collagen. Collagen (previous page) is the most abundant protein in the human body and is the 'glue' that literally sticks us together. How does the inflexibility of proline permit it to be in a helix? The answer is probably the parallel abundance in collagen of glycine, which contains the smallest side group and therefore has the greatest flexibility.

As an interesting sidelight of the presence of proline in collagen is the chemical modification of prolines, by the addition of hydroxyl groups, after the protein is made. Such 'post-translational modifications' are not uncommon. Threonine, serine, and tyrosine frequently have their hydroxyl side-chains phosphorylated. Lysines in collagen too are hydroxylated post-translationally. The hydroxylated prolines and lysines play a role in the formation of interchain hydrogen bonds and crosslinking of triple helices during the assembly of collagen fibrils. These bonds provide structural integrity to the collagen. The enzymes that add hydroxyls to proline and lysine require vitamin C (ascorbic acid) for their activity. Lack of vitamin C leads to the production of weakened collagen fibrils, resulting in a condition called scurvy.

The carbonyl oxygen of the peptide bond can exist in resonance with the C-N bond, giving the peptide bond characteristics of a double bond and imposing limitations for rotation around it. If we treat the peptide bond as a double bond, then the arrangements of adjacent carbon bonds around it can be thought of as being in the cis or trans configurations. In proteins, not surprisingly, the preferred arrangement of these groups is strongly trans (1000/1). Of the 20 amino acids, the one that favors peptide bonds in the cis configuration most commonly is proline, but even for proline, the trans isomer is strongly preferred.

Figure 3.2.5: *Collagen.*

Ramachandran Plots

Another consequence of considering the peptide bond as a double bond is that it reduces the number of variable rotational angles of the polypeptide backbone. The terms phi and psi refer to rotational angles about the bonds between the N-alpha carbon and alpha carbon-carbonyl carbon respectively (previous page). Given the bulkiness of R-groups, the phenomenon of steric hindrance and the tendency of close side chains to interact with each other, one might expect to find a bias in the values of phi and psi. Indeed, that is exactly what is observed. Dr. G.N. Ramachandran proposed such a result and, in a plot that bears his name, depicted the theoretical

likelihood of each angle appearing in a polypeptide. More recent observations of actual phi and psi angles in data from the PDB protein database bear out Dr. Ramachandran's predictions. In the plot above, beta strands fit nicely in the darker blue section at the top and alpha helices fit in the yellow section near the middle.

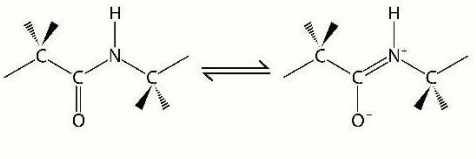


Figure 8.3.6: Peptide bond resonance.

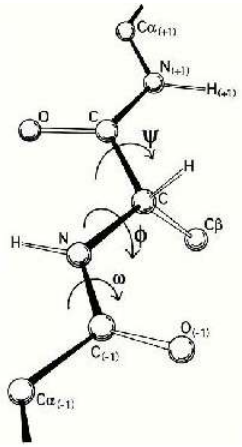


Figure 8.3.7: Phi and psi angles.

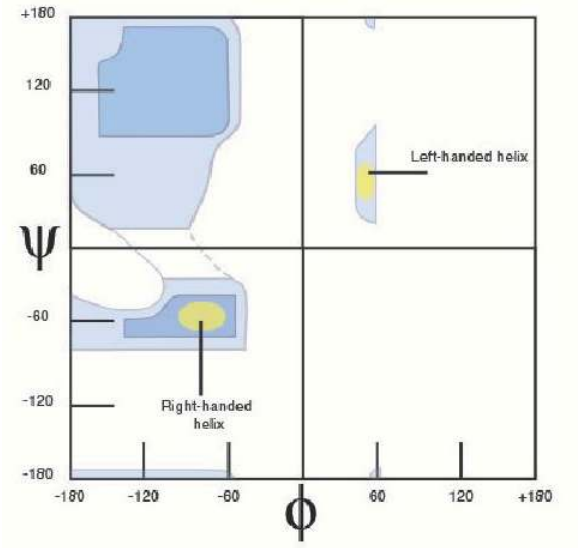


Figure 8.3.8: Ramachandran Plot.

Tertiary Structure

In contrast to secondary structures, which arise from interactions between amino acids close in primary structure, tertiary structure arises from interactions between amino acids more distant in primary structure. Such interactions are not possible in an endlessly stretching fiber because each amino acid placed between two amino acids causes them to be moved farther away from each other in what is essentially the two dimensions of a secondary structure. For distant amino acids to interact, they must be brought into closer proximity and this requires bending and folding of the polypeptide chain. Proteins with such structures are referred to as ‘globular’ and they are, by far, the most abundant class of proteins. Indeed, it is in globular proteins that we have the most vivid images of the results of folding. “Folds" in polypeptides arise as a result of ‘bends’ between regions of secondary structure (such as alpha helix or beta strands). Such structures may be preferred due to incompatibility of a given amino acid side chain for a secondary structure

formed by the amino acids preceding it. Bends occur commonly in proteins and proline is often implicated. Bends do not have the predictable geometry of alpha helices or beta strands and are often referred to as random coils. Thus, even though protein structure can be described easily as regions of secondary structure separated by bends, the variability of bend structures makes prediction of tertiary structure from amino acid sequence enormously more difficult than identifying/predicting regions of secondary structure.

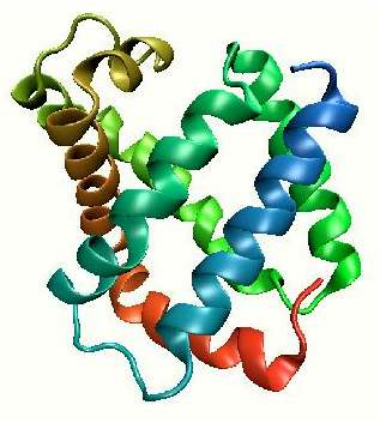


Figure 8.3.9: *The structure of Myoglobin*

Hydrophobic Effect

It is at the level of tertiary structure that the characteristic arrangement of hydrophobic and hydrophilic amino acids in a protein occurs. In an aqueous environment, for a protein to remain soluble, it must have favorable interactions with the water around it, hence, the positioning of hydrophilic amino acids externally. Another impetus for the folding phenomenon is a bit harder to understand. It is known as the hydrophobic effect. At a chemical level, it makes sense – hydrophobic amino acids will 'prefer' to interact with each other internally and away from water. The driving force for this phenomenon, though, is a bit more conceptually difficult. Consider a bottle containing oil and water. As everyone knows, the two liquids will not mix and instead will form separate layers. A reasonable question might be why they do this instead of one existing as tiny globules inside of the other. The answer to that question, as well as the positioning of hydrophobic amino acids in the interior of water soluble proteins, is the hydrophobic effect. To understand the hydrophobic effect, perform the followingexperiment – take the water-oil mixture and shake it vigorously. This will force the layers to mix and one will observe that tiny globules of both water and oil can, in fact, be found initially in the layer of each. Over time, though, the tiny globules break up and merge with the appropriate layer. This is due to the phenomenon of entropy and consideration of surface area. First, the sum of the surface area of the embedded tiny globs is far greater than the area of the region between the two layers after mixing is over. The smaller the globs, the more the surface area of interaction between the oil and the water. The minimum possible surface area of interaction occurs when there are no globs at all – just two layers and nothing else.



Figure 8.3.10: *A hydrophobic effect causes the water on this leaf to assume a spherical shape.*

How does this relate to entropy? Interactions between the water-hydrophobic layers causes the molecules at the interface to arrange themselves precisely/regularly so as to minimize their interactions. Ordering thus occurs at the layer interfaces. The maximum amount of ordering occurs when the maximum surface areas of oil and water interact. Small globules give rise to more exposed surface area between the water and hydrophobic layers and, as a consequence, more ordering. Since entropy in a closed system tends to increase, it will tend to reduce the amount of ordering, if left alone. Thus, one can increase the ordering on a nanoscopic

scale (forming globules) by applying energy in the form of shaking. When left alone, however, the system will increase its disorder by reducing the interactions between hydrophobic groups and hydrophilic ones.

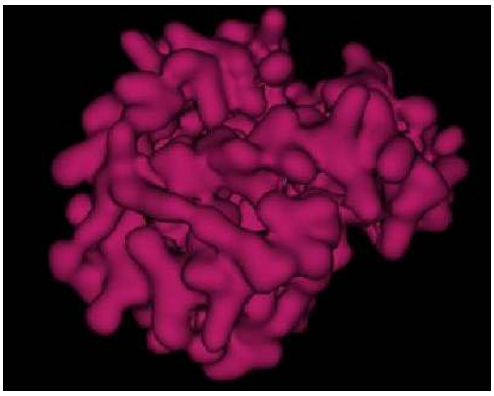


Figure 8.3.11: Oxygenated Myoglobin.

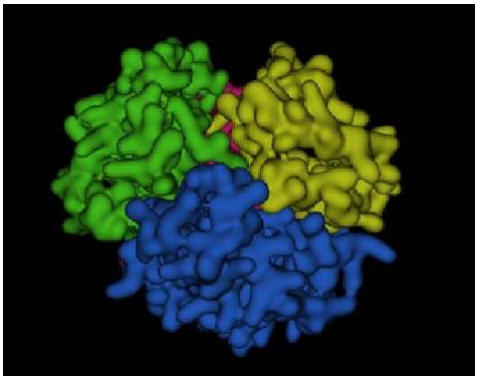


Figure 8.3.12: *Hemoglobin in the absence of oxygen.*

In the oil water mixture, this causes the tiny globs to break up and produce the two layers we are familiar with because this is the minimum surface area that can be made between the two layers and thus the least ordering. In proteins, hydrophobic amino acid side chains are 'shielded' from water by placement internal to the protein, thus also reducing interfaces between hydrophobic residues and water. In both cases, entropy is increased, due to the reduced organization of the layers. Once formed, the interactions between the hydrophobic amino acid side chains helps to stabilize the overall protein structure.

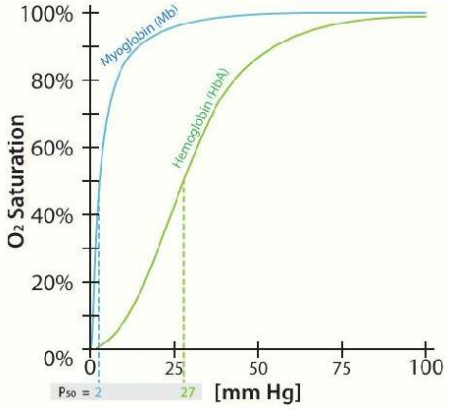


Figure 8.3.13

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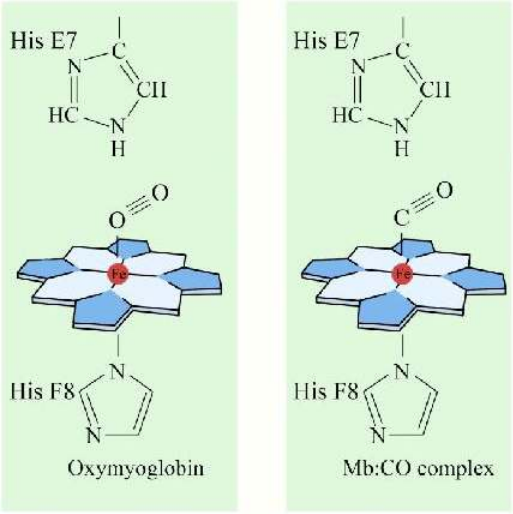


Figure 8.3.14: *Oxygen and Carbon Monoxide binding to heme.*

Quaternary Structure

The last level of protein structure we will consider is that of quaternary structure. In order to have quaternary structure, a protein must have multiple polypeptide subunits because the structure involves the arrangement of those subunits with respect to each other. Consider hemoglobin, the oxygen-carrying protein of our blood. It contains two identical subunits known as alpha and two other identical ones known as beta. These are arranged together in a fashion as shown on the previous page. By contrast, the related oxygen storage protein known as myoglobin only contains a single subunit. Hemoglobin has quaternary structure, but myoglobin does not. Multiple subunit proteins are common in cells and they give rise to very useful properties not found in single subunit proteins. In the case of hemoglobin, the multiple subunits confer the property of cooperativity – variable affinity for oxygen depending on the latter's concentration. In the case of enzymes, it can impart allosterism – the ability to have the activity of the enzyme altered by interaction with an effector molecule. We will discuss allosterism in detail in the next chapter.

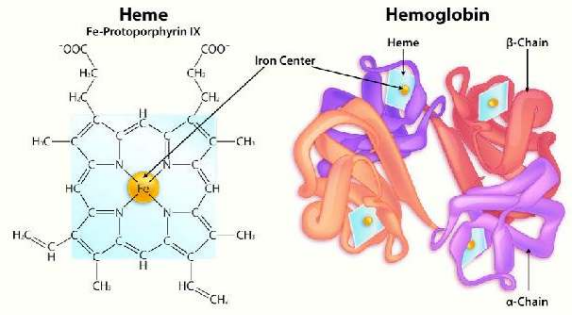


Figure 8.3.15: *Hemoglobin.*

Other Protein Structural Features

Not everything found in a protein is an amino acid. Proteins frequently have other chemical groups, known as prosthetic groups, bound to them, that are necessary for the function of a protein. Examples include the porphyrin ring of heme in myoglobin and hemoglobin that carries an iron so that oxygen can be bound. Metals are frequently employed by enzymes in their catalysis. Several vitamins (referred to as coenzymes), such as thiamine (B1) and riboflavin(B2) are modified and chemically bound to enzymes to help them perform specific catalytic functions.

Cooperativity

An interesting and important aspect of some proteins is the phenomenon of cooperativity. Cooperativity refers to the fact that binding of one ligand molecule by a protein favors the binding of additional molecules of the same type. Hemoglobin, for example, exhibits cooperativity when the binding of an oxygen molecule by the iron of the heme group in one of the four subunits causes a

slight conformation change in the subunit. This happens because the heme iron is attached to a histidine side chain and binding of oxygen 'lifts' the iron along with the histidine ring (also known as the imidazole ring).

Since each hemoglobin subunit interacts with and influences the other subunits, they too are induced to change shape slightly when the first subunit binds to oxygen (a transition described as going from the T-state to the R-state). These shape changes favor each of the remaining subunits binding oxygen, as well. This is very important in the lungs where oxygen is picked up by hemoglobin, because the binding of the first oxygen molecule facilitates the rapid uptake of more oxygen molecules. In the tissues, where the oxygen concentration is lower, the oxygen leaves hemoglobin and the proteins .ips from the R-state back to the T-state.

Cooperativity is only one of many fascinating structural aspects of hemoglobin that help the body to receive oxygen where it is needed and pick it up where it is abundant. Hemoglobin also assists in the transport of the product of cellular respiration (carbon dioxide) from the tissues producing it to the lungs where it is exhaled. Let us consider these individually.

Bohr Effect

The Bohr Effect was first described over 100 years ago by Christian Bohr. Shown graphically (above left), the observed effect is that hemoglobin's affinity for oxygen decreases as the pH decreases and/or as the concentration of carbon dioxide increases. Binding of the protons by histidine helps to facilitate structural changes in the protein and also with the uptake of carbon dioxide. Physiologically, this has great significance because actively respiring tissues (such as contracting muscles) require oxygen and release protons and carbon dioxide. The higher the concentration of protons and carbon dioxide, the more oxygen is released to feed the tissues that need it most.

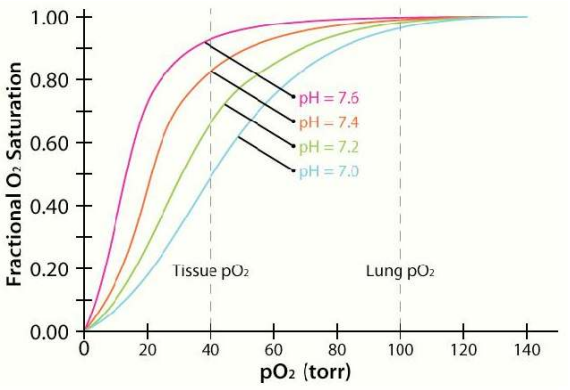


Figure 8.3.16: *The Bohr Effect.*

2,3 BPG

Another molecule affecting the release of oxygen by hemoglobin is 2,3 bisphosphoglycerate (also called 2,3 BPG or just BPG). Like protons and carbon dioxide, 2,3 BPG is produced by actively respiring tissues, as a byproduct of glucose metabolism. The 2,3 BPG molecule fits into the 'hole of the donut' of adult hemoglobin. Such binding of 2,3 BPG favors the T (tight) state of hemoglobin, which has a reduced affinity for oxygen. In the absence of 2,3 BPG, hemoglobin can exist in the R (relaxed) state, which has a high affinity for oxygen.

Fetal Hemoglobin

Adult hemoglobin releases oxygen when it binds 2,3 BPG. This is in contrast to fetal hemoglobin, which has a slightly different configuration (α2Γ2) than adult hemoglobin (α2ß). Fetal hemoglobin has a greater affinity for oxygen than maternal hemoglobin, allowing the fetus to obtain oxygen effectively from the mother's blood. Part of the reason for fetal hemoglobin's greater affinity for oxygen is that it doesn't bind 2,3 BPG.

Another significant fact about 2,3 BPG is that its concentration is higher in the blood of smokers than it is of non-smokers. Consequently, hemoglobin in a smoker's blood spends more time in the T state than the R state. That is a problem when it is in the lungs, where being in the R state is necessary to maximally load the hemoglobin with oxygen. A high blood level of 2,3 BPG is one of the reasons smokers have trouble breathing when they exercise – they have reduced oxygen carrying capacity.

Last, though it is not related directly to 2,3 BPG, smokers have another reason why their oxygen carrying capacity is lower than that of non-smokers. Cigarette smoke contains carbon monoxide and this molecule, which has almost identical dimensions to molecular oxygen, competes effectively with oxygen for binding to the iron atom of heme. Part of carbon monoxide's toxicity is due to its ability to bind hemoglobin and prevent oxygen from binding.

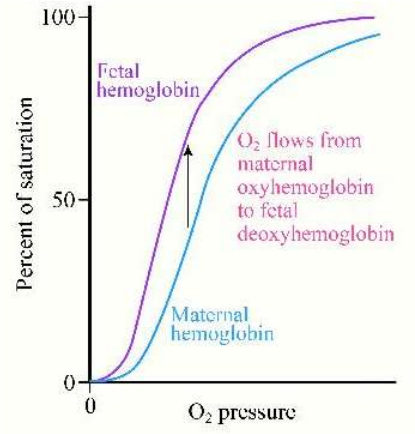


Figure 8.3.17*: Fetal hemoglobin binding of oxygen.*

Denaturation

For proteins, function is dependent on precise structure. Loss of the precise, folded structure of a protein is known as denaturation and is usually accompanied by loss of function. Anyone who has ever worked to purify an enzyme knows how easy it is for one to lose its activity. A few enzymes, such as ribonuclease, are remarkably stable under even very harsh conditions. For most others, a small temperature or pH change can drastically affect activity. The reasons for these differences vary, but relate to 1) the strength of the forces holding the structure together and 2) the ability of a protein to refold itself after being denatured. Let us consider these separately below.

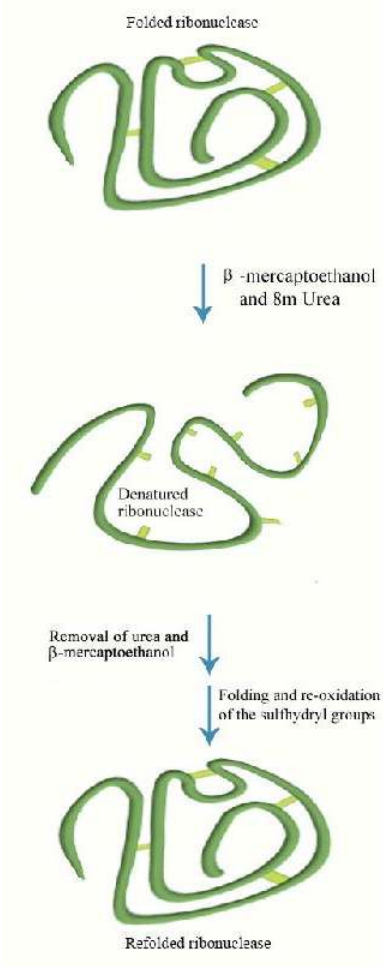


Figure 8.3.18: *Denaturation and renaturation of ribonuclease.*

Forces Stabilizing Structures

Amino acids are linked one to the other by peptide bonds. These covalent bonds are extraordinarily stable at neutral pHs, but can be broken by hydrolysis with heat under acidic conditions. Peptide bonds, however, only stabilize primary structure and, in fact, are the only relevant force responsible for it. Secondary structure, on the other hand, is generally stabilized by weaker forces, including hydrogen bonds. Hydrogen bonds are readily disrupted by heat, urea, or guanidinium chloride.

Forces stabilizing tertiary structure include ionic interactions, disulfide bonds, hydrophobic interactions, metallic bonds, and hydrogen
bonds. Of these, the ionic interactions are most sensitive to pH changes. Hydrophobic bonds are most sensitive to detergents. Thus, washing one's hands helps to kill bacteria by denaturing critical proteins they need to survive. Metallic bonds are sensitive to oxidation/reduction. Breaking disulfide bonds requires either a strong oxidizing agent, such as performic acid or a strong reducing agent
on another disulfide, such as mercaptoethanol or dithiothreitol.

Quaternary structures are stabilized by the same forces as tertiary structure and have the same sensitivities.

Refolding Denatured Proteins

All of the information for protein folding is contained in the primary structure of the protein. It may seem curious then that most proteins do not refold into their proper, fully active form after they have been denatured and the denaturant is removed. A few do, in fact, refold correctly under these circumstances. A good example is bovine ribonuclease (also called RNase). Its catalytic activity is very resistant to heat and urea. However, if one treats the enzyme with mercaptoethanol (which breaks disulfide bonds) prior to urea treatment and

heating, activity is lost, indicating that the covalent disulfide bonds help stabilize the overall enzyme structure. If one allows the enzyme
mixture to cool back down to room temperature, over time some enzyme activity reappears, indicating that ribonuclease can re-fold under the proper conditions.

Irreversible Denaturation

Most enzymes, however, do not behave like ribonuclease. Once denatured, their activity cannot be recovered to any significant extent. This may seem to contradict the idea that folding information is inherent to the sequence of amino acids in the protein. It does not. The reason most enzymes can't refold properly is due to two phenomena. First, normal folding may occur as proteins are being made. Interactions among amino acids early in the synthesis are not "confused" by interactions with amino acids later in the synthesis because those amino acids aren't present as protein synthesis starts. In many cases, the proper folding of newly made polypeptides is also assisted by special proteins called chaperones. Chaperones bind to newly made proteins, preventing interactions that might result in misfolding. Thus, early folding and the assistance of chaperones eliminate some potential "wrong-folding" interactions that can occur if the entire sequence was present when folding started.

Denatured full-length polypeptides have many more potential wrong folds that can occur. A second reason most proteins don't refold properly after denaturation is probably that folding, like any other natural phenomenon, is driven by energy minimization. Though the folded structure may have a low energy, the path leading to it may not be all downhill. Like a chemical reaction that has energies of activation that must be overcome for the reaction to occur, folding likely has peaks and valleys of energy that do not automatically lead directly to the proper fold. Again, folding during synthesis leads the protein along a better-defined path through the energy maze of folding that denatured full-length proteins can't navigate.

Prions and Misfolding

Folding and the stability of folded proteins is an important consideration for so-called "infectious" proteins known as prions. These mysterious proteins, which are implicated in diseases, such as mad cow disease and the related human condition known as Creutzfeldt-Jakob disease, result from the improper folding of a brain protein known as PrP. The misfolded protein has two important properties that lead to the disease. First, it tends to aggregrate into large complexes called amyloid plaques that damage/destroy nerve cells in the brain, leading ultimately to dementia and loss of brain function.

Second, and probably worse, the misfolded protein "induces" other copies of the same protein to misfold as well. Thus, a misfolded protein acts something like a catalytic center and the disease progresses rapidly. The question arises as to how the PrP protein misfolds to begin with, but the answer to this is not clear. There are suggestions that exposure in the diet to misfolded proteins may be a factor, but this is disputed. An outbreak of mad cow disease in Britain in the 1980s was followed by a rise in the incidence of a rare form of human Creutzfeld-Jakob disease called variant CJD (v-CJD), lending some credence to the hypothesis. It is possible that misfolding of many proteins occurs sporadically without consequence or observation, but if PrP misfolds, the results are readily apparent. Thus, Creutzfeld-Jakob disease may ultimately give insights into the folding process itself.

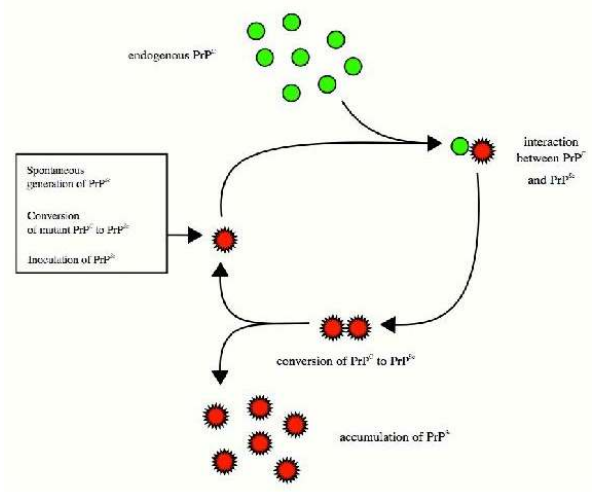


Figure 8.3.19: *Prion protein misfolding.*

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8.4: Nucleic Acids

Determination of the structure of the most common form of DNA, known as the B form, was one of the most important scientific advances of the 20th century. Using data from Rosalind Franklin, James Watson and Francis Crick initiated the modern era of molecular biology with their paper in the April 25, 1953 issue of Nature. Arguably, that single page paper has had more scientific impact per word than any other research article ever published. Today, every high school biology student knows the double helical structure in which G pairs with C and A pairs with T. The DNA molecule is a polymer of nucleoside monophosphates with phosphodiester bonds between the phosphate and the 5' end of one deoxyribose and the 3' end of the next one. In the B form the DNA helix has a repeat of 10.5 base pairs per turn, with sugars and phosphate forming the covalent "backbone" of the molecule and the adenine, guanine, cytosine, and thymine bases oriented in the middle where they form the now familiar base-pairs that look like the rungs of a ladder.

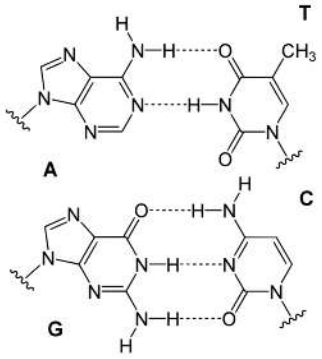


Figure 8.4.1*: A-T Base pairs (top) and G-C base pairs (bottom).*

Hydrogen bonds help to hold the base pairs together, with two hydrogen bonds per A-T pair and three hydrogen bonds per G-C pair. The two strands of a DNA duplex run in opposite directions. The 5' end of one strand is paired with the 3' end of the other strand and vice-versa at the other end of the duplex. The B form of DNA has a prominent major groove and a minor groove tracing the path of the helix (shown at left). Proteins, such as transcription factors bind in these grooves and access the hydrogen bonds of the base pairs to "read" the sequence therein.

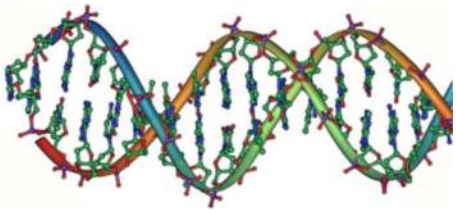


Figure 8.4.2: *DNA double helix.*

Other forms of DNA besides the B form are known. One of these, the 'A' form, was identified by Rosalind Franklin in the same issue of Nature as Watson and Crick's paper. Though the A structure is a relatively minor form of DNA and resembles the B form, it turns out to be important in the duplex form of RNA and in RNA-DNA hybrids. Both the A form and the B form of DNA have the helix oriented in what is termed the right-handed form.

These stand in contrast to another form of DNA, known as the Z form. Z-DNA, as it is known, has the same base-pairing rules as the B and A forms, but instead has the helices twisted in the opposite direction, making a left-handed helix (Figure 8.4.3). The Z form has a sort of zig-zag shape, giving to the name Z DNA. In addition, the helix is rather stretched out compared to the A and B forms. Why are there different forms of DNA. The answer relates to both superhelical tension and sequence bias. Sequence bias means that certain sequences tend to favor the "flipping" of B form DNA into other forms. Z DNA forms are favored by long stretches of alternating Gs and Cs.

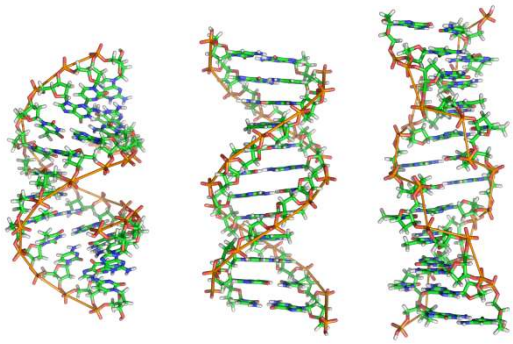


Figure 8.4.3: *A, B, and Z forms of DNA*

Superhelicity

Short stretches of linear DNA duplexes exist in the B form and have 10.5 base pairs per turn. Double helices of DNA in the cell can vary in the number of base pairs per turn they contain. There are several reasons for this. For example, during DNA replication, strands of DNA at the site of replication get unwound at the rate of 6000 rpm by an enzyme called helicase. The effect of such local unwinding at one place in a DNA has the effect increasing the winding ahead of it. Unrelieved, such 'tension' in a DNA duplex can result in structural obstacles to replication.

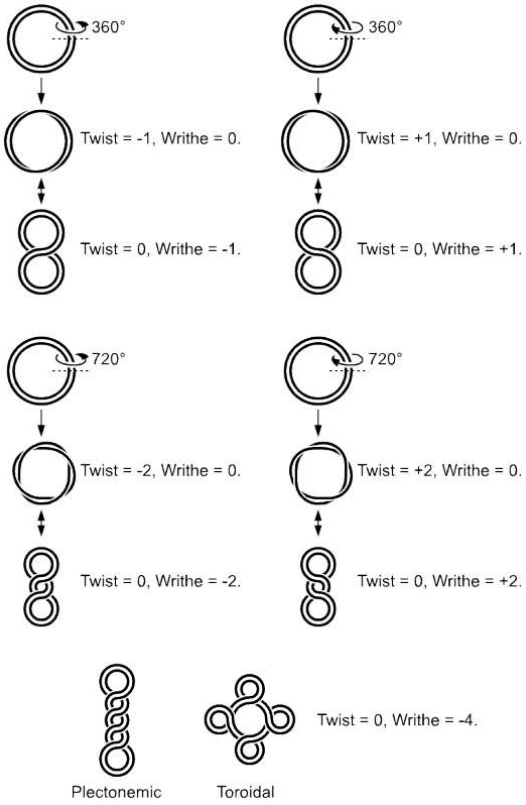


Figure 8.4.4: *Topoisomers of DNA*

Such adjustments can occur in three ways. First, tension can provide the energy for 'flipping' DNA structure. Z-DNA can arise as a means of relieving the tension. Second, DNA can 'supercoil' to relieve the tension. In this method, the strands of the duplex can cross each other repeatedly, much like a rubber band will coil up if one holds one section in place and twists another part of it. Third, enzymes called topoisomerases can act to relieve or, in some cases, increase the tension by adding or removing twists in the DNA.

RNA Structures

With respect to structure, RNAs are more varied than their DNA cousins. Created by copying regions of DNA, cellular RNAs are synthesized as single strands, but they often have self-complementary regions leading to “fold-backs" containing duplex regions. The structure of tRNAs and rRNAs are excellent examples. The base-pairing rules of DNA are the same in RNA (with U in RNA replacing the T from DNA), but in addition, base pairing between G and U can also occur in RNA. This latter fact leads to many more possible duplex regions in RNA that can exist compared to single strands of DNA.

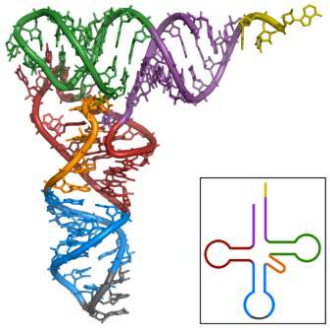


Figure 8.4.5: *3D structure of tRNA (left) and 2D projection (right).*

RNA structure, like protein structure, has importance, in some cases, for catalytic function. Like random coils in proteins that give rise to tertiary structure, single-stranded regions of RNA that link duplex regions give these molecules a tertiary structure, as well. Catalytic RNAs, called ribozymes, catalyze important cellular reactions, including the formation of peptide bonds. DNA, which is usually present in cells in strictly duplex forms (no tertiary structure, per se), is not known to be involved in catalysis.

RNA structures are important for reasons other than catalysis. The 3D arrangement of tRNAs is important for enzymes that attach amino acids to them to do so properly. Small RNAs called siRNAs found in the nucleus of cells appear to play roles in both gene regulation and in cellular defenses against viruses. The key to the mechanisms of these actions is the formation of short fold-back RNA structures that are recognized by cellular proteins and then chopped into smaller units. One strand is copied and used to base pair with specific mRNAs to prevent the synthesis of proteins from them.

Denaturing Nucleic Acids

Like proteins, nucleic acids can be denatured. Forces holding duplexes together include hydrogen bonds between the bases of each strand that, like the hydrogen bonds in proteins, can be broken with heat or urea. (Another important stabilizing force for DNA arises from the stacking interactions between the bases in a strand.) Single strands absorb light at 260 nm more strongly than double strands (hyperchromic effect), allowing one to easily follow denaturation. For DNA, strand separation and strand hybridization are important aspects of the technique known as the polymerase chain reaction (PCR). Strand separation of DNA duplexes is accomplished in the method by heating them to boiling. Hybridization is an important aspect of the method that requires complementary single strands to “find" each other and form a duplex. Thus, DNAs (and RNAs too) can renature readily, unlike most proteins. Considerations for efficient hybridization (also called annealing) include temperature, salt concentration, strand concentration, and magnesium ion levels.

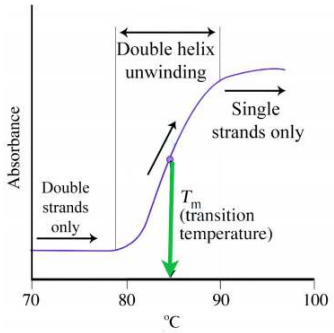


Figure 8.4.6: *Hyperchromic effect.*

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8.5: Carbohydrates

The last class of macromolecules we will consider structurally here is the carbohydrates. Built of sugars or modified sugars, carbohydrates have several important functions, including structural integrity, cellular identification, and energy storage.

Monosaccharides

Simple sugars, also known as monosaccharides, can generally be written in the form $C_x(H_2O)_x$. It is for this reason they are referred to as carbo-hydrates. By convention, the letters 'ose' at the end of a biochemical name flags a molecule as a sugar. Thus, there are glucose, galactose, sucrose, and many other '-oses'. Other descriptive nomenclature involves use of a prefix that tells how many carbons the sugar contains. For example, glucose, which contains six carbons, is described as a hexose. The following list shows the prefixes for numbers of carbons in a sugar:

- Tri- = 3
- Tetr- = 4
- Pent- = 5
- Hex- =6
- Hept- = 7
- Oct- = 8

Other prefixes identify whether the sugar contains an aldehyde group (aldo-) or a ketone (keto) group. Prefixes may be combined. Glucose, which contains an aldehyde group, can be described as an aldo-hexose. The list that follows gives some common sugars and some descriptors.

- Ribose = aldo-pentose
- Glucose = aldo-hexose
- Galactose = aldo-hexose
- Mannose = aldo-hexose
- Glyceraldehyde = aldo-triose
- Erythrose – aldo-tetrose
- Fructose = keto-hexose
- Ribulose = keto-pentose
- Sedoheptulose = keto-heptose
- Dihydroxyacetone = keto-triose

Stereoisomer Nomenclature

Sugars of a given category (hexoses, for example) differ from each other in the stereoisomeric configuration of their carbons. Two sugars having the same number of carbons (hexoses, for example) and the same chemical form (aldoses, for example), but differing in the stereoisomeric configuration of their carbons are called diastereomers. Biochemists use D and L nomenclature to describe sugars, as explained below.

D-sugars predominate in nature, though L-forms of some sugars, such as fucose, do exist. The D and L designation is a bit more complicated than it would appear on the surface. To determine if a sugar is a D-sugar or an L-sugar, one simply examines the configuration of the highest numbered asymmetric carbon. If the hydroxyl is written to the right, it is a D-sugar. If the hydroxyl is on the left, it is an L-sugar. That part is simple. The confusion about D and L arises because L sugars of a given name (glucose, for example) are mirror images of D sugars of the same name. The figure on the previous page shows the structure of D- and L-glucose. Notice that D-glucose is not converted into L-glucose simply by .ipping the configuration of the fifth carbon in the molecule. There is another name for sugars that are mirror images of each other. They are called enantiomers. Thus, L-glucose and D-glucose are enantiomers, but D-Erythrose and D-Threose are diastereomers.

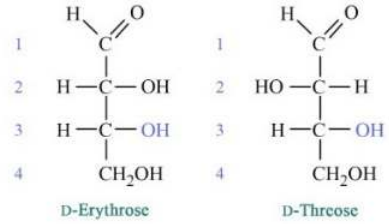


Figure 8.5.1: *Diastereomers.*

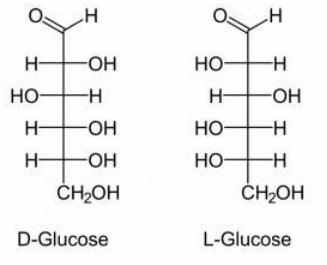


Figure 8.5.2: *Enantiomers.*

Sugars of 5-7 carbons can fairly easily form ring structures (called Haworth structures). For aldoses like glucose, this involves formation of a hemi-acetal. For ketoses like fructose, it involves formation of a hemi-ketal. The bottom line for both is that the oxygen that was part of the aldehyde or the ketone group is the one that becomes a part of the ring. More important than the oxygen, though, is the fact that the carbon attached to it (carbon #1 in aldoses or #2 in ketoses) becomes asymmetric as a byproduct of the cyclization. This new asymmetric carbon is called the anomeric carbon and it has two possible configurations, called alpha and beta.

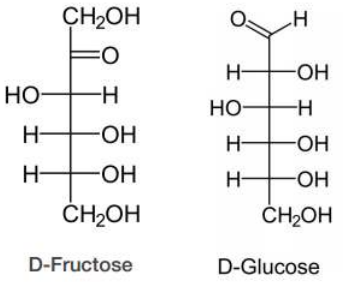


Figure 8.5.3: *Ketose and Aldose.*

A solution of glucose will contain a mixture of alpha and beta forms. Whether the alpha or the beta arises upon cyclization is partly determined by geometry and partly random. Thus, one can find a bias for one form, but usually not that form exclusively. A given molecule of sugar will flip between alpha and beta over time. A requirement for this is that the hydroxyl on the anomeric carbon is unaltered, thus facilitating flipping back to the straight chain form followed by recyclization. If the hydroxyl becomes chemically altered in any way (for example, replacement of its hydrogen by a methyl group), a glycoside is formed. Glycosides are locked in the same alpha or beta configuration they were in when the modification was made. Glycosides are commonly found in nature. Sucrose, for example , is a di-glycoside – both the glucose and the fructose have had their anomeric hydroxyls altered by being joined together.

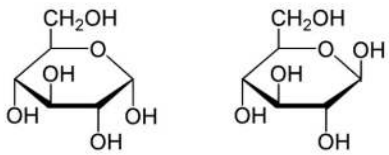


Figure 8.5.4: *alpha-D Glucose (left) and beta-D Glucose (right)*

The last considerations for sugars relative to their structure are their chemical reactivity and modification. The aldehyde group of aldoses is susceptible to oxidation, whereas ketoses are less so. Sugars that are readily oxidized are called ‘ reducing sugars ’ because their oxidation causes other reacting molecules to be reduced. Reducing sugars can easily be identified in a chemical test. Chemical modification of sugars occurs readily in cells. As we will see, phosphorylation of sugars occurs routinely during metabolism. Oxidation of sugars to create carboxyl groups also can occur. Reduction of aldehyde/ketone groups of sugars creates what are called sugar alcohols, and other modifications, such as addition of sulfates and amines also readily occur.

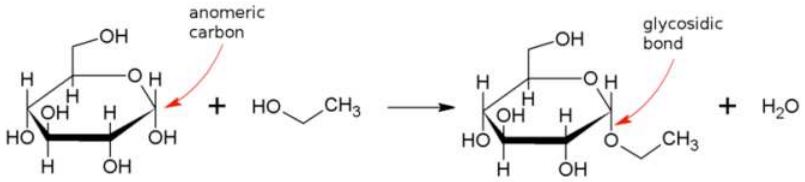


Figure 8.5.5: Glycoside formation

Boat/Chair Conformations

Independent of stereoisomerization, sugars in ring form of a given type (such as glucose) can “twist" themselves into alternative conformations called boat and chair. Note that this rearrangement does not change the relative positions of hydroxyl groups. All that has changed is the shape of the molecule. As shown for glucose, one can see that the beta-hydroxyl of glucose is closer to the CH_2OH (carbon #6) in the boat form than it is in the chair form. Steric hindrance can be a factor in favoring one configuration over another.

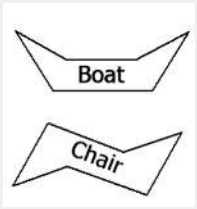


Figure 8.5.6: *Boat and Chair*

Disaccharides

Sugars are readily joined together (and broken apart) in cells. Sucrose (Figure 8.5.7), which is common table sugar, is made by joining the anomeric hydroxyl of alpha-D-glucose to the anomeric hydroxyl of beta-D-fructose. Not all disaccharides join the anomeric hydroxyls of both sugars. For example, lactose (milk sugar) is made by linking the anomeric hydroxyl of galactose in the beta configuration to the hydroxyl of carbon #4 of glucose.

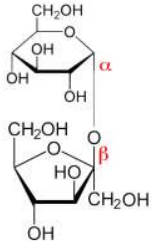


Figure 8.5.7: Sucrose

Oligosaccharides

The term ‘oligosaccharide’ is used to describe polymers of sugars of 5-15 units, typically. Oligosaccharides are not commonly found free in cells, but instead are found covalently attached to proteins, which are then said to be glycosylated. Oligosaccharides attached to proteins may be **N-linked** (through asparagine) or **O-linked** (though serine or threonine). O-linked sugars are added only in the Golgi apparatus while N-linked sugars are attached starting in the endoplasmic reticulum and then completed in the Golgi.

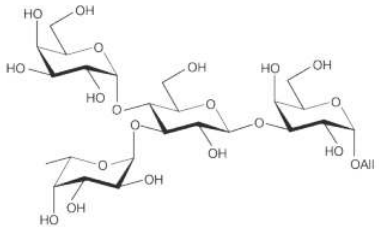


Figure 8.5.8: *An oligosaccharide.*

Oligosaccharides often function as identity markers, both of cells and proteins. On the cell surface, glycoproteins with distinctive oligosaccharides attached establish the identity of each cell. The types of oligosaccharides found on the surface of blood cells is a determinant of blood type. The oligosaccharides that are attached to proteins may also determine their cellular destinations. Improper glycosylation or sugar modification patterns can result in the failure of proteins to reach the correct cellular compartment. For example, inclusion cell (I-cell) disease arises from a defective phosphotransferase in the Golgi. This enzyme normally catalyzes the addition of a phosphate to a mannose sugar attached to a protein destined for the lysosome. In the absence of a functioning enzyme, the unphosphorylated glycoprotein never makes it to the lysosome and is instead exported out of the cell where it accumulates in the blood and is excreted in the urine. Individuals with I-cell disease suffer developmental delays, abnormal skeletal development, and restricted joint movement.

Polysaccharides

Polysaccharides, as their name implies, are made by joining together many sugars. The functions for polysaccharides are varied. They include energy storage, structural strength, and lubrication. Polysaccharides involved in energy storage include the plant polysaccharides, amylose and amylopectin. The polysaccharide involved in energy storage in animals is called glycogen and it is mostly found in the muscles and liver.

Amylose/Amylopectin

Amylose is the simplest of the polysaccharides, being comprised solely of glucose units joined in an alpha 1-4 linkage. Amylose is broken down by the enzyme alpha-amylase, found in saliva. Amylopectin is related to amylose in being composed only of glucose, but it differs in how the glucose units are joined together. Alpha 1-4 linkages predominate, but every 30-50 residues, a ‘branch’ arises from an alpha 1-6 linkage. Branches make the structure of amylopectin more complex than that of amylose.

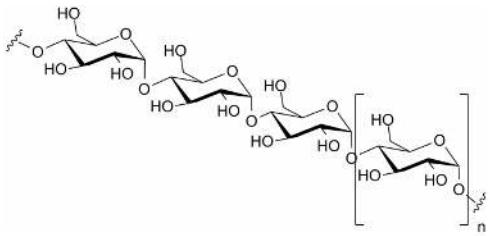


Figure 8.5.9: Amylose.

Glycogen

Glycogen is a polysaccharide that is physically related to amylopectin in being built only of glucose and in having a mix of alpha 1-4 and alpha 1-6 bonds. Glycogen, however, has many more alpha 1-6 branches than amylopectin, with such bonds occurring about every 10 residues. One might wonder why such branching occurs more abundantly in animals than in plants. A plausible explanation is based on the method by which these molecules are broken down. The breakdown of these polysaccharides is catalyzed by enzymes, known as phosphorylases, that clip glucose residues from the ends of glycogen chains and attach a phosphate to them in the process, producing glucose-1-phosphate. More highly branched polysaccharides have more ends to clip, and this translates to more glucose-1-phosphates that can be removed simultaneously by numerous phosphorylases. Since glucose is used for energy by muscles, glucose concentrations can be increased faster the more branched the glycogen is. Plants, which are immobile do not have needs for such immediate release of glucose and thus have less need for highly branched polysaccharides.

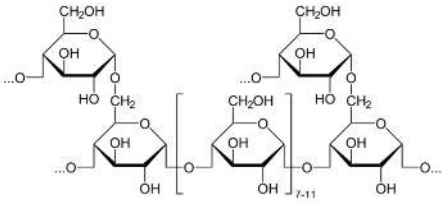


Figure 8.5.10: *Glycogen Structure*

Cellulose

Another important polysaccharide containing only glucose is cellulose. It is a polymer of glucose used to give plant cell walls structural integrity and has the individual units joined solely in a beta 1-4 configuration. That simple structural change makes a radical diff erence in its digestibility. Humans are unable to break down cellulose and it passes through the digestive system as roughage. Ruminant animals, such as cattle, however have bacteria in their rumens that contain the enzyme cellulase. It breaks the beta 1-4 links of the glucoses in cellulose to release the sugars for energy.

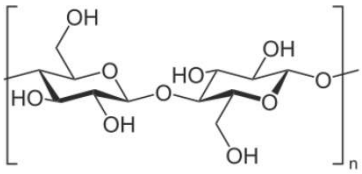


Figure 8.5.11: *The repeating structure of cellulose.*

Another polysaccharide used for structural integrity is known as chitin. Chitin makes up the exoskeleton of insects and is a polymer of a modified form of glucose known as N-acetyl-glucosamine.

Glycosaminoglycans

Yet another category of polysaccharides are the glycosaminoglycans (also called mucopolysaccharides), some examples of which include keratan sulfate, heparin, hyaluronic acid (right), and chondroitin sulfate. The polysaccharide compounds are linked to proteins, but differ from glycoproteins in having a much larger contingent of sugar residues and, further, the sugars are considerably more chemically modified. Each of them contains a repeating unit of a disaccharide that contains at least one negatively charged residue. The result is a polyanionic substance that, in its interactions with water, makes for a “slimy" feel. Glycosaminoglycans are found in snot, and in synovial fluid, which lubricates joints. Heparin is a glycosaminoglycan that helps to prevent blood from clotting.

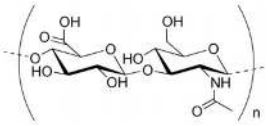


Figure 8.5.12: *The repeating unit of a glycosaminoglycan structure.*

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8.6: Lipids and Membranes

Lipids are a broad class of molecules that all share the characteristic that they have at least a portion of them that is hydrophobic. The class of molecules includes fats, oils (and their substituent fatty acids), steroids, fat-soluble vitamins, prostaglandins, glycerophospholipids, and sphingolipids. Interestingly, each of these can be derived from acetyl-CoA.

Fatty Acids

Arguably, the most important lipids in our cells are the fatty acids, because they are components of all of the other lipids, except some of the steroids and fat-soluble vitamins. Consisting of a carboxyl group linked to a long aliphatic tail, fatty acids are described as either saturated (no double bonds) or unsaturated (one or more double bonds). Fatty acids with more than one double bond are described as polyunsaturated. Increasing the amount of unsaturated fatty acids (and the amount of unsaturation in a given fatty acid) in a fat decreases its melting temperature. This is also a factor in membrane fluidity. If the melting temperature of a fat is decreased sufficiently so that it is a liquid at room temperature, it is referred to as an oil. It is worth noting that organisms like fish, which live in cool environments, have fats with more unsaturation. This is why fish oil is a rich source of polyunsaturated fatty acids.

	Number of Carbon Atoms	Unsaturation	Formula	Melting Point (°C)
Palmitoleic	16	$16:1-\Delta^9$	$CH_3(CH_2)_5CH{=}CH(CH_2)_7CO_2H$	-0.5
Oleic	18	$18:1-\Delta^9$	$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H$	16
Linoleic	18	$18:2-\Delta^{9,12}$	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7CO_2H$	-5
Linolenic	18	$18:3-\Delta^{9,12,15}$	$CH_3(CH_2CH{=}CH)_3(CH_2)_7CO_2H$	-11
Arachidonic	20	$20:4-\Delta^{5,8,11,14}$	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_3CO_2H$	-50

Figure 3.5.1: *Important unsaturated fatty acids.*

Biochemically, the double bonds found in fatty acids are predominantly in the cis configuration. So-called trans fats arise as a chemical by-product of partial hydrogenation of vegetable oil (small amounts of trans fats also occur naturally). In humans, consumption of trans fats raises low density lipoprotein (LDL) levels and lowers high density lipoprotein (HDL) levels. Each is thought to contribute to the risk of developing coronary artery disease. The most common fatty acids in our body include palmitate, stearate, oleate, linolenate, linoleate, and arachidonate. Fatty acids are numbered by two completely different schemes. The delta numbering scheme has the carboxyl group as #1, whereas the omega number scheme starts at the other end of the fatty acid with the methyl group as #1. Fatty acids are described as essential if they must be in the diet (can't be synthesized by the organism). Animals, including humans, cannot synthesize fatty acids with double bonds beyond position delta 9, so linoleic and linolenic acids are considered essential in these organisms.

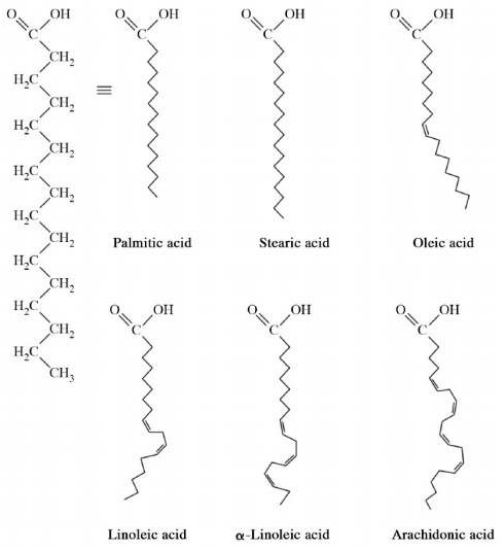


Figure 3.5.2: *Fatty acids.*

In animal cells, fats are the primary energy storage forms. They are also known as triacylglycerols, since they consist of a glycerol molecule esterified to three fatty acids. Fats are synthesized by replacing the phosphate on phosphatidic acid with a fatty acid. Fats

are stored in the body in specialized cells known as adipocytes. Enzymes known as lipases release fatty acids from fats by hydrolysis reactions. Of the various lipases acting on fat, the one that acts first, triacylglycerol lipase, is regulated hormonally.

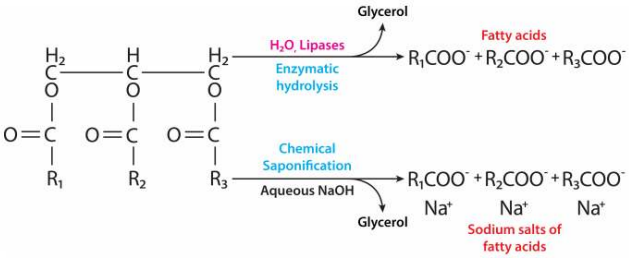


Figure 3.5.3: *Hydrolysis of fat.*

Membrane Lipids

The predominant lipids found in membranes are glycerophospholipids (phosphoglycerides) and sphingolipids. The former are related to fats structurally as both are derived from phosphatidic acid. Phosphatidic acid is a simple glycerophospholipid that is usually converted into phosphatidyl compounds. These are made by esterifying various groups, such as ethanolamine, serine, choline, inositol, and others to the phosphate. All of these compounds form lipid bilayers in aqueous solution, due to the amphiphilic nature of their structure.

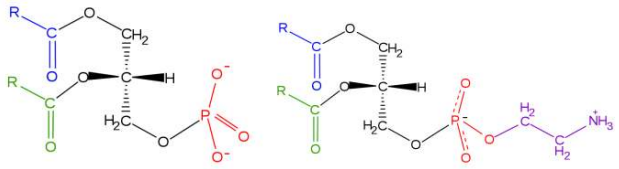


Figure 3.5.4: *Phosphatic Acid (Left) and Phosphatidyl Ethanolamine (Right)*

Though structurally similar to glycerophospholipids, sphingolipids are synthesized completely independently of them, starting with palmitic acid and the amino acid serine. The figure on the right shows the structure of several sphingolipids. LIke the glycerophospholipids, sphingolipids are amphiphilic, but unlike them, they may have simple (in cerebrosides) or complex (in gangliosides) carbohydrates attached at one end. Most sphingolipids, except sphingomyelin, do not contain phosphate.

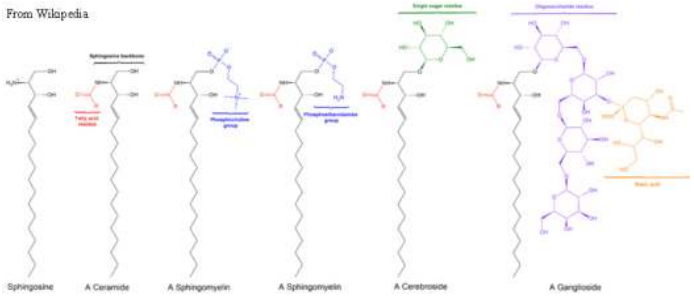


Figure 3.5.5: *The structures of several sphingolipids.*

Steroids, such as cholesterol are also found in membranes. Cholesterol, in particular, may play an important role in membrane fluidity. Membranes can be thought of a being more “frozen" or more “fluid." Fluidity is important for cellular membranes. When heated, membranes move from a more “frozen" character to that of a more “fluid" one as the temperature rises. The mid-point of this transition, referred to as the Tm, is influenced by the fatty acid composition of the lipid bilayer compounds. Longer and more saturated fatty acids will favor higher Tm values, whereas unsaturation and short fatty acids will favor lower Tm values. Interestingly, cholesterol does not change the Tm value, but instead widens the transition range between frozen and fluid forms of the membrane.

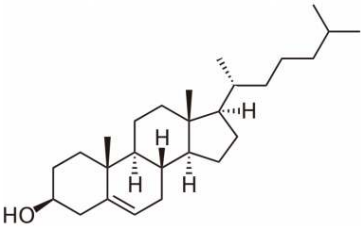


Figure 3.5.6: *Cholesterol*

Lipid Bilayers

The membrane around cells contains many components, including cholesterol, proteins, glycolipids, glycerophospholipids and sphingolipids. The last two of these will, in water, form what is called a lipid bilayer, which serves as a boundary for the cell that is largely impermeable to the movement of most materials across it. With the notable exceptions of water, carbon dioxide, carbon monoxide, and oxygen, most polar/ionic compounds require transport proteins to help them to efficiently navigate across the bilayer. The orderly movement of these compounds is critical for the cell to be able to 1) get food for energy; 2) export materials; 3) maintain osmotic balance; 4) create gradients for secondary transport; 5) provide electromotive force for nerve signaling; and 6) store energy in electrochemical gradients for ATP production (oxidative phosphorylation or photosynthesis). In some cases, energy is required to move the substances (active transport). In other cases, no external energy is required and they move by diffusion through specific cellular channels.

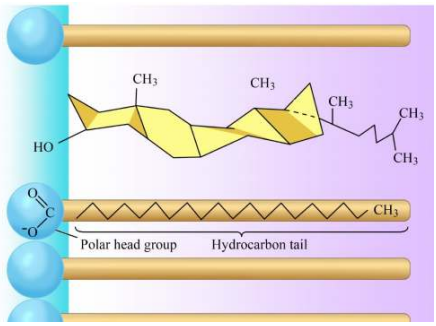


Figure 3.5.7: *Cholesterol in a lipid bilayer.*

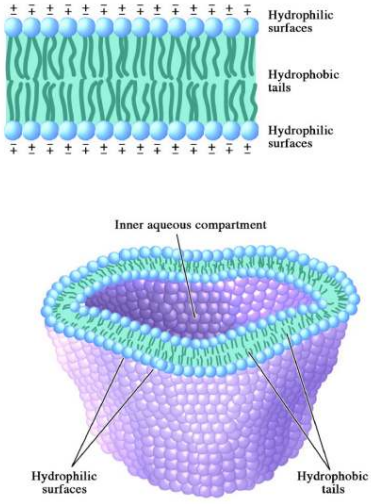


Figure 3.5.8: Lipid bilayer structure.

The spontaneous ability of these compounds to form lipid bilayers is exploited in the formation of artificial membranous structures called liposomes. Liposomes have some uses in delivering their contents into cells via membrane fusion.

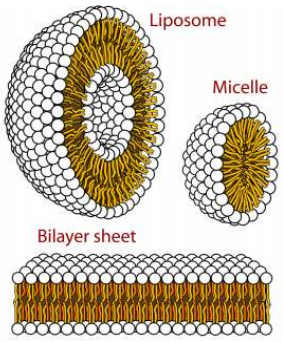


Figure 3.5.9: *Liposome, Micelle, and Bilayer Sheet.*

Membrane Proteins

Other significant components of cellular membranes include proteins. We can put them into several categories. Integral membrane proteins are embedded in the membrane and project through both sides of the lipid bilayer. Peripheral membrane proteins are embedded in or tightly associated with part of the bilayer, but do not project completely through both sides. Associated membrane proteins are found near membranes, but may not be embedded in them. Their association may arise as a result of interaction with other proteins or molecules in the lipid bilayer. Anchored membrane proteins are not themselves embedded in the lipid bilayer, but instead are attached to a molecule (typically a fatty acid) that is embedded in the membrane.

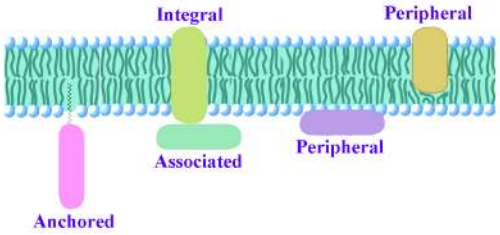


Figure 3.5.10: Types of membrane proteins.

The geometry of the lipid bilayer is such that is hydrophobic on its interior and hydrophilic on the exterior. Such properties also dictate the amino acid side chains of proteins that interact with the bilayer. For most membrane proteins, the polar amino acids are found where the protein projects through the bilayer (interacting with aqueous/polar substances) and the non-polar amino acids are embedded within the non-polar portion of the bilayer containing the fatty acid tails.

Glycolipids and glycoproteins play important roles in cellular identification. Blood types, for example, differ from each other in the structure of the carbohydrate chains projecting out from the surface of the glycoprotein in their membranes.

Cells have hundreds of membrane proteins and the protein composition of a membrane varies with its function and location. Mitochondrial membranes are among the most densely packed with proteins. The plasma membrane has a large number of integral proteins involved in communicating information across the membrane (signaling) or in transporting materials into the cell.

Membrane Transport

Materials, such as food and waste must be moved across a cell's lipid bilayer. There are two means of accomplishing this - passive processes and active processes. Passive processes have as their sole driving force the process of diffusion. In these systems, molecules always move from a higher concentration to a lower concentration. These can occur directly across a membrane (water, oxygen, carbon dioxide, and carbon monoxide) or through special transport proteins (glucose transport proteins of red blood cells, for example). In each case, no cellular energy is expended in the movement of the molecules. On the other hand, active processes require energy to accomplish such transport. A common energy source is ATP (see Na+/K+ ATPase), but many other energy sources are employed. For example, the sodium-glucose transporter uses a sodium gradient as a force for actively transporting glucose into a cell. Thus, it is important to know that not all active transport uses ATP energy. Proteins, such as the sodium-glucose transporter that move two molecules in the same direction across the membrane are called symporters (also called synporters). If the action of a protein in moving ions across a membrane results in a change in charge, the protein is described as electrogenic and if there is no change in charge the protein is described as electro-neutral.

Sodium-Potassium ATPase

Another important integral membrane protein is the Na+/K+ ATPase (Figure 3.5.11), which transports sodium ions out of the cell and potassium ions into the cell. The protein, which is described as an anti-port (molecules moved in opposite directions across the membrane) uses the energy of ATP to create ion gradients that are important both in maintaining cellular osmotic pressure and (in nerve cells) for creating the ion gradients necessary for signal transmission. The transport system moves three atoms of sodium out of the cell and two atoms of potassium into the cell for each ATP hydrolyzed.

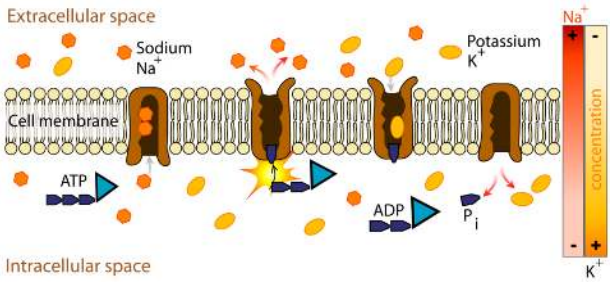


Figure 3.5.11: *Sodium-Potassium ATPase.*

Bacteriorhodopsin

An interesting integral membrane protein is bacteriorhodopsin. The protein has three identical polypeptide chains, each rotated by 120 degrees relative to the others. Each chain has seven transmembrane alpha helices and contains one molecule of retinal (Vitamin A) buried deep within each cavity (shown in purple in lower figure at left). Vitamin A is light sensitive an isomerizes rapidly between a cis and a trans form in the presence of light. The changing conformation of the vitamin A is used to transport protons through the protein and out of the bacterium, creating a proton gradient across the cell membrane, which is used ultimately to make ATP. It is not too difficult to imagine engineering an organism (say a transparent fish) to contain bacteriorhodopsin in its mitochondrial inner membrane. When light is shone upon it, the bacteriorhodopsin could be used to generate a proton gradient (much like electron transport does) and power oxidative phosphorylation. Such a fish would be partly photosynthetic in that it would be deriving energy from light, but would differ from plants in being unable to assimilate carbon dioxide in a series of “dark reactions."

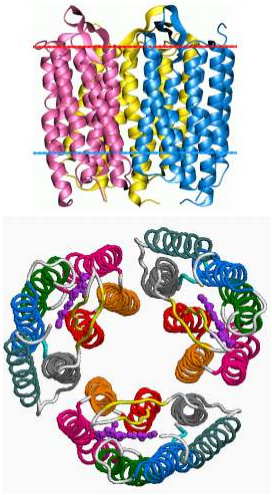


Figure 3.5.12: *Bacteriorhodopsin*

Fat Soluble Vitamins

Other lipids of note include the fat-soluble vitamins - A, D, E, and K. Vitamin A comes in three primary chemical forms, retinol (storage in liver), retinal (role in vision), and retinoic acid (roles in growth and development). Vitamin D (cholecalciferol) plays important roles in the intestinal absorption of calcium and phosphate and thus in healthy bones. Derived from ultimately from cholesterol, the compound can be synthesized in a reaction catalyzed by ultraviolet light. Vitamin E (tocopherol) is the vitamin about which the least is known. It consists of a group of eight fat-soluble compounds of which the alpha-isomer has the most

biological activity. Vitamin K (the name comes from the German for coagulation vitamin) is essential for blood clotting. It is used as a co-factor for the enzyme that modifies prothrombin to increase its affinity for calcium, allowing it to be positioned closer to the site of a wound.

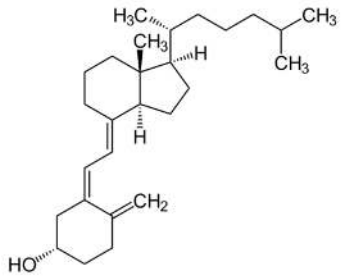


Figure 3.5.13: *Vitamin D*

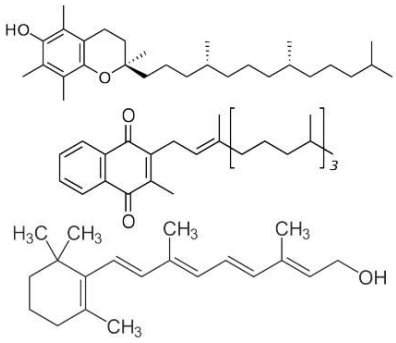


Figure 3.5.14: *Top to bottom - Vitamins E, K, and A*

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CHAPTER OVERVIEW

9: Cells

9.1: Case Study- The Importance of Cells
9.2: Discovery of Cells and Cell Theory
9.3: Variation in Cells
9.4: Plasma Membrane
9.5: Connections between Cells and Cellular Activities
9.6: Cytoplasm and Cytoskeleton

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9.1: CASE STUDY- THE IMPORTANCE OF CELLS

CASE STUDY: MORE THAN JUST TIRED

We all get tired sometimes, especially if we have been doing a lot of physical activity. But for Jasmin, a 34-year-old former high school track star who is now a recreational runner, her tiredness was going far beyond what she thought should be normal for someone who is generally in good physical shape. She was experiencing extreme fatigue after her runs, as well as muscle cramping, spasms, and an unusual sense of heaviness in her legs. At first, she chalked it up to getting older, but her exhaustion and pain worsened to the point where this former athlete could no longer run for more than a few minutes at a time. She also began to experience other unusual symptoms, such as blurry vision and vomiting for no apparent reason.



Figure **9.1.1**: Exhausted

Concerned, she went to her doctor. Her doctor ran many tests and consulted with several specialists. After several months, Jasmin is finally diagnosed with a mitochondrial disease. Jasmin is surprised. She has an 8-year-old niece with a mitochondrial disease, but her niece's symptoms started when she was very young, and included seizures and learning disabilities. How can Jasmin have the same disease but different symptoms? Why did she not have problems until adulthood while her niece had symptoms at an early age? And what are mitochondria anyway?

CHAPTER OVERVIEW: CELLS

As you will learn in this chapter, mitochondria are important structures within our cells. This chapter will describe cells, which are the basic unit of structure and function in all living organisms. Specifically, you will learn:

- How cells were discovered, their common structures, and the principles of cell theory.
- The importance of size and shape in the functions of cells.
- The differences between eukaryotic cells (such as those in humans and other animals) and prokaryotic cells (such as bacteria).
- The structures and functions of parts of cells including mitochondria, the plasma membrane, cytoplasm, cytoskeleton, nucleus, ribosomes, Golgi apparatus, endoplasmic reticulum, vesicles, and vacuoles.
- How the processes of passive and active transport move substances into and out of cells and help maintain homeostasis.
- How organisms obtain the energy needed for life, including how the sugar glucose is broken down to produce ATP through the processes of aerobic cellular respiration and anaerobic respiration.

As you read this chapter, think about the following questions related to Jasmin's disease:

1. What are mitochondria? What is their structure, function, and where did they come from during evolution?
2. Why are fatigue and "exercise intolerance," such as Jasmin's extreme exhaustion after running, common symptoms of mitochondrial diseases?
3. Why do you think Jasmin has symptoms that affect so many different parts of her body including her legs, eyes, and digestive system?

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9.2: DISCOVERY OF CELLS AND CELL THEORY

A BIG BLUE CELL

What is this incredible object? Would it surprise you to learn that it is a human cell? The cell is actually too small to see with the unaided eye. It is visible here in such detail because it is being viewed with a very powerful microscope. Cells may be small in size, but they are extremely important for life. Like all other living things, you are made of cells. Cells are the basis of life, and without cells, life as we know it would not exist. You will learn more about these amazing building blocks of life when you read this section.

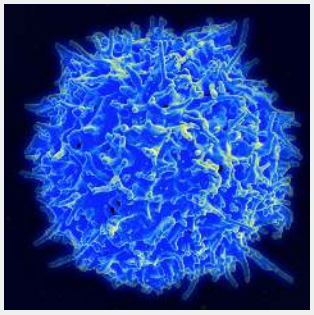


Figure **9.2.1**: Healthy human T-cell

If you look at a living matter with a microscope — even a simple light microscope — you will see that it consists of cells. **Cells** are the basic units of the structure and function of living things. They are the smallest units that can carry out the processes of life. All organisms are made up of one or more cells, and all cells have many of the same structures and carry out the same basic life processes. Knowing the structure of cells and the processes they carry out is necessary to understanding life itself.

DISCOVERY OF CELLS

The first time the word *cell* was used to refer to these tiny units of life was in 1665 by a British scientist named Robert Hooke. Hooke was one of the earliest scientists to study living things under a microscope. The microscopes of his day were not very strong, but Hooke was still able to make an important discovery. When he looked at a thin slice of cork under his microscope, he was surprised to see what looked like a honeycomb. Hooke made the drawing in the figure below to show what he saw. As you can see, the cork was made up of many tiny units, which Hooke called cells.

Soon after Robert Hooke discovered cells in cork, Anton van Leeuwenhoek in Holland made other important discoveries using a microscope. Leeuwenhoek made his own microscope lenses, and he was so good at it that his microscope was more powerful than other microscopes of his day. In fact, Leeuwenhoek's microscope was almost as strong as modern light microscopes. Using his microscope, Leeuwenhoek was the first person to observe human cells and bacteria.

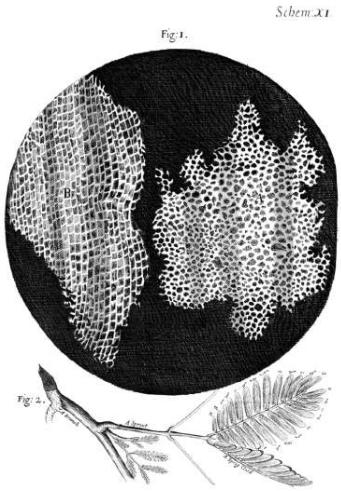


Figure **9.2.2**: Robert Hooke sketched these cork cells as they appeared under a simple light microscope.

CELL THEORY

By the early 1800s, scientists had observed the cells of many different organisms. These observations led two German scientists, named Theodor Schwann and Matthias Jakob Schleiden, to propose that cells are the basic building blocks of all living things. Around 1850, a German doctor named Rudolf Virchow was studying cells under a microscope when he happened to see them dividing and forming new cells. He realized that living cells produce new cells through division. Based on this realization, Virchow proposed that living cells arise only from other living cells.

The ideas of all three scientists — Schwann, Schleiden, and Virchow — led to **cell theory**, which is one of the fundamental theories unifying all of biology. Cell theory states that:

- All organisms are made of one or more cells.
- All the life functions of organisms occur within cells.
- All cells come from already existing cells.

SEEING INSIDE CELLS

Starting with Robert Hooke in the 1600s, the **microscope** opened up an amazing new world — the world of life at the level of the cell. As microscopes continued to improve, more discoveries were made about the cells of living things. However, by the late 1800s, light microscopes had reached their limit. Objects much smaller than cells, including the structures inside cells, were too small to be seen with even the strongest light microscope.

Then, in the 1950s, a new type of the microscope was invented. Called the electron microscope, it used a beam of electrons instead of light to observe extremely small objects. With an electron microscope, scientists could finally see the tiny structures inside cells. In fact, they could even see individual molecules and atoms. The electron microscope had a huge impact on biology. It allowed scientists to study organisms at the level of their molecules and led

to the emergence of the field of cell biology. With the electron microscope, many more cell discoveries were made. Figure **9.2.3** shows how the cell structures called **organelles** appear when scanned by an electron microscope.

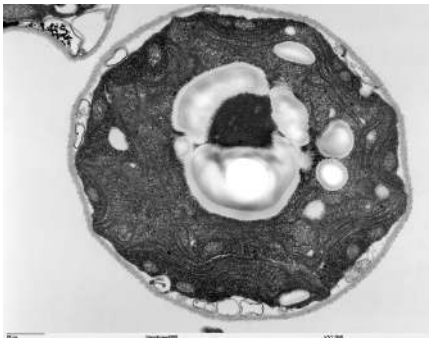


Figure **9.2.3**: An electron microscope produced this image of the structures inside a cell.

STRUCTURES SHARED BY ALL CELLS

Although cells are diverse, all cells have certain parts in common. These parts include a plasma membrane, cytoplasm, ribosomes, and DNA.

1. The **plasma membrane** (also called the cell membrane) is a thin coat of phospholipids that surrounds a cell. It forms the physical boundary between the cell and its environment, so you can think of it as the "skin" of the cell.
2. **Cytoplasm** refers to all of the cellular material inside the plasma membrane. The Cytoplasm is made up of a watery substance called cytosol and contains other cell structures such as ribosomes.
3. **Ribosomes** are structures in the cytoplasm where proteins are made.
4. **DNA** is a nucleic acid found in cells. It contains the genetic instructions that cells need to make proteins.

These parts are common to all cells, from organisms as different as bacteria and human beings. How did all known organisms come to have such similar cells? The similarities show that all life on Earth has a common evolutionary history.

REVIEW

1. Describe cells.
2. Explain how cells were discovered.
3. Outline how cell theory developed.
4. Identify structures shared by all cells.
5. *True or False.* Cork is not a living organism.
6. *True or False.* Some organisms are made of only one cell.
7. *True or False.* Ribosomes are found outside of the cytoplasm of a cell.
8. Proteins are made on _____ .
9. What are the differences between a light microscope and an electron microscope?
10. The first microscopes were made around
    A. 1965
    B. 1665
    C. 1950
    D. 1776
11. Which of these scientists made each of the following discoveries? (Anton van Leeuwenhoek; Robert Hooke; Rudolf Virchow)
    A. Observed some of the first cells and first used the term "cell"
    B. Observed the first human cells
    C. Observed cells dividing
12. Robert Hooke sketched what looked like honeycombs, or repeated circular or square units when he observed plant cells under a microscope.
    A. What is each unit?
    B. Of the shared parts of all cells, what makes up the outer surface of each unit?
    C. Of the shared parts of all cells, what makes up the inside of each unit?

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9.3: VARIATION IN CELLS

BACTERIA ATTACK!

Figure **9.3.1** shows a bacterial cell (colored green) attacking human red blood cells. The bacterium causes a disease called relapsing fever. The bacterial and human cells look very different in size and shape. Although all living cells have certain things in common — such as a plasma membrane and cytoplasm — different types of cells, even within the same organism, may have their own unique structures and functions. Cells with different functions generally have different shapes that suit them for their particular job. Cells vary not only in shape but also in size, as this example shows. In most organisms, however, even the largest cells are no bigger than the period at the end of this sentence. Why are cells so small?



Figure **9.3.1**: Bacterial cell attacking a human red blood cell

EXPLAINING CELL SIZE

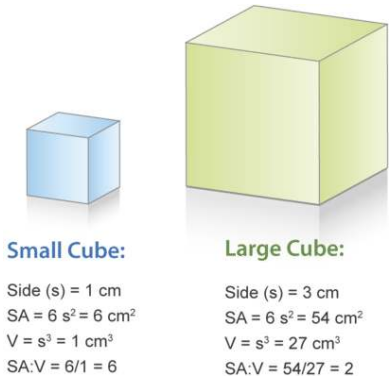


Figure **9.3.2**: Surface Area to Volume Comparison. A larger cube has a smaller surface area (SA) to volume (V) ratio than a smaller cube. This also holds true for cells and limits how large they can be.

Table **9.3.1**: Characteristics of small and large cubes

Characteristic	Small Cube	Large Cube
sides (S)	$1cm$	$3cm$
Surface Area (SA)	$6S^2 = 6 \times 1^2 = 6cm^2$	$6S^2 = 6 \times 3^2 = 54cm^2$
Volume (V)	$S^3 = 1^3 = 1cm^3$	$S^3 = 3^3 = 27cm^3$
SA:V	$SA/V = 6/1 = 6$	$SA/V = 54/27 = 2$

Most organisms, even very large ones, have microscopic cells. Why don't cells get bigger instead of remaining tiny and multiplying? What limits cell size?

The answers to these questions are clear once you know how a cell functions. To carry out life processes, a cell must be able to quickly pass substances into and out of the cell. For example, it must be able to pass nutrients and oxygen into the cell and waste products out of the cell. Anything that enters or leaves a cell must cross its outer surface. It is this need to pass substances across the surface that limits how large a cell can be.

Look at the two cubes in Figure **9.3.2**. As this figure and table show, a larger cube has less surface area relative to its volume than a smaller cube. This relationship also applies to cells; a larger cell has less surface area relative to its volume than a smaller cell. A cell with a larger volume also needs more nutrients and oxygen and produces more wastes. Because all of these substances must pass through the surface of the cell, a cell with a large volume will not have enough surface area to allow it to meet its needs. The larger the cell is, the smaller its ratio of surface area to volume, and the harder it will be for the cell to get rid of its wastes and take in necessary substances. This is what limits the size of the cell.

CELL FORM AND FUNCTION

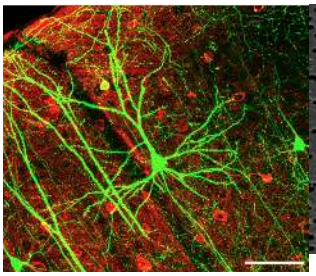


Figure **9.3.3**: Human nerve cell

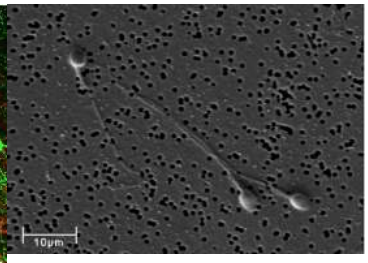


Figure **9.3.4**: Human sperm cells

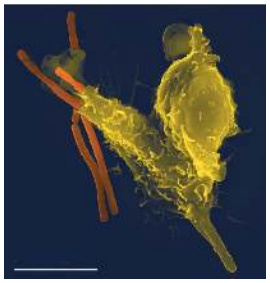


Figure **9.3.5**: Human white blood cell

Cells with different functions often have different shapes. The cells in Figure **9.3.3** - Figure **9.3.5** are just a few examples of the many different shapes that human cells may have. Each type of cell in the figure has characteristics that help it do its job. For example, the job of the nerve cell is to carry messages to other cells. The nerve cell has many long extensions that reach out in all directions, allowing it to pass messages to many other cells at once. Do you see the tail of each tiny sperm cell? Its tail helps a sperm cell "swim" through fluids in the female reproductive tract in order to reach an egg cell. The white blood cell has the job of destroying bacteria and other pathogens. Figure **9.3.5** shows the large white blood cell (in yellow) engulfing and destroying bacteria (in orange).

CELLS WITH AND WITHOUT A NUCLEUS

There is a basic cell structure that is present in many but not all living cells: the nucleus. The nucleus of a cell is a structure in the cytoplasm that is surrounded by a membrane (the nuclear membrane) and contains DNA. Based on whether or not they have a nucleus, there are two basic types of cells: prokaryotic cells and eukaryotic cells.

PROKARYOTIC CELLS

Prokaryotic cells are cells without a nucleus. The DNA in prokaryotic cells is in the cytoplasm rather than enclosed within a nuclear membrane. Prokaryotic cells are found in single-celled organisms, such as the bacterium represented by the model below. Organisms with prokaryotic cells are called **prokaryotes**. They were the first type of organisms to evolve and are still the most common organisms today.

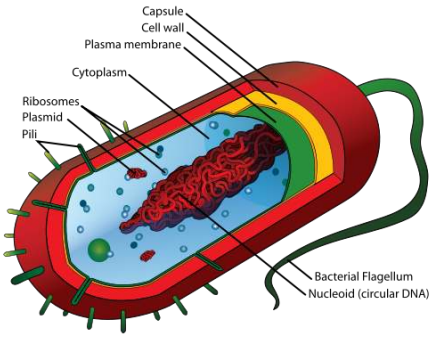


Figure **9.3.6**: Prokaryotic Cell. This diagram shows the structure of a typical prokaryotic cell, a bacterium. Like other prokaryotic cells, this bacterial cell lacks a nucleus but has other cell parts, including a plasma membrane, cytoplasm, ribosomes, and DNA.

Table **9.3.2**: Prokaryotic cell structures

Cell Structure	Description
Flagellum	Long projection(s) outside of the cell in some bacteria; aids in the motility
Pili	Small projections outside of the cell; aid in attachment
Capsule	A thick protective layer outside the cell wall of some bacteria
Cell wall	Outer layer of bacterial cells; more chemically complex than eukaryotic cell walls
Plasma Membrane	Phospholipid bilayer marking the outside of the cytoplasm
Cytoplasm	The fluid portion of the cell
Ribosome	Involved in protein synthesis
Nucleoid	Circular DNA found in the cytoplasm
Plasmid	Small loops of DNA found in some bacteria

EUKARYOTIC CELLS

Eukaryotic cells are cells that contain a nucleus. A typical eukaryotic cell is represented by the model below. Eukaryotic cells are usually larger than prokaryotic cells. They are found in some single-celled and all multicellular organisms. Organisms with eukaryotic cells are called **eukaryotes**, and they range from fungi to people.

Besides a nucleus, eukaryotic cells also contain other organelles. An **organelle** is a structure within the cytoplasm that performs a specific job in the cell. Organelles called mitochondria, for example, provide energy to the cell, and organelles called vacuoles store substances in the cell. Organelles allow eukaryotic cells to carry out more functions than prokaryotic cells can.

Table **9.3.3**: Eukaryotic cell structures

Structure	Location	Description
Flagellum	Outside the cell	A projection used for locomotion in some eukaryotic cells
Plasma Membrane	Outer layer of cell	Phospholipid bilayer enclosing the cytoplasm
Cytoplasm	Bound by the plasma membrane	Entire region between the plasma membrane and the nuclear envelope, consisting of organelles suspended in the gel-like cytosol, the cytoskeleton, and various chemicals
Golgi Vesicles (Golgi Apparatus)	Cytoplasm	A series of stacked membranes that sorts, tags, and packages lipids and proteins for distribution
Ribosomes	free-floating or on rough ER	Involved in protein synthesis
Rough Endoplasmic Reticulum	Cytoplasm	Interconnected membranous structures that are studded with ribosomes and engage in protein modification and phospholipid synthesis
Smooth Endoplasmic Reticulum	Cytoplasm	Interconnected membranous structures that have few or no ribosomes on its cytoplasmic surface and synthesize carbohydrates, lipids, and steroid hormones; detoxifies certain chemicals (like pesticides, preservatives, medications, and environmental pollutants), and stores calcium ions
Mitochondria	Cytoplasm	(singular = mitochondrion) cellular organelles responsible for carrying out cellular respiration, resulting in producing ATP, the cell's main energy-carrying molecule
Peroxisome	Cytoplasm	The small, round organelle that contains hydrogen peroxide, and detoxifies many poisons
Lysosome	Cytoplasm	Organelle in an animal cell that functions as the cell's digestive component; it breaks down proteins, polysaccharides, lipids, nucleic acids, and even worn-out organelles
Secretory Vesicle	Cytoplasm	Small, membrane-bound sac that functions in cellular storage and transport; its membrane is capable of fusing with the plasma membrane and the membranes of the endoplasmic reticulum and Golgi apparatus
Centrosome (with 2 centrioles)	Cytoplasm	Region in animal cells made of two centrioles that serve as an organizing center for microtubules
Actin Filaments	Cytoskeleton	The cytoskeleton's narrowest element; it provides rigidity and shape to the cell and enables cellular movements
Intermediate Filaments	Cytoskeleton	Cytoskeletal component, comprised of several fibrous protein intertwined strands, that bears tension, supports cell-cell junctions, and anchors cells to extracellular structures
Microtubules	Cytoskeleton	The cytoskeleton's widest element; provides a track along which vesicles move through the cell, pulls replicated chromosomes to opposite ends of a dividing cell, and is the structural element of centrioles
Cytoskeleton	Throughout cell	Protein fiber network that collectively maintains the cell's shape, secures some organelles in specific positions and allows cytoplasm and vesicles to move within the cell
Nucleus	Cytoplasm	Cell organelle that houses the cell's DNA and directs ribosome and protein synthesis
Nuclear Pore	Nucleus	Pores in the nuclear envelope allow substances to enter and exit the nucleus.
Nuclear Envelope	Nucleus	Double-membrane structure that constitutes the nucleus' outermost portion
Chromatin	Nucleus	Protein-DNA complex that serves as the chromosomes' building material
Nucleolus	Nucleus	Darkly staining body within the nucleus that is responsible for assembling ribosome subunits

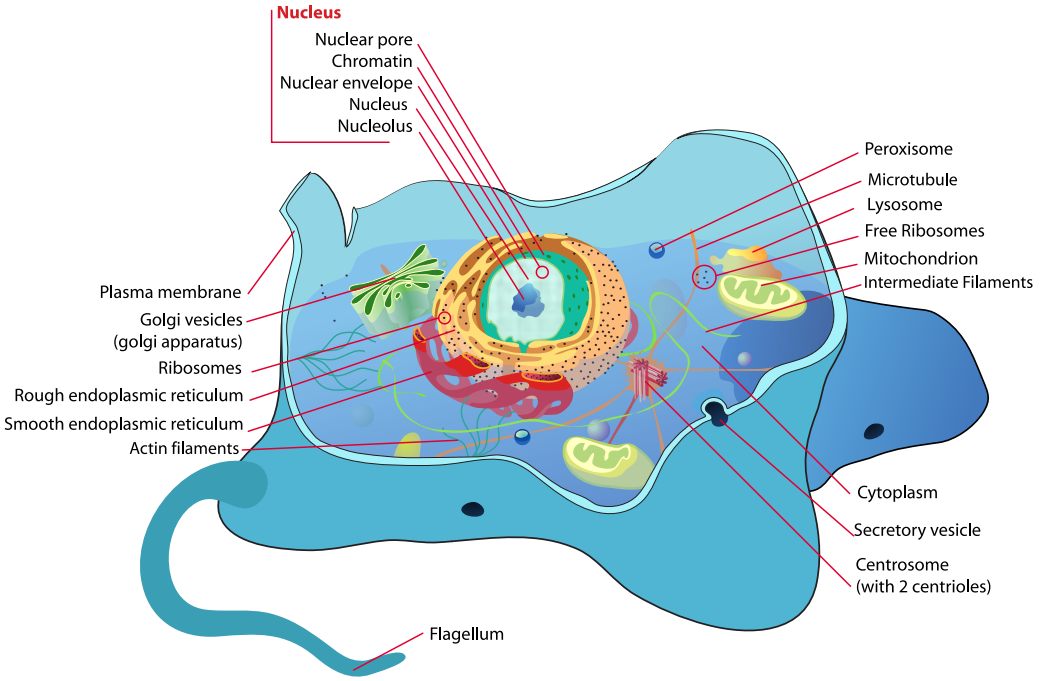


Figure **9.3.7**: Eukaryotic Cell. Compare and contrast the eukaryotic cell shown here with the prokaryotic cell. What similarities and differences can you identify?

REVIEW

1. Explain why most cells are very small.
2. Discuss variations in the form and function of cells.
3. Compare and contrast prokaryotic and eukaryotic cells.
4. *True or False.* Prokaryotic cells do not have mitochondria.
5. *True or False.* Prokaryotic cells do not have DNA.
6. *True or False.* All single-celled organisms are prokaryotes.
7. Which was the first type of organism to evolve – eukaryotes or prokaryotes? Based on their structures, does this make sense to you? Explain your answer.
8. Do human cells have organelles? Explain your answer.
9. Which are usually larger – prokaryotic or eukaryotic cells? What do you think this means for their relative ability to take in needed substances and release wastes? Discuss your answer.
10. DNA in eukaryotes is enclosed within the _____ _____.
11. Name three different types of cells in humans.
12. Which organelle provides energy in eukaryotic cells?
13. What is the function of a vacuole in a cell?

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9.4: PLASMA MEMBRANE

A BAG FULL OF JELL-O

This simple, cut-away model of an animal cell (Figure **9.4.1**) shows that a cell resembles a plastic bag full of Jell-O. Its basic structure is a plasma membrane filled with cytoplasm. Like Jell-O containing mixed fruit, the cytoplasm of the cell also contains various structures, such as a nucleus and other organelles. Your body is made up of trillions of cells, but all of them perform the same basic life functions. They all obtain and use energy, respond to the environment, and reproduce. How do your cells carry out these basic functions and keep themselves — and you — alive? To answer these questions, you need to know more about the structures that make up cells, starting with the plasma membrane.



Figure **9.4.1**: Animal cell model

The plasma membrane is a structure that forms a barrier between the cytoplasm inside the cell and the environment outside the cell. Without the plasma membrane, there would be no cell. The membrane also protects and supports the cell and controls everything that enters and leaves it. It allows only certain substances to pass through while keeping others in or out. To understand how the plasma membrane controls what passes into or out of the cell, you need to know its basic structure.

PHOSPHOLIPID BILAYER

The **plasma membrane** is composed mainly of **phospholipids**, which consist of fatty acids and alcohol. The phospholipids in the plasma membrane are arranged in two layers, called a **phospholipid bilayer**, with a hydrophobic, or water-hating, interior and a hydrophilic, or water-loving, exterior. Each phospholipid molecule has a head and two tails. The head “loves” water (hydrophilic) and the tails “fear” water (hydrophobic). The water-fearing tails are on the interior of the membrane, whereas the water-loving heads point outwards, toward either the cytoplasm or the fluid that surrounds the cell. The polar head group and fatty acid chains are attached by a 3-carbon glycerol unit. Figure **9.4.2** shows a single phospholipid next to a phospholipid bilayer.

Molecules that are hydrophobic can easily pass through the plasma membrane if they are small enough because they are water-hating like the interior of the membrane. Molecules that are hydrophilic, on the other hand, cannot pass through the plasma membrane — at least not without help — because they are water-loving like the exterior of the membrane.

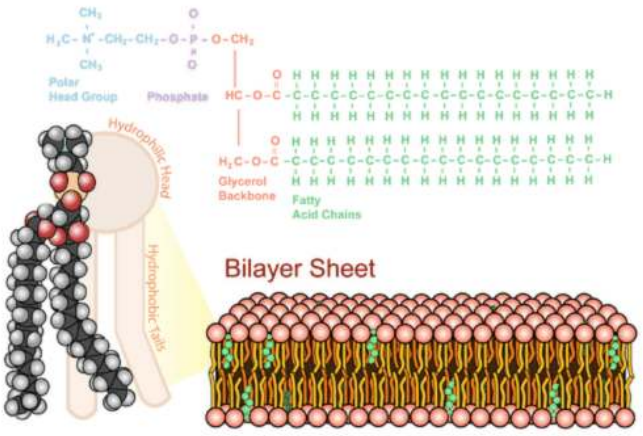


Figure **9.4.2**: Phospholipid and a phospholipid Bilayer.

OTHER MOLECULES IN THE PLASMA MEMBRANE

The plasma membrane also contains other molecules, primarily other lipids and proteins. The green molecules in Figure **9.4.2**, for example, are the lipid cholesterol. Molecules of the steroid lipid cholesterol help the plasma membrane keep its shape. (Figure **9.4.3**) shows the cholesterol molecules as yellow structures within the center of the phospholipid bilayer. Other structures shown in (Figure **9.4.3**):

- Protein channels. These span the full membrane and have a space within them because they are used to transport materials into or out of the cell.
- Transmembrane proteins. The root "trans" explains that these span (go "across") the membrane. Transmembrane proteins can have a variety of functions.
- Peripheral proteins. These are found only on one side of the membrane. They can be found on either the cytoplasmic side or the outside of the membrane.
- Glycoproteins. These consist of a protein in the plasma membrane with chains of carbohydrates projecting out of the cell.
- Glycolipids. These are chains of carbohydrates attached directly to a lipid in the membrane. Both glycoproteins and glycolipids act as labels to identify the cell.
- Filaments of cytoskeleton are found along the cytoplasmic side of the membrane and provide a scaffolding for the membrane.

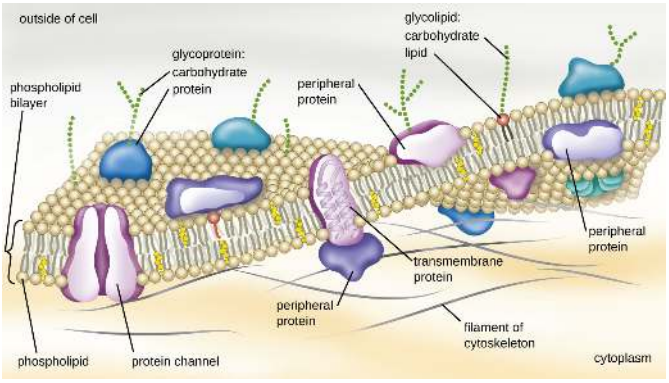


Figure **9.4.3**: The figure illustrates the major components of the phospholipid bilayer.

ADDITIONAL FUNCTIONS OF THE PLASMA MEMBRANE

The plasma membrane may have extensions, such as whip-like **flagella** or brush-like **cilia**, that give it other functions. In single-celled organisms, like those shown below, these membrane extensions may help the organisms move. In multicellular organisms, the extensions have different functions. For example, the cilia on human lung cells sweep foreign particles and mucus toward the mouth and nose.

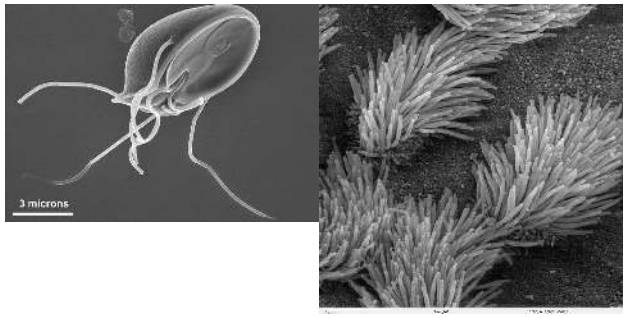


Figure **9.4.4**: Flagella of Giardia (left) and cilia of human respiratory mucosa (right). Flagella and cilia are extensions of the plasma membrane of many cells.

FEATURE: MY HUMAN BODY

If you smoke and need another reason to quit, here's a good one. We usually think of lung cancer as a major disease caused by smoking. But smoking can have devastating effects on the body's ability to protect itself from repeated, serious respiratory infections, such as bronchitis and pneumonia.

Cilia are microscopic, hair-like projects on cells that line the respiratory, reproductive, and digestive systems. Cilia in the respiratory system line most of your airways where they have the job of trapping and removing dust, germs, and other foreign particles before they can make you sick. Cilia secrete mucus that traps particles, and they move in a continuous wave-like motion that sweeps the mucus and particles upward toward the throat, where they can be expelled from the body. When you are sick and cough up phlegm, that's what you are doing.

Smoking prevents cilia from performing these important functions. Chemicals in tobacco smoke paralyze the cilia so they can't sweep mucus out of the airways and they also inhibit the cilia from producing mucus. Fortunately, these effects start to wear off soon after the last exposure to tobacco smoke. If you stop smoking, your cilia will return to normal. Even if prolonged smoking has destroyed cilia, they will regrow and resume functioning in a matter of months after you stop smoking.

REVIEW

1. What are the general functions of the plasma membrane?
2. Describe the phospholipid bilayer of the plasma membrane.
3. Identify other molecules in the plasma membrane, and state their functions.
4. Why do some cells have plasma membrane extensions such as flagella and cilia?
5. Explain why hydrophilic molecules cannot easily pass through the cell membrane. What type of molecule in the cell membrane might help hydrophilic molecules pass through it?
6. Which part of a phospholipid molecule in the plasma membrane is made of fatty acid chains? Is this part hydrophobic or hydrophilic?
7. The two layers of phospholipids in the plasma membrane are called a phospholipid _____.
8. *True or False.* The flagella on your lung cells sweep foreign particles and mucus toward your mouth and nose.
9. *True or False.* Small hydrophobic molecules can easily pass through the plasma membrane.
10. *True or False.* The side of the cell membrane that faces the cytoplasm is hydrophilic.
11. Steroid hormones can pass directly through cell membranes. Why do you think this is the case?
12. Some antibiotics work by making holes in the plasma membrane of bacterial cells. How do you think this kills the cells?
13. What is the name of the long, whip-like extensions of the plasma membrane that helps some single-celled organisms move?

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9.5: Connections between Cells and Cellular Activities

Skills to Develop

- Describe the extracellular matrix
- List examples of the ways that plant cells and animal cells communicate with adjacent cells
- Summarize the roles of tight junctions, desmosomes, gap junctions, and plasmodesmata

You already know that a group of similar cells working together is called a tissue. As you might expect, if cells are to work together, they must communicate with each other, just as you need to communicate with others if you work on a group project. Let's take a look at how cells communicate with each other.

Extracellular Matrix of Animal Cells

Most animal cells release materials into the extracellular space. The primary components of these materials are proteins, and the most abundant protein is collagen. Collagen fibers are interwoven with carbohydrate-containing protein molecules called proteoglycans. Collectively, these materials are called the extracellular matrix (Figure 9.5.1). Not only does the extracellular matrix hold the cells together to form a tissue, but it also allows the cells within the tissue to communicate with each other. How can this happen?

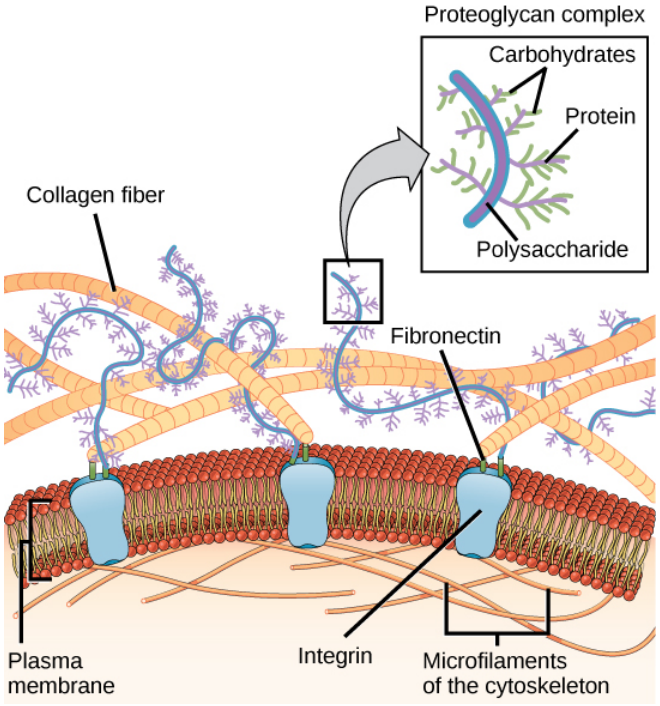


Figure 9.5.1: The extracellular matrix consists of a network of proteins and carbohydrates.

Cells have protein receptors on the extracellular surfaces of their plasma membranes. When a molecule within the matrix binds to the receptor, it changes the molecular structure of the receptor. The receptor, in turn, changes the conformation of the microfilaments positioned just inside the plasma membrane. These conformational changes induce chemical signals inside the cell that reach the nucleus and turn "on" or "off" the transcription of specific sections of DNA, which affects the production of associated proteins, thus changing the activities within the cell.

Blood clotting provides an example of the role of the extracellular matrix in cell communication. When the cells lining a blood vessel are damaged, they display a protein receptor called tissue factor. When tissue factor binds with another factor in the extracellular matrix, it causes platelets to adhere to the wall of the damaged blood vessel, stimulates the adjacent smooth muscle cells in the blood vessel to contract (thus constricting the blood vessel), and initiates a series of steps that stimulate the platelets to produce clotting factors.

Intercellular Junctions

Cells can also communicate with each other via direct contact, referred to as intercellular junctions. There are some differences in the ways that plant and animal cells do this. Plasmodesmata are junctions between plant cells, whereas animal cell contacts include tight junctions, gap junctions, and desmosomes.

Plasmodesmata

In general, long stretches of the plasma membranes of neighboring plant cells cannot touch one another because they are separated by the cell wall that surrounds each cell. How then, can a plant transfer water and other soil nutrients from its roots, through its stems, and to its leaves? Such transport uses the vascular tissues (xylem and phloem) primarily. There also exist structural modifications called plasmodesmata (singular = plasmodesma), numerous channels that pass between cell walls of adjacent plant cells, connect their cytoplasm, and enable materials to be transported from cell to cell, and thus throughout the plant (Figure 9.5.2).

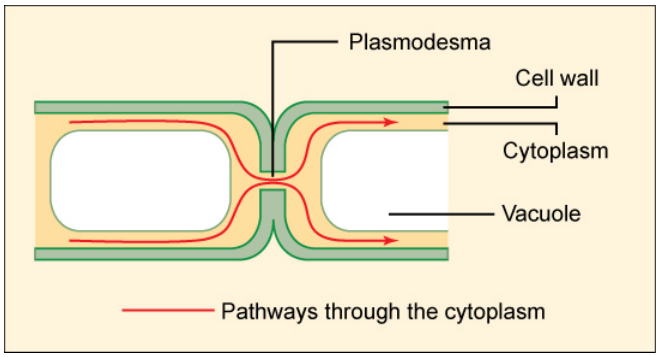


Figure 9.5.2: A plasmodesma is a channel between the cell walls of two adjacent plant cells. Plasmodesmata allow materials to pass from the cytoplasm of one plant cell to the cytoplasm of an adjacent cell.

Tight Junctions

A tight junction is a watertight seal between two adjacent animal cells (Figure 9.5.3). The cells are held tightly against each other by proteins (predominantly two proteins called claudins and occludins).

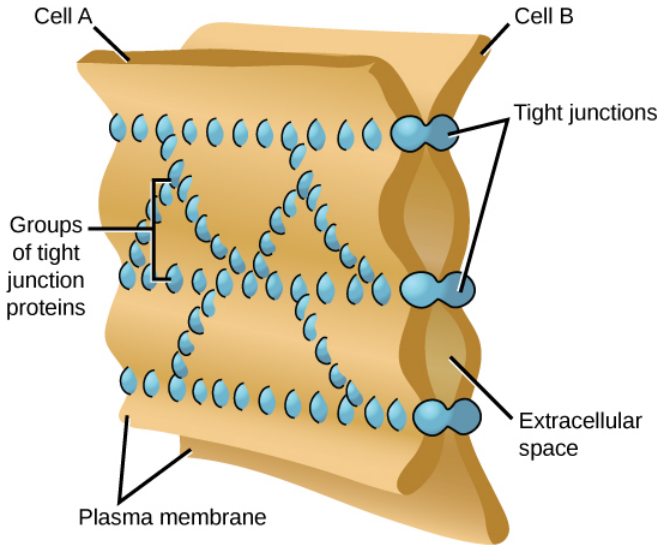


Figure 9.5.3: Tight junctions form watertight connections between adjacent animal cells. Proteins create tight junction adherence. (credit: modification of work by Mariana Ruiz Villareal)

This tight adherence prevents materials from leaking between the cells; tight junctions are typically found in epithelial tissues that line internal organs and cavities, and comprise most of the skin. For example, the tight junctions of the epithelial cells lining your urinary bladder prevent urine from leaking out into the extracellular space.

Desmosomes

Also found only in animal cells are desmosomes, which act like spot welds between adjacent epithelial cells (Figure 9.5.4). Short proteins called cadherins in the plasma membrane connect to intermediate filaments to create desmosomes. The cadherins join two adjacent cells together and maintain the cells in a sheet-like formation in organs and tissues that stretch, like the skin, heart, and muscles.

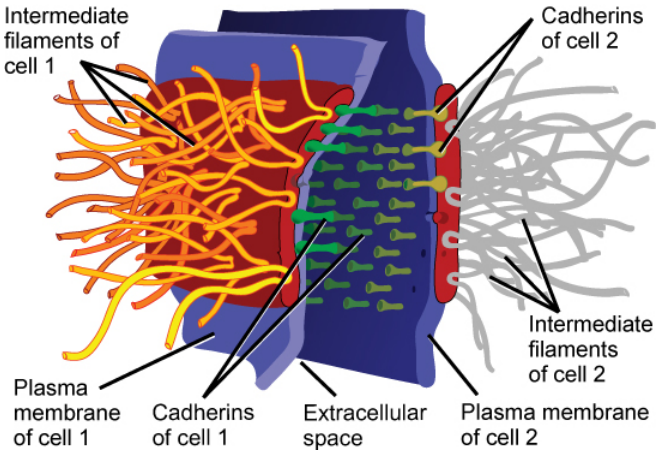


Figure 9.5.4: A desmosome forms a very strong spot weld between cells. It is created by the linkage of cadherins and intermediate filaments. (credit: modification of work by Mariana Ruiz Villareal)

Gap Junctions

Gap junctions in animal cells are like plasmodesmata in plant cells in that they are channels between adjacent cells that allow for the transport of ions, nutrients, and other substances that enable cells to communicate (Figure 9.5.5). Structurally, however, gap junctions and plasmodesmata differ.

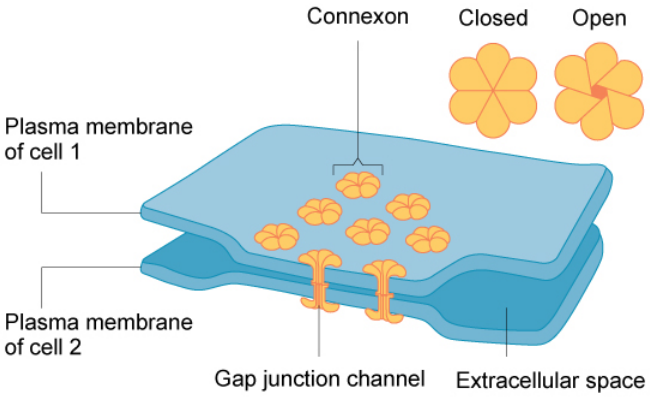


Figure 9.5.5: A gap junction is a protein-lined pore that allows water and small molecules to pass between adjacent animal cells. (credit: modification of work by Mariana Ruiz Villareal)

Gap junctions develop when a set of six proteins (called connexins) in the plasma membrane arrange themselves in an elongated donut-like configuration called a connexon. When the pores (“doughnut holes”) of connexons in adjacent animal cells align, a channel between the two cells forms. Gap junctions are particularly important in cardiac muscle: The electrical signal for the muscle to contract is passed efficiently through gap junctions, allowing the heart muscle cells to contract in tandem.

Summary

Animal cells communicate via their extracellular matrices and are connected to each other via tight junctions, desmosomes, and gap junctions. Plant cells are connected and communicate with each other via plasmodesmata.

When protein receptors on the surface of the plasma membrane of an animal cell bind to a substance in the extracellular matrix, a chain of reactions begins that changes activities taking place within the cell. Plasmodesmata are channels between adjacent plant cells, while gap junctions are channels between adjacent animal cells. However, their structures are quite different. A tight junction is a watertight seal between two adjacent cells, while a desmosome acts like a spot weld.

Glossary

desmosome
: linkages between adjacent epithelial cells that form when cadherins in the plasma membrane attach to intermediate filaments

extracellular matrix
: material (primarily collagen, glycoproteins, and proteoglycans) secreted from animal cells that provides mechanical protection and anchoring for the cells in the tissue

gap junction
: channel between two adjacent animal cells that allows ions, nutrients, and low molecular weight substances to pass between cells, enabling the cells to communicate

plasmodesma
: (plural = plasmodesmata) channel that passes between the cell walls of adjacent plant cells, connects their cytoplasm, and allows materials to be transported from cell to cell

tight junction
: firm seal between two adjacent animal cells created by protein adherence

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9.6: CYTOPLASM AND CYTOSKELETON

A PEEK INSIDE THE CELL

Figure **9.6.1** may look like a colorful work of abstract art or maybe an ultra-modern carpet design, but it's neither. It is actually a model of the interior of a cell. It's an artist's representation of what you might see if you could take a peek inside one of these basic building blocks of living things. A cell's interior is obviously a crowded and busy space. It contains cytoplasm, dissolved substances, and many structures; and it's a hive of countless biochemical activities all going on at once.

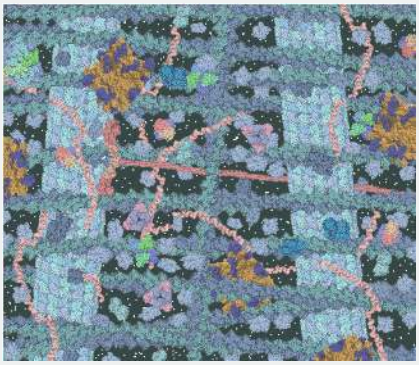


Figure **9.6.1**: Picture of cytosol, showing microtubules (light blue), actin filaments (dark blue), ribosomes (yellow and purple), soluble proteins (light blue), kinesin (red), small molecules (white) and RNA (pink).

CYTOPLASM

The **cytoplasm** is a thick, usually colorless solution that fills each cell and is enclosed by the cell membrane. Cytoplasm presses against the cell membrane, filling out the cell and giving it its shape. Sometimes cytoplasm acts like a watery solution and sometimes it takes on a more gel-like consistency. In eukaryotic cells, the cytoplasm includes all of the material inside the cell but outside the nucleus, which contains its own watery substance called **nucleoplasm**. All of the organelles in eukaryotic cells, such as the endoplasmic reticulum and mitochondria, are located in the cytoplasm. The cytoplasm helps to keep them in place. It is also the site of most metabolic activities in the cell, and it allows materials to pass easily throughout the cell.

The portion of the cytoplasm surrounding organelles is called cytosol, which is the liquid part of the cytoplasm. It is composed of about 80 percent water and also contains dissolved salts, fatty acids, sugars, amino acids, and proteins such as enzymes. These dissolved substances are needed to keep the cell alive and carry out metabolic processes. For example, enzymes dissolved in cytosol break down larger molecules into smaller products that can then be used by organelles of the cell. Waste products are also dissolved in the cytosol before they are taken in by vacuoles or expelled from the cell.

Though prokaryotic cells do not have organelles (they do have ribosomes), they still have cytoplasm. It is within the cytoplasm that most cellular activities occur, including the many metabolic pathways that occur within organelles, such as photosynthesis and aerobic respiration.

CYTOSKELETON

Although cytoplasm may appear to have no form or structure, it is actually highly organized. A framework of protein scaffolds called the **cytoskeleton** provides the cytoplasm and the cell with structure. The cytoskeleton consists of thread-like filaments and tubules that criss-cross the cytoplasm. You can see these filaments and tubules in the cells in Figure **9.6.2**. As its name suggests, the cytoskeleton is like a cellular “skeleton.” It helps the cell maintain its shape and also helps to hold cell structures such as organelles in place within the cytoplasm.

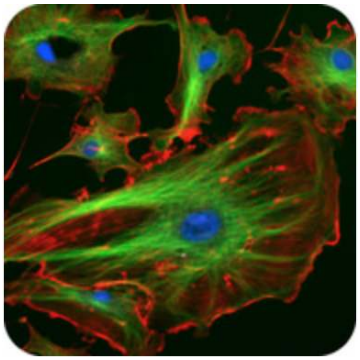


Figure **9.6.2**: Cytoskeleton. The cytoskeleton gives the cell an internal structure, like the frame of a house. In this photograph, actin filaments and tubules of the cytoskeleton are green and red, respectively. The blue dots are cell nuclei.

The eukaryotic cytoskeleton is made up of a network of long, thin protein fibers. These threadlike proteins continually rebuild to adapt to the cell's constantly changing needs. Three main kinds of cytoskeleton fibers are microtubules, intermediate filaments, and microfilaments (Table **9.6.1**).

- **Microtubules** are the thickest of the cytoskeleton structures. They are most commonly made of filaments which are polymers of alpha and beta-tubulin and radiate outwards from an area near the nucleus called the centrosome. Two forms of tubulin form dimers (pairs) which come together to form the hollow cylinders. The cylinders are twisted around each other to form the microtubules. Microtubules help the cell keep its shape. They hold organelles in place and allow them to move around the cell, and they form the mitotic spindle during cell division. Microtubules also make up parts of cilia and flagella, the organelles that help a cell move.
- **Microfilaments** are made of two thin **actin** chains that are twisted around one another. Microfilaments are mostly concentrated just beneath the cell membrane, where they support the cell and help the cell keep its shape. Microfilaments form cytoplasmatic extensions, such as **microvilli** and pseudopodia, which allow certain cells to move. The actin and myosin protein interact to cause a contraction in muscle cells. Microfilaments

are found in almost every cell and are numerous in muscle cells and in cells that move by changing shape, such as phagocytes (white blood cells that search the body for bacteria and other invaders).

- **Intermediate filaments (IF)** differ in make-up from one cell type to another. The IF may be composed of **vimentin**, **keratin**, **desmin**, or **lamin**. Each cell type can have a unique combination of IFs. For example, intermediate filaments made of keratin are found in skin, hair, and nail cells. IFs organize the inside structure of the cell by holding organelles and providing strength. They are also structural components of the nuclear envelope. Intermediate filaments made of the protein keratin are found in skin, hair, and nail cells.

Table **9.6.1**: Cytoskeleton Structure

Characteristic	Microtubules	Intermediate Filaments	Microfilaments
Fiber Diameter	About 25 nm	8 to 11 nm	Around 7 nm
Protein Composition	Tubulin with two subunits, alpha, and beta-tubulin	One of the different types of proteins such as lamin, vimentin, desmin, and keratin	Actin
Shape	Hollow cylinders made of two protein chains twisted around each other	Protein fiber coils twisted into each other	Two actin chains twisted around one another
Main Functions	Organelle and vesicle movement; form mitotic spindles during cell reproduction; cell motility (in cilia and flagella)	Organize cell shape; positions organelles in cytoplasm structural support of the nuclear envelope and sarcomeres; involved in cell-to-cell and cell-to-matrix junctions	Keep cellular shape; allows movement of certain cells by forming cytoplasmatic extensions or contraction of actin fibers; involved in some cell-to-cell or cell-to-matrix junctions

FEATURE: HUMAN BIOLOGY IN THE NEWS

News about an important study of the cytoplasm of eukaryotic cells appeared early in 2016. Researchers in Dresden, Germany discovered that when cells are deprived of adequate nutrients, they may essentially shut down and become dormant. Specifically, when cells do not get enough nutrients, they shut down their metabolism, their energy level drops, and the pH of their cytoplasm decreases. Their normally liquid cytoplasm also assumes a solid state. The cells appear dead and as though a kind of rigor mortis has set in. The researchers think that these changes protect the sensitive structures inside the cells and allow the cells to survive difficult conditions. If nutrients are returned to the cells, they can emerge from their dormant state unharmed. They will continue to grow and multiply when conditions improve.

This important basic science research was carried out on a nonhuman organism: one-celled fungi called yeasts. Nonetheless, it may have important implications for humans because yeasts have eukaryotic cells with many of the same structures as human cells. Yeast cells appear to be able to "trick" death by shutting down all life processes in a controlled way. Researchers hope to learn with the continued research on whether human cells can be taught this "trick" as well.

REVIEW

1. Describe the composition of cytoplasm.
2. What are some of the functions of cytoplasm?
3. Outline the structure and functions of the cytoskeleton.
4. Is the cytoplasm made of cells? Why or why not?
5. Name two types of cytoskeletal structures.
6. *True or False.* The cytoplasm is usually green.
7. *True or False.* The nucleus of a cell is filled with cytoplasm.
8. In Figure **9.6.2** of the different cytoskeletal structures above (shown in red and green), what do you notice about these different structures?
9. Describe one example of a metabolic process that occurs in the cytosol.
10. In eukaryotic cells, all of the material inside of the cell but outside of the nucleus is called the _____.
11. What is the liquid part of the cytoplasm called?
12. What chemical substance makes up most of the cytosol?
13. When yeast cells deprived of nutrients go dormant, their cytoplasm assumes a solid-state. What effect do you think a solid cytoplasm would have on normal cellular processes? Explain your answer.
14. What is the difference between cytoplasm and cytosol?
15. Name the three main parts of the cytoskeleton.
16. List two functions of the eukaryotic cytoskeleton

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CHAPTER OVERVIEW

10: Membranes and Transport

10.1: Cell Transport
10.2: Active Transport and Homeostasis

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10.1: CELL TRANSPORT

LETTING IN THE LIGHT

Look at the big windows and glass doors in this house. Imagine all the light they must let in on a sunny day. Now imagine living in a house that has walls without any windows or doors. Nothing could enter or leave. Or imagine living in a house with holes in the walls instead of windows and doors. Things could enter or leave, but you couldn't control what came in or went out. Only if a house has walls with windows and doors that can be opened or closed you can control what enters or leaves. For example, windows and doors allow you to let in light and the family dog and keep out rain and bugs.



Figure **10.1.1**: A house with windows

TRANSPORT ACROSS MEMBRANES

If a cell were a house, the plasma membrane would be walls with windows and doors. Moving things in and out of the cell is an important role of the plasma membrane. It controls everything that enters and leaves the cell. There are two basic ways that substances can cross the plasma membrane: passive transport, which requires no energy; and active transport, which requires energy. Passive transport is explained in this section and Active transport is explained in the next section, Active Transport and Homeostasis. Various types of cell transport are summarized in the concept map in Figure **10.1.2**.

TRANSPORT WITHOUT ENERGY

Passive transport occurs when substances cross the plasma membrane without any input of energy from the cell. No energy is needed because the substances are moving from an area where they have a higher concentration to an area where they have a lower concentration. Water solutions are very important in biology. When water is mixed with other molecules this mixture is called a **solution**. Water is the **solvent** and the dissolved substance is the **solute**. A solution is characterized by the solute. For example, water and sugar would be characterized as a sugar solution. More the particles of a solute in a given volume, the higher the concentration. The particles of solute always move from an area where it is more concentrated to an area where it is less concentrated. It's a little like a ball rolling down a hill. It goes by itself without any input of extra energy.

The different categories of cell transport are outlined in Figure **10.1.2**. Cell transport can be classified as follows:

- Passive Transport which includes
  - Simple Diffusion
  - Osmosis
  - Facilitated Diffusion
- Active Transport can involve either a pump or a vesicle
  - Pump Transport can be
    - primary
    - secondary
  - Vesicle Transport can involve
    - Exocytosis
    - Endocytosis which includes
      - Pinocytosis
      - Phagocytosis
      - Receptor-Mediated Endocytosis

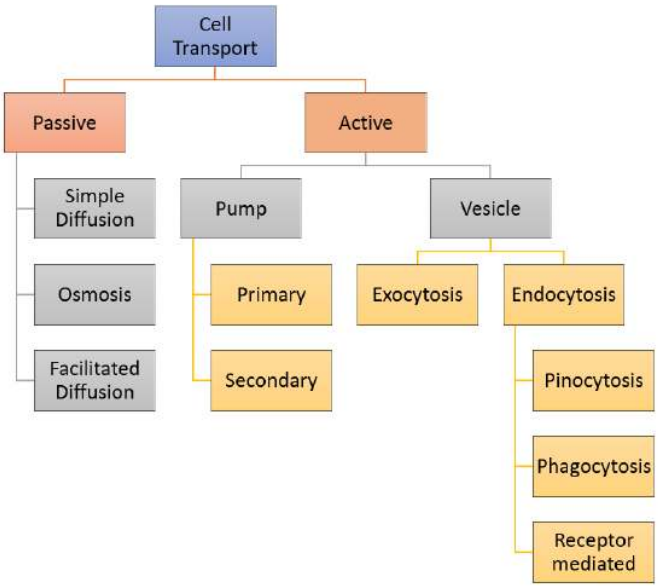


Figure **10.1.2**: The Cell Transport Concept Map illustrates various types of cell transports that happen at the plasma membrane

SIMPLE DIFFUSION

Diffusion Although you may not know what diffusion is, you have experienced the process. Can you remember walking into the front door of your home and smelling a pleasant aroma coming from the kitchen? It was the diffusion of particles from the kitchen to the front door of the house that allowed you to detect the odors. **Diffusion** is defined as the net movement of particles from an area of greater concentration to an area of lesser concentration.

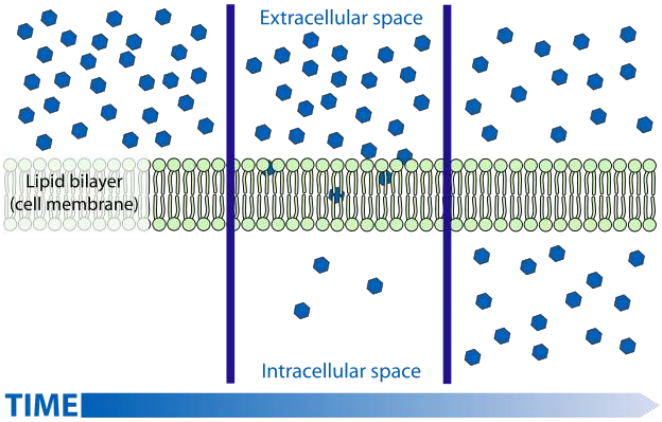


Figure **10.1.3**. Simple diffusion shows as a timeline with the outside of the cell (extracellular space) separated from the inside of the cell (intracellular space) by the cell membrane. In the beginning of the timeline there are many molecules outside of the cell and none inside. Over time, they diffuse into the cell until there is an equal amount outside and inside.

The molecules in a gas, a liquid, or a solid are in constant motion due to their kinetic energy. Molecules are in constant movement and collide with each other. These collisions cause the molecules to move in random directions. Over time, however, more molecules will be propelled into the less concentrated area. Thus, the net movement of molecules is always from more tightly packed areas to less tightly packed areas. Many things can diffuse. Odors diffuse through the air, salt diffuses through water and nutrients diffuse from the blood to the body tissues. This spread of particles through the random motion from an area of high concentration to an area of lower concentration is known as diffusion. This unequal distribution of molecules is called a concentration gradient. Once the molecules become uniformly distributed, a dynamic equilibrium exists. The equilibrium is said to be dynamic because molecules continue to move, but despite this change, there is no net change in concentration over time. Both living and nonliving systems experience the process of diffusion. In living systems, diffusion is responsible for the movement of a large number of substances, such as gases and small uncharged molecules, into and out of cells.

OSMOSIS

Osmosis is a specific type of diffusion; it is the passage of water from a region of high water concentration through a semi-permeable membrane to a region of low water concentration. Water moves in or out of a cell until its concentration is the same on both sides of the plasma membrane.

Semi-permeable membranes are very thin layers of material that allow some things to pass through them but prevent other things from passing through. Cell membranes are an example of semi-permeable membranes. Cell membranes allow small molecules such as oxygen, water carbon dioxide, and oxygen to pass through but do not allow larger molecules like glucose, sucrose, proteins, and starch to enter the cell directly.

The classic example used to demonstrate osmosis and osmotic pressure is to immerse cells into sugar solutions of various concentrations. There are three possible relationships that cells can encounter when placed into a sugar solution. Figure **10.1.4** shows what happens in osmosis through the semi-permeable membrane of the cells.

A. The concentration of solute in the solution can be **greater than** the concentration of solute in the cells. This cell is described as being in a **hypertonic solution** (hyper = greater than normal). The net flow or water will be out of the cell.
B. The concentration of solute in the solution can be **equal to** the concentration of solute in cells. In this situation, the cell is in an **isotonic solution** (iso = equal or the same as normal). The amount of water entering the cell is the same as the amount leaving the cell.
C. The concentration of solute in the solution can be **less than** the concentration of solute in the cells. This cell is in a **hypotonic solution** (hypo = less than normal). The net flow of water will be into the cell.

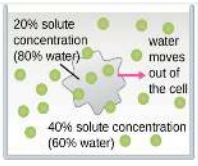


Figure **10.1.4.*A***: **Hypertonic solution.** A solution that has a higher solute concentration than another solution. Water particles will move out of the cell, causing crenation.

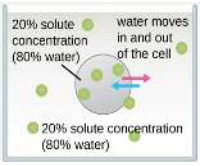


Figure **10.1.4.*B***: **Isotonic solution.** A solution that has the same solute concentration as another solution. There is no net movement of water particles, and the overall concentration on both sides of the cell membrane remains constant.

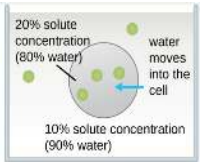


Figure **10.1.4.*C***: **Hypotonic solution.** A solution that has a lower solute concentration than another solution. Water particles will move into the cell, causing the cell to expand and eventually lyse.

Figure **10.1.5** demonstrates the specific outcomes of osmosis in red blood cells.

A. **Hypertonic solution.** The red blood cell will appear to shrink as the water flows out of the cell and into the surrounding environment.
B. **Isotonic solution.** The red blood cell will retain its normal shape in this environment as the amount of water entering the cell is the same as the amount leaving the cell.
C. **Hypotonic solution**. The red blood cell in this environment will become visibly swollen and potentially rupture as water rushes into the cell.

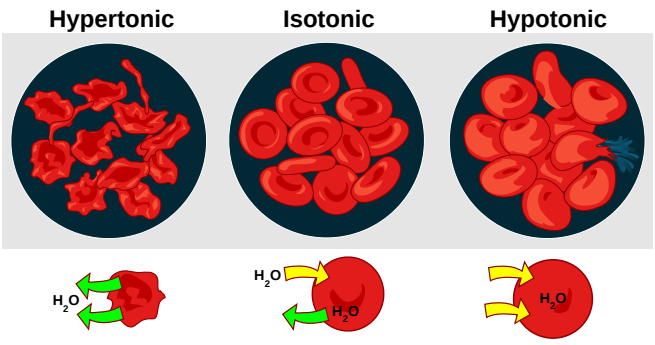


Figure **10.1.5**: Osmosis demonstration with Red Blood cells places in a hypertonic, isotonic, and hypotonic solution.

FACILITATED DIFFUSION

Water and many other substances cannot simply diffuse across a membrane. Hydrophilic molecules, charged ions, and relatively large molecules such as glucose all need help with diffusion. The help comes from special proteins in the membrane known as **transport proteins**. Diffusion with the help of transport proteins is called **facilitated diffusion**. There are several types of transport proteins, including channel proteins and carrier proteins (Figure **10.1.6**)

- Channel proteins form pores, or tiny holes, in the membrane. This allows water molecules and small ions to pass through the membrane without coming into contact with the hydrophobic tails of the lipid molecules in the interior of the membrane.
- Carrier proteins bind with specific ions or molecules, and in doing so, they change shape. As carrier proteins change shape, they carry the ions or molecules across the membrane.

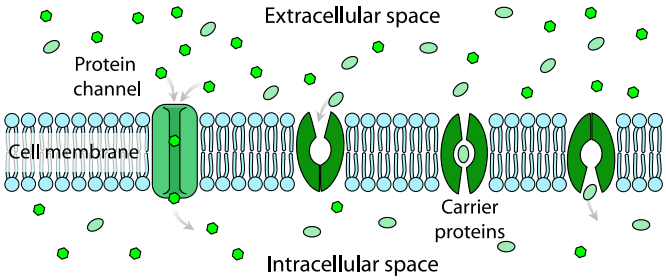


Figure **10.1.6**: Facilitated Diffusion Across a Cell Membrane. Channel proteins and carrier proteins help substances diffuse across a cell membrane. In this diagram, the channel and carrier proteins are helping substances move into the cell (from the extracellular space to the intracellular space). The channel protein has an opening that allows the substances to cross. In a carrier protein, the substance binds to the protein, which then causes the protein to changes shape, thereby releasing the substance into the cell.

REVIEW

1. What is the main difference between passive and active transport?
2. Summarize three different ways that passive transport can occur, and give an example of a substance that is transported in each way.
3. Explain how transport across the plasma membrane is related to the homeostasis of the cell.
4. Why can generally only very small, hydrophobic molecules across the cell membrane by simple diffusion?
5. Explain how facilitated diffusion assists in osmosis in cells. Be sure to define osmosis and facilitated diffusion in your answer.
6. Imagine a hypothetical cell with a higher concentration of glucose inside the cell than outside. Answer the following questions about this cell, assuming all transport across the membrane is passive, not active.
   A. Can the glucose simply diffuse across the cell membrane? Why or why not?
   B. Assuming that there are glucose transport proteins in the cell membrane, which way would glucose flow – into or out of the cell? Explain your answer.
   C. If the concentration of glucose was equal inside and outside of the cell, do you think there would be a net flow of glucose across the cell membrane in one direction or the other? Explain your answer.
7. What are the similarities and differences between channel proteins and carrier proteins?
8. *True or False.* Only active transport, not passive transport, involves transport proteins.
9. *True or False.* Oxygen and carbon dioxide can squeeze between the lipid molecules in the plasma membrane.
10. *True or False.* Ions easily diffuse across the cell membrane by simple diffusion.
11. Controlling what enters and leaves the cell is an important function of the:
    A. nucleus
    B. vesicle
    C. plasma membrane
    D. Golgi apparatus

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10.2: ACTIVE TRANSPORT AND HOMEOSTASIS

LIKE PUSHING A HUMVEE UPHILL

You can tell by their faces that these airmen are expending a lot of energy trying to push this Humvee up a slope. The men are participating in a competition that tests their brute strength against that of other teams. The Humvee weighs about 13,000 pounds, so it takes every ounce of energy they can muster to move it uphill against the force of gravity. Transport of some substances across a plasma membrane is a little like pushing a Humvee uphill — it can't be done without adding energy.



Figure **10.2.1**: Pushing a machine up a hill.

WHAT IS ACTIVE TRANSPORT?

Some substances can pass into or out of a cell across the plasma membrane without any energy required because they are moving from an area of higher concentration to an area of lower concentration. This type of transport is called passive transport as you learned in the last section. Other substances require energy to cross a plasma membrane often because they are moving from an area of lower concentration to an area of higher concentration. This type of transport is called **active transport**. The energy for active transport comes from the energy-carrying molecule called ATP (adenosine triphosphate). Active transport may also require transport proteins, such as carrier proteins, which are embedded in the plasma membrane. Two types of active transport are pump and vesicle transport.

PUMP

Two pump mechanisms (primary and secondary active transports) exist for the transport of small-molecular weight material and macromolecules. The **primary active transport** moves ions across a membrane and creates a difference in charge across that membrane. The primary active transport system uses ATP to move a substance, such as an ion, into the cell, and often at the same time, a second substance is moved out of the cell. The **sodium-potassium pump** is a mechanism of active transport that moves sodium ions out of the cell and potassium ions into the cells — in all the trillions of cells in the body! Both ions are moved from areas of lower to higher concentration, so energy is needed for this "uphill" process. The energy is provided by ATP. The sodium-potassium pump also requires carrier proteins. Carrier proteins bind with specific ions or molecules, and in doing so, they change shape. As carrier proteins change shape, they carry the ions or molecules across the membrane. Figure **10.2.2** shows in greater detail how the sodium-potassium pump works and the specific roles played by carrier proteins in this process.

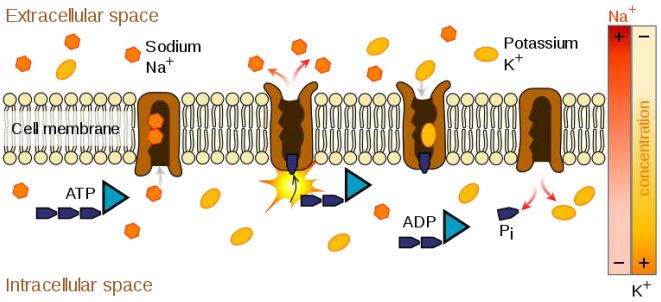


Figure **10.2.2**: The sodium-potassium pump. The sodium-potassium pump moves sodium ions (Na^+) out of the cell and potassium ions (K^+) into the cell. First, three sodium ions bind with a carrier protein in the cell membrane. Then, the carrier protein receives a phosphate group from ATP. When ATP loses a phosphate group, energy is released. The carrier protein changes shape, and as it does, it pumps the three sodium ions out of the cell. At that point, two potassium ions bind to the carrier protein. The process is reversed, and the potassium ions are pumped into the cell.

To appreciate the importance of the sodium-potassium pump, you need to know more about the roles of sodium and potassium in the body. Both are essential dietary minerals, meaning you have to obtain them in the foods you eat. Both sodium and potassium are also electrolytes, meaning that they dissociate into ions (charged particles) in solution, which allows them to conduct electricity. Normal body functions require a very narrow range of concentrations of sodium and potassium ions in body fluids, both inside and outside of cells.

- Sodium is the principal ion in the fluid outside of cells. Normal sodium concentrations are about 10 times higher outside than inside of cells.
- Potassium is the principal ion in the fluid inside of cells. Normal potassium concentrations are about 30 times higher inside than outside of cells.

These differences in concentration create an electrical gradient across the cell membrane, called the membrane potential. the **secondary active transport** describes the movement of material using the energy of the electrochemical gradient established by the primary active transport. Using the energy of the electrochemical gradient created by the primary active transport system, other substances such as amino acids and glucose can be brought into the cell through membrane channels. ATP itself is formed through secondary active transport using a hydrogen ion gradient in the mitochondrion. Tightly controlling the membrane potential is critical for vital body functions, including the transmission of nerve impulses and the contraction of muscles. A large percentage of the

body's energy goes to maintaining this potential across the membranes of its trillions of cells with the sodium-potassium pump.

VESICLE TRANSPORT

Some molecules, such as proteins, are too large to pass through the plasma membrane, regardless of their concentration inside and outside the cell. Very large molecules cross the plasma membrane with a different sort of help, called **vesicle transport**. Vesicle transport requires energy, so it is also a form of active transport. There are two types of vesicle transport: endocytosis and exocytosis.

ENDOCYTOSIS

Endocytosis is a type of vesicle transport that moves a substance into the cell. The plasma membrane completely engulfs the substance, a vesicle pinches off from the membrane, and the vesicle carries the substance into the cell. It is used by all cells of the body because most substances important to them are polar and consist of big molecules, and thus cannot pass through the hydrophobic plasma membrane. When an entire cell or other solid particle is engulfed, the process is called **phagocytosis**. When fluid is engulfed, the process is called **pinocytosis**. When the content is taken in specifically with the help of receptors on the plasma membrane, it is called **receptor-mediated endocytosis**.

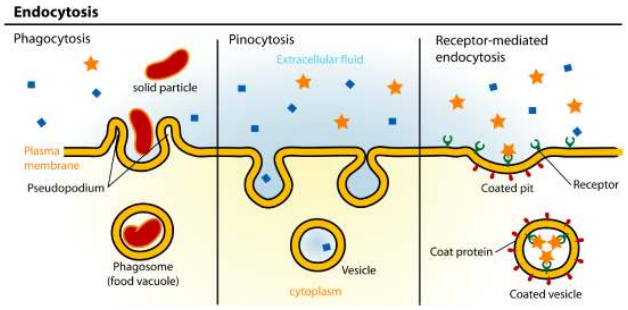


Figure **10.2.3**: (On the right) Phagocytosis is when the plasma membrane wraps around a solid particle outside the cell using projections called pseudopodia. The membrane then pinches off to form a phagosome (food vacuole). (Middle)Pinocytosis is when the membrane folds to form a vesicle that carries substances dissolved in the extracellular fluid. (On the left) Receptor-mediated endocytosis occurs when the receptors on the plasma membrane bind to specific particles. The coated pit region of the membrane forms a coated vesicle containing the receptors with their bound particles.

A targeted variation of endocytosis employs binding proteins in the plasma membrane that are specific for certain substances. The particles bind to the proteins and the plasma membrane invaginates, bringing the substance and the proteins into the cell. If passage across the membrane of the target of **receptor-mediated endocytosis** is ineffective, it will not be removed from the tissue fluids or blood. Instead, it will stay in those fluids and increase in concentration. Some human diseases are caused by a failure of receptor-mediated endocytosis. For example, the form of cholesterol termed low-density lipoprotein or LDL (also referred to as “bad” cholesterol) is removed from the blood by receptor-mediated endocytosis. In the human genetic disease familial hypercholesterolemia, the LDL receptors are defective or missing entirely. People with this condition have life-threatening levels of cholesterol in their blood because their cells cannot clear the chemical from their blood.

EXOCYTOSIS

Exocytosis is a type of vesicle transport that moves a substance out of the cell. A vesicle containing the substance moves through the cytoplasm to the cell membrane. Then, the vesicle membrane fuses with the cell membrane, and the substance is released outside the cell.

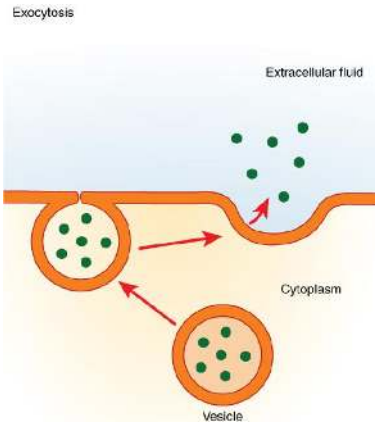


Figure **10.2.4**: Exocytosis is much like endocytosis in reverse. Material destined for export is packaged into a vesicle inside the cell. The membrane of the vesicle fuses with the cell membrane, and the contents are released into the extracellular space.

HOMEOSTASIS AND CELL FUNCTION

For a cell to function normally, a stable state must be maintained inside the cell. For example, the concentration of salts, nutrients, and other substances must be kept within a certain range. The process of maintaining stable conditions inside a cell (or an entire organism) is homeostasis. Homeostasis requires constant adjustments because conditions are always changing both inside and outside the cell. The processes described in this and previous lessons play important roles in homeostasis. By moving substances into and out of cells, they keep conditions within normal ranges inside the cells and the organism as a whole.

FEATURE:FEATURE: MY HUMAN BODY

Maintaining the proper balance of sodium and potassium in body fluids by active transport is necessary for life itself, so it's no surprise that getting the right balance of sodium and potassium in the diet is important for good health. Imbalances may increase the risk of high blood pressure, heart disease, diabetes, and other disorders.

If you are like the majority of Americans, sodium and potassium are out of balance in your diet. You are likely to consume too much sodium and too little potassium. Follow these guidelines to help ensure that these minerals are in balance in the foods you eat:

- Total sodium intake should be less than 2300 mg/day. Most salt in the diet is found in processed foods or added with a salt shaker. Stop adding salt and start checking food labels for sodium content. Foods considered low in sodium have less than 140 mg/serving (or 5% daily value).
- Total potassium intake should be 4700 mg/day. It's easy to add potassium to the diet by choosing the right foods, and there are plenty of choices. Most fruits and vegetables are high in potassium, but especially potatoes, bananas, oranges, apricots, plums, leafy greens, tomatoes, lima beans, and avocado. Other foods with substantial amounts of potassium are fish, meat, poultry, and whole grains.

REVIEW

1. Define active transport.
2. What is the sodium-potassium pump? Why is it so important?
3. Name two types of vesicle transport. Which type moves substances out of the cell?
4. What are the similarities and differences between phagocytosis and pinocytosis?
5. The sodium-potassium pump is a:
   A. Phospholipid
   B. Protein
   C. Carbohydrate
   D. Ion
6. What is the functional significance of the shape change of the carrier protein in the sodium-potassium pump after the sodium ions bind?
7. A potentially deadly poison derived from plants called ouabain blocks the sodium-potassium pump and prevents it from working. What do you think this does to the sodium and potassium balance in cells? Explain your answer.
8. True or False. The sodium-potassium pump uses one protein to pump both sodium and potassium.
9. True or False. Vesicles are made of the nuclear membrane.
10. What is an electrical gradient across the cell membrane called?
11. Chemical signaling molecules called neurotransmitters are released from nerve cells (neurons) through vesicles. This is an example of:
    A. Pinocytosis
    B. Phagocytosis
    C. Endocytosis
    D. Exocytosis
12. The energy for active transport comes from
    A. ATP
    B. RNA
    C. Carrier proteins
    D. Sodium ions
13. Transport proteins that move substances into and out of a cell are located in which structure?

EXPLORE MORE

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CHAPTER OVERVIEW

11: Energy and Metabolism

11.1: Prelude to Metabolism

11.2: Energy and Metabolism

11.3: Potential, Kinetic, Free, and Activation Energy

11.4: The Laws of Thermodynamics

11.5: ATP- Adenosine Triphosphate

11.6: Enzymes

11.E: Metabolism (Exercises)

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11.1: Prelude to Metabolism

Virtually every task performed by living organisms requires energy. Energy is needed to perform heavy labor and exercise, but humans also use a great deal of energy while thinking, and even during sleep. In fact, the living cells of every organism constantly use energy. Nutrients and other molecules are imported, metabolized (broken down) and possibly synthesized into new molecules, modified if needed, transported around the cell, and may be distributed to the entire organism. For example, the large proteins that make up muscles are actively built from smaller molecules. Complex carbohydrates are broken down into simple sugars that the cell uses for energy. Just as energy is required to both build and demolish a building, energy is required for both the synthesis and breakdown of molecules. Additionally, signaling molecules such as hormones and neurotransmitters are transported between cells. Pathogenic bacteria and viruses are ingested and broken down by cells. Cells must also export waste and toxins to stay healthy, and many cells must swim or move surrounding materials via the beating motion of cellular appendages like cilia and flagella.



Figure 11.1.1: A hummingbird needs energy to maintain prolonged periods of flight. The bird obtains its energy from taking in food and transforming the nutrients into energy through a series of biochemical reactions. The flight muscles in birds are extremely efficient in energy production. (credit: modification of work by Cory Zanker)

The cellular processes listed above require a steady supply of energy. From where, and in what form, does this energy come? How do living cells obtain energy, and how do they use it? This chapter will discuss different forms of energy and the physical laws that govern energy transfer. This chapter will also describe how cells use energy and replenish it, and how chemical reactions in the cell are performed with great efficiency.

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11.2: Energy and Metabolism

Skills to Develop

- Explain what metabolic pathways are and describe the two major types of metabolic pathways
- Discuss how chemical reactions play a role in energy transfer

Scientists use the term bioenergetics to discuss the concept of energy flow (Figure 11.2.1) through living systems, such as cells. Cellular processes such as the building and breaking down of complex molecules occur through stepwise chemical reactions. Some of these chemical reactions are spontaneous and release energy, whereas others require energy to proceed. Just as living things must continually consume food to replenish what has been used, cells must continually produce more energy to replenish that used by the many energy-requiring chemical reactions that constantly take place. All of the chemical reactions that take place inside cells, including those that use energy and those that release energy, are the cell's metabolism.

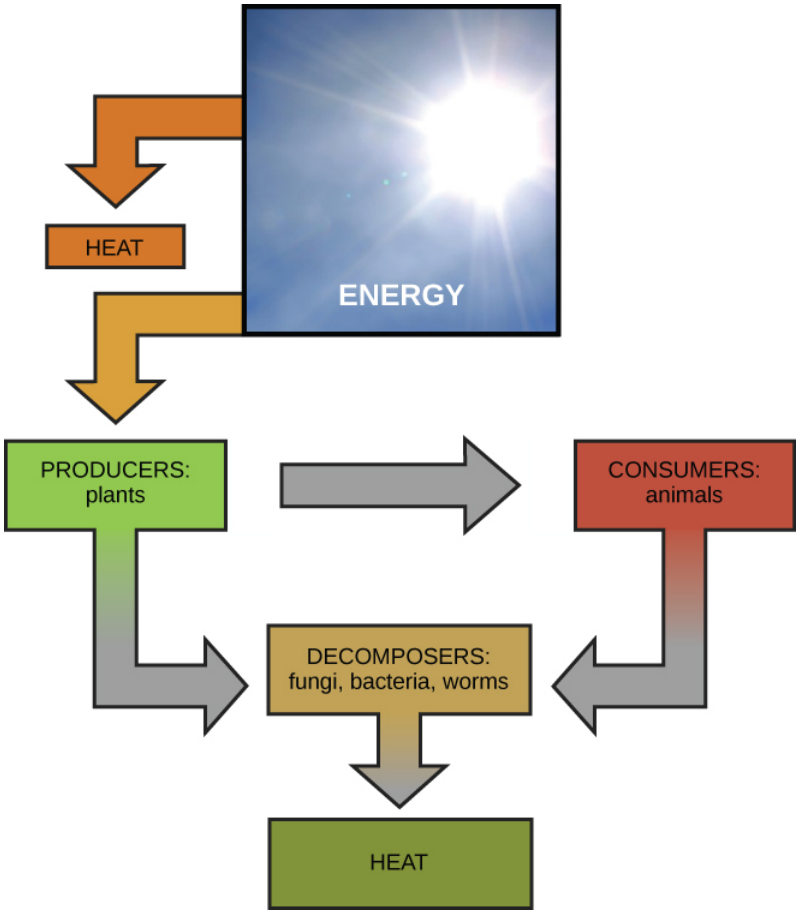


Figure 11.2.1: Most life forms on earth get their energy from the sun. Plants use photosynthesis to capture sunlight, and herbivores eat those plants to obtain energy. Carnivores eat the herbivores, and decomposers digest plant and animal matter.

Metabolism of Carbohydrates

The metabolism of sugar (a simple carbohydrate) is a classic example of the many cellular processes that use and produce energy. Living things consume sugar as a major energy source, because sugar molecules have a great deal of energy stored within their bonds. The breakdown of glucose, a simple sugar, is described by the equation:

$$C_6H_{12}O_6 + 6\,O_2 \rightarrow 6\,CO_2 + 6\,H_2O + (\text{energy})$$

Carbohydrates that are consumed have their origins in photosynthesizing organisms like plants (Figure 6.1.2). During photosynthesis, plants use the energy of sunlight to convert carbon dioxide gas (CO_2) into sugar molecules, like glucose

($C_6H_{12}O_6$). Because this process involves synthesizing a larger, energy-storing molecule, it requires an input of energy to proceed. The synthesis of glucose is described by this equation (notice that it is the reverse of the previous equation):

$$6\,CO_2 + 6\,H_2O + (\text{energy}) \rightarrow C_6H_{12}O_6 + 6\,O_2$$

During the chemical reactions of photosynthesis, energy is provided in the form of a very high-energy molecule called ATP, or adenosine triphosphate, which is the primary energy currency of all cells. Just as the dollar is used as currency to buy goods, cells use molecules of ATP as energy currency to perform immediate work. The sugar (glucose) is stored as starch or glycogen. Energy-storing polymers like these are broken down into glucose to supply molecules of ATP.

Solar energy is required to synthesize a molecule of glucose during the reactions of photosynthesis. In photosynthesis, light energy from the sun is initially transformed into chemical energy that is temporally stored in the energy carrier molecules ATP and NADPH (nicotinamide adenine dinucleotide phosphate). The stored energy in ATP and NADPH is then used later in photosynthesis to build one molecule of glucose from six molecules of CO_2. This process is analogous to eating breakfast in the morning to acquire energy for your body that can be used later in the day. Under ideal conditions, energy from 18 molecules of ATP is required to synthesize one molecule of glucose during the reactions of photosynthesis. Glucose molecules can also be combined with and converted into other types of sugars. When sugars are consumed, molecules of glucose eventually make their way into each living cell of the organism. Inside the cell, each sugar molecule is broken down through a complex series of chemical reactions. The goal of these reactions is to harvest the energy stored inside the sugar molecules. The harvested energy is used to make high-energy ATP molecules, which can be used to perform work, powering many chemical reactions in the cell. The amount of energy needed to make one molecule of glucose from six molecules of carbon dioxide is 18 molecules of ATP and 12 molecules of NADPH (each one of which is energetically equivalent to three molecules of ATP), or a total of 54 molecule equivalents required for the synthesis of one molecule of glucose. This process is a fundamental and efficient way for cells to generate the molecular energy that they require.



Figure 11.2.2: Plants, like this oak tree and acorn, use energy from sunlight to make sugar and other organic molecules. Both plants and animals (like this squirrel) use cellular respiration to derive energy from the organic molecules originally produced by plants. (credit “acorn”: modification of work by Noel Reynolds; credit “squirrel”: modification of work by Dawn Huczek)

Metabolic Pathways

The processes of making and breaking down sugar molecules illustrate two types of metabolic pathways. A metabolic pathway is a series of interconnected biochemical reactions that convert a substrate molecule or molecules, step-by-step, through a series of metabolic intermediates, eventually yielding a final product or products. In the case of sugar metabolism, the first metabolic pathway synthesized sugar from smaller molecules, and the other pathway broke sugar down into smaller molecules. These two opposite processes—the first requiring energy and the second producing energy—are referred to as anabolic (building) and catabolic (breaking down) pathways, respectively. Consequently, metabolism is composed of building (anabolism) and degradation (catabolism).

Evolution Connection: Evolution of Metabolic Pathways

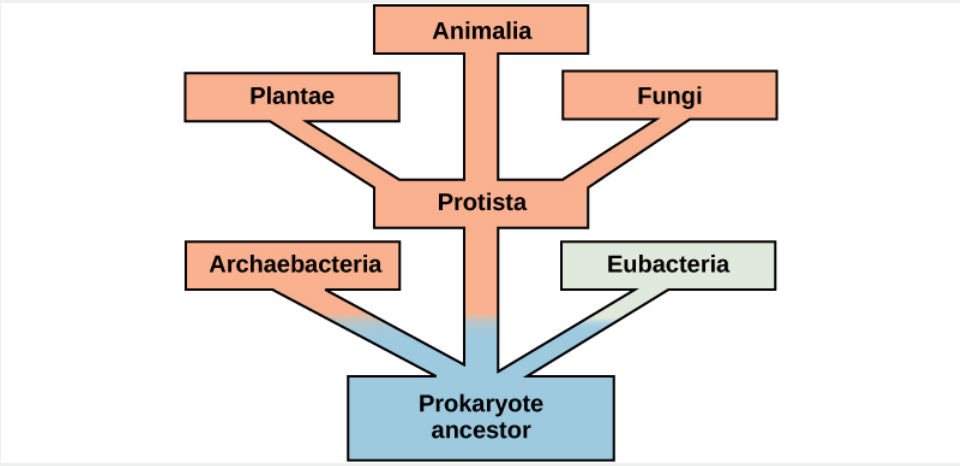


Figure 11.2.3: This tree shows the evolution of the various branches of life. The vertical dimension is time. Early life forms, in blue, used anaerobic metabolism to obtain energy from their surroundings.

There is more to the complexity of metabolism than understanding the metabolic pathways alone. Metabolic complexity varies from organism to organism. Photosynthesis is the primary pathway in which photosynthetic organisms like plants (the majority of global synthesis is done by planktonic algae) harvest the sun's energy and convert it into carbohydrates. The by-product of photosynthesis is oxygen, required by some cells to carry out cellular respiration. During cellular respiration, oxygen aids in the catabolic breakdown of carbon compounds, like carbohydrates. Among the products of this catabolism are CO2 and ATP. In addition, some eukaryotes perform catabolic processes without oxygen (fermentation); that is, they perform or use anaerobic metabolism.

Organisms probably evolved anaerobic metabolism to survive (living organisms came into existence about 3.8 billion years ago, when the atmosphere lacked oxygen). Despite the differences between organisms and the complexity of metabolism, researchers have found that all branches of life share some of the same metabolic pathways, suggesting that all organisms evolved from the same ancient common ancestor (Figure 11.2.3). Evidence indicates that over time, the pathways diverged, adding specialized enzymes to allow organisms to better adapt to their environment, thus increasing their chance to survive. However, the underlying principle remains that all organisms must harvest energy from their environment and convert it to ATP to carry out cellular functions.

Anabolic and Catabolic Pathways

Anabolic pathways require an input of energy to synthesize complex molecules from simpler ones. Synthesizing sugar from CO_2 is one example. Other examples are the synthesis of large proteins from amino acid building blocks, and the synthesis of new DNA strands from nucleic acid building blocks. These biosynthetic processes are critical to the life of the cell, take place constantly, and demand energy provided by ATP and other high-energy molecules like NADH (nicotinamide adenine dinucleotide) and NADPH (Figure 11.2.4).

ATP is an important molecule for cells to have in sufficient supply at all times. The breakdown of sugars illustrates how a single molecule of glucose can store enough energy to make a great deal of ATP, 36 to 38 molecules. This is a catabolic pathway. Catabolic pathways involve the degradation (or breakdown) of complex molecules into simpler ones. Molecular energy stored in the bonds of complex molecules is released in catabolic pathways and harvested in such a way that it can be used to produce ATP. Other energy-storing molecules, such as fats, are also broken down through similar catabolic reactions to release energy and make ATP (Figure 11.2.4).

It is important to know that the chemical reactions of metabolic pathways don't take place spontaneously. Each reaction step is facilitated, or catalyzed, by a protein called an enzyme. Enzymes are important for catalyzing all types of biological reactions—those that require energy as well as those that release energy.

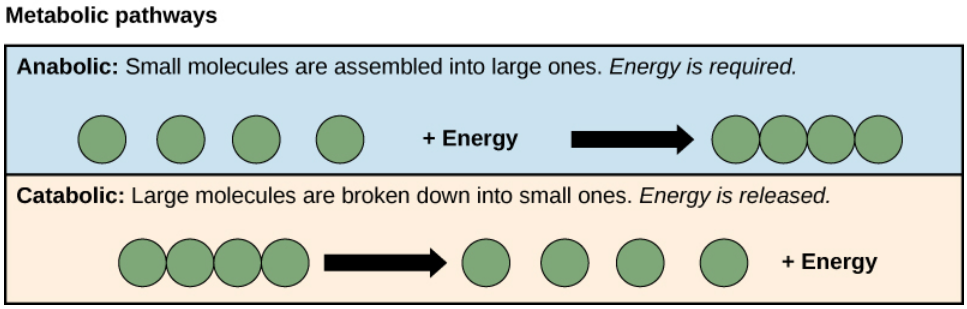


Figure 11.2.4: Anabolic pathways are those that require energy to synthesize larger molecules. Catabolic pathways are those that generate energy by breaking down larger molecules. Both types of pathways are required for maintaining the cell's energy balance.

Summary

Cells perform the functions of life through various chemical reactions. A cell's metabolism refers to the chemical reactions that take place within it. There are metabolic reactions that involve the breaking down of complex chemicals into simpler ones, such as the breakdown of large macromolecules. This process is referred to as catabolism, and such reactions are associated with a release of energy. On the other end of the spectrum, anabolism refers to metabolic processes that build complex molecules out of simpler ones, such as the synthesis of macromolecules. Anabolic processes require energy. Glucose synthesis and glucose breakdown are examples of anabolic and catabolic pathways, respectively.

Glossary

anabolic
(also, anabolism) pathways that require an input of energy to synthesize complex molecules from simpler ones

bioenergetics
study of energy flowing through living systems

catabolic
(also, catabolism) pathways in which complex molecules are broken down into simpler ones

metabolism
all the chemical reactions that take place inside cells, including anabolism and catabolism

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11.3: Potential, Kinetic, Free, and Activation Energy

Skills to Develop

- Define “energy”
- Explain the difference between kinetic and potential energy
- Discuss the concepts of free energy and activation energy
- Describe endergonic and exergonic reactions

Energy is defined as the ability to do work. As you’ve learned, energy exists in different forms. For example, electrical energy, light energy, and heat energy are all different types of energy. While these are all familiar types of energy that one can see or feel, there is another type of energy that is much less tangible. This energy is associated with something as simple as an object held above the ground. In order to appreciate the way energy flows into and out of biological systems, it is important to understand more about the different types of energy that exist in the physical world.

Types of Energy

When an object is in motion, there is energy associated with that object. In the example of an airplane in flight, there is a great deal of energy associated with the motion of the airplane. This is because moving objects are capable of enacting a change, or doing work. Think of a wrecking ball. Even a slow-moving wrecking ball can do a great deal of damage to other objects. However, a wrecking ball that is not in motion is incapable of performing work. Energy associated with objects in motion is called kinetic energy. A speeding bullet, a walking person, the rapid movement of molecules in the air (which produces heat), and electromagnetic radiation like light all have kinetic energy.

Now what if that same motionless wrecking ball is lifted two stories above a car with a crane? If the suspended wrecking ball is unmoving, is there energy associated with it? The answer is yes. The suspended wrecking ball has energy associated with it that is fundamentally different from the kinetic energy of objects in motion. This form of energy results from the fact that there is the *potential* for the wrecking ball to do work. If it is released, indeed it would do work. Because this type of energy refers to the potential to do work, it is called potential energy. Objects transfer their energy between kinetic and potential in the following way: As the wrecking ball hangs motionless, it has 0 kinetic and 100 percent potential energy. Once it is released, its kinetic energy begins to increase because it builds speed due to gravity. At the same time, as it nears the ground, it loses potential energy. Somewhere mid-fall it has 50 percent kinetic and 50 percent potential energy. Just before it hits the ground, the ball has nearly lost its potential energy and has near-maximal kinetic energy. Other examples of potential energy include the energy of water held behind a dam (Figure 11.3.1), or a person about to skydive out of an airplane.



Figure 11.3.1: Water behind a dam has potential energy. Moving water, such as in a waterfall or a rapidly flowing river, has kinetic energy. (credit “dam”: modification of work by "Pascal"/Flickr; credit “waterfall”: modification of work by Frank Gualtieri)

Potential energy is not only associated with the location of matter (such as a child sitting on a tree branch), but also with the structure of matter. A spring on the ground has potential energy if it is compressed; so does a rubber band that is pulled taut. The very existence of living cells relies heavily on structural potential energy. On a chemical level, the bonds that hold the atoms of

molecules together have potential energy. Remember that anabolic cellular pathways require energy to synthesize complex molecules from simpler ones, and catabolic pathways release energy when complex molecules are broken down. The fact that energy can be released by the breakdown of certain chemical bonds implies that those bonds have potential energy. In fact, there is potential energy stored within the bonds of all the food molecules we eat, which is eventually harnessed for use. This is because these bonds can release energy when broken. The type of potential energy that exists within chemical bonds, and is released when those bonds are broken, is called chemical energy (Figure 11.3.2). Chemical energy is responsible for providing living cells with energy from food. The release of energy is brought about by breaking the molecular bonds within fuel molecules.

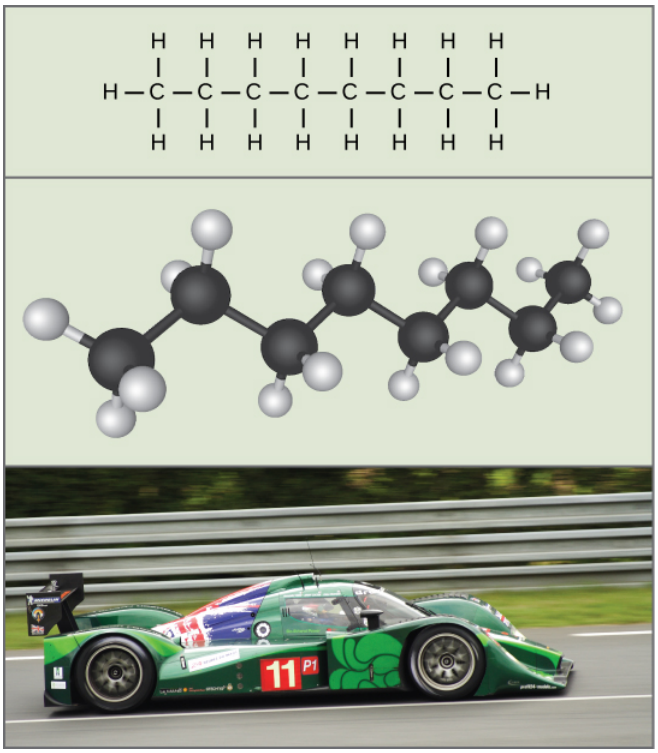


Figure 11.3.2: The molecules in gasoline (octane, the chemical formula shown) contain chemical energy within the chemical bonds. This energy is transformed into kinetic energy that allows a car to race on a racetrack. (credit "car": modification of work by Russell Trow)

Link to Learning

Visit this site and select "A simple pendulum" on the menu (under "Harmonic Motion") to see the shifting kinetic (K) and potential energy (U) of a pendulum in motion.

Free Energy

After learning that chemical reactions release energy when energy-storing bonds are broken, an important next question is how is the energy associated with chemical reactions quantified and expressed? How can the energy released from one reaction be compared to that of another reaction? A measurement of free energy is used to quantitate these energy transfers. Free energy is called Gibbs free energy (abbreviated with the letter G) after Josiah Willard Gibbs, the scientist who developed the measurement. Recall that according to the second law of thermodynamics, all energy transfers involve the loss of some amount of energy in an

unusable form such as heat, resulting in entropy. Gibbs free energy specifically refers to the energy associated with a chemical reaction that is available after entropy is accounted for. In other words, Gibbs free energy is usable energy, or energy that is available to do work.

Every chemical reaction involves a change in free energy, called delta G (ΔG). The change in free energy can be calculated for any system that undergoes such a change, such as a chemical reaction. To calculate ΔG, subtract the amount of energy lost to entropy (denoted as ΔS) from the total energy change of the system. This total energy change in the system is called enthalpy and is denoted as ΔH . The formula for calculating ΔG is as follows, where the symbol T refers to absolute temperature in Kelvin (degrees Celsius + 273):

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

The standard free energy change of a chemical reaction is expressed as an amount of energy per mole of the reaction product (either in kilojoules or kilocalories, kJ/mol or kcal/mol; 1 kJ = 0.239 kcal) under standard pH, temperature, and pressure conditions. Standard pH, temperature, and pressure conditions are generally calculated at pH 7.0 in biological systems, 25 degrees Celsius, and 100 kilopascals (1 atm pressure), respectively. It is important to note that cellular conditions vary considerably from these standard conditions, and so standard calculated ΔG values for biological reactions will be different inside the cell.

Endergonic Reactions and Exergonic Reactions

If energy is released during a chemical reaction, then the resulting value from the above equation will be a negative number. In other words, reactions that release energy have a $\Delta G < 0$. A negative ΔG also means that the products of the reaction have less free energy than the reactants, because they gave off some free energy during the reaction. Reactions that have a negative ΔG and consequently release free energy are called exergonic reactions. Think: *ex*ergonic means energy is *ex*iting the system. These reactions are also referred to as spontaneous reactions, because they can occur without the addition of energy into the system. Understanding which chemical reactions are spontaneous and release free energy is extremely useful for biologists, because these reactions can be harnessed to perform work inside the cell. An important distinction must be drawn between the term spontaneous and the idea of a chemical reaction that occurs immediately. Contrary to the everyday use of the term, a spontaneous reaction is not one that suddenly or quickly occurs. The rusting of iron is an example of a spontaneous reaction that occurs slowly, little by little, over time.

If a chemical reaction requires an input of energy rather than releasing energy, then the ΔG for that reaction will be a positive value. In this case, the products have more free energy than the reactants. Thus, the products of these reactions can be thought of as energy-storing molecules. These chemical reactions are called endergonic reactions, and they are non-spontaneous. An endergonic reaction will not take place on its own without the addition of free energy.

Let's revisit the example of the synthesis and breakdown of the food molecule, glucose. Remember that the building of complex molecules, such as sugars, from simpler ones is an anabolic process and requires energy. Therefore, the chemical reactions involved in anabolic processes are endergonic reactions. On the other hand, the catabolic process of breaking sugar down into simpler molecules releases energy in a series of exergonic reactions. Like the example of rust above, the breakdown of sugar involves spontaneous reactions, but these reactions don't occur instantaneously. Figure 11.3.3 shows some other examples of endergonic and exergonic reactions. Later sections will provide more information about what else is required to make even spontaneous reactions happen more efficiently.

Art Connection



(a)



(b)



(c)



(d)

Figure 11.3.3: Shown are some examples of endergonic processes (ones that require energy) and exergonic processes (ones that release energy). These include (a) a compost pile decomposing, (b) a chick hatching from a fertilized egg, (c) sand art being destroyed, and (d) a ball rolling down a hill. (credit a: modification of work by Natalie Maynor; credit b: modification of work by USDA; credit c: modification of work by "Athlex"/Flickr; credit d: modification of work by Harry Malsch)

Look at each of the processes shown, and decide if it is endergonic or exergonic. In each case, does enthalpy increase or decrease, and does entropy increase or decrease?

An important concept in the study of metabolism and energy is that of chemical equilibrium. Most chemical reactions are reversible. They can proceed in both directions, releasing energy into their environment in one direction, and absorbing it from the environment in the other direction (Figure 11.3.4). The same is true for the chemical reactions involved in cell metabolism, such as the breaking down and building up of proteins into and from individual amino acids, respectively. Reactants within a closed system will undergo chemical reactions in both directions until a state of equilibrium is reached. This state of equilibrium is one of the lowest possible free energy and a state of maximal entropy. Energy must be put into the system to push the reactants and products away from a state of equilibrium. Either reactants or products must be added, removed, or changed. If a cell were a closed system, its chemical reactions would reach equilibrium, and it would die because there would be insufficient free energy left to perform the work needed to maintain life. In a living cell, chemical reactions are constantly moving towards equilibrium, but never reach it. This is because a living cell is an open system. Materials pass in and out, the cell recycles the products of certain chemical reactions into other reactions, and chemical equilibrium is never reached. In this way, living organisms are in a constant energy-requiring, uphill battle against equilibrium and entropy. This constant supply of energy ultimately comes from sunlight, which is used to produce nutrients in the process of photosynthesis.

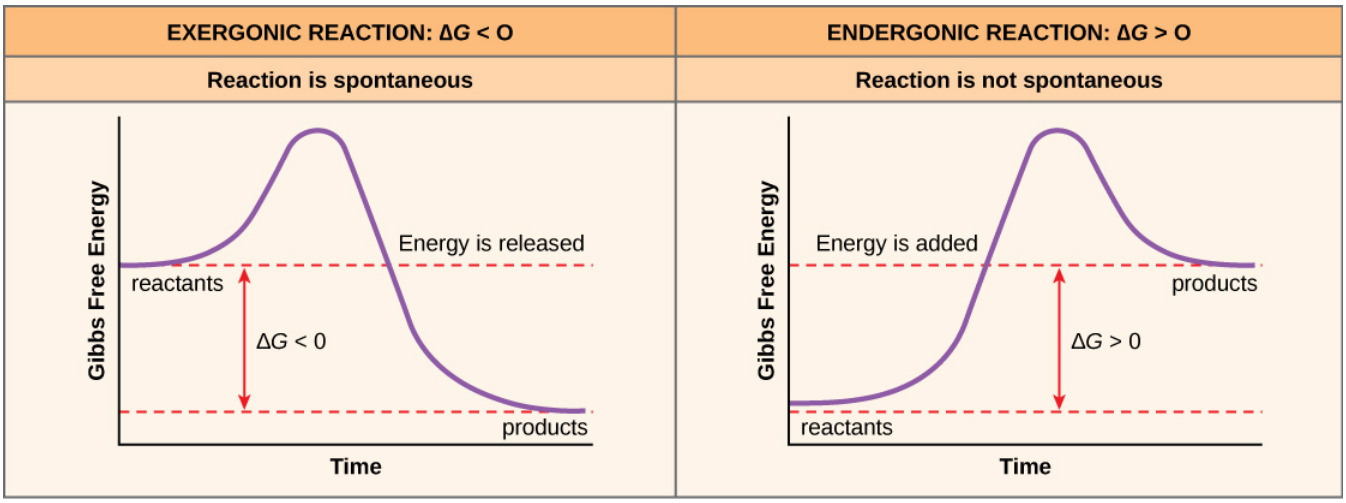


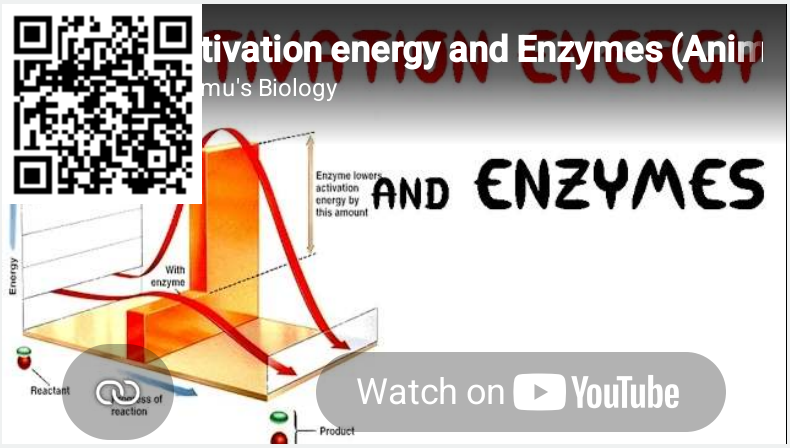
Figure 11.3.4: Exergonic and endergonic reactions result in changes in Gibbs free energy. Exergonic reactions release energy; endergonic reactions require energy to proceed.

Activation Energy

There is another important concept that must be considered regarding endergonic and exergonic reactions. Even exergonic reactions require a small amount of energy input to get going before they can proceed with their energy-releasing steps. These reactions have a net release of energy, but still require some energy in the beginning. This small amount of energy input necessary for all chemical reactions to occur is called the activation energy (or free energy of activation) and is abbreviated E_A (Figure 11.3.5).

Why would an energy-releasing, negative ΔG reaction actually require some energy to proceed? The reason lies in the steps that take place during a chemical reaction. During chemical reactions, certain chemical bonds are broken and new ones are formed. For example, when a glucose molecule is broken down, bonds between the carbon atoms of the molecule are broken. Since these are energy-storing bonds, they release energy when broken. However, to get them into a state that allows the bonds to break, the molecule must be somewhat contorted. A small energy input is required to achieve this contorted state. This contorted state is called the transition state, and it is a high-energy, unstable state. For this reason, reactant molecules don't last long in their transition state, but very quickly proceed to the next steps of the chemical reaction. Free energy diagrams illustrate the energy profiles for a given reaction. Whether the reaction is exergonic or endergonic determines whether the products in the diagram will exist at a lower or higher energy state than both the reactants and the products. However, regardless of this measure, the transition state of the reaction exists at a higher energy state than the reactants, and thus, E_A is always positive.

Link to Learning



Watch an animation of the move from free energy to transition state at this site.

Where does the activation energy required by chemical reactants come from? The source of the activation energy needed to push reactions forward is typically heat energy from the surroundings. Heat energy (the total bond energy of reactants or products in a chemical reaction) speeds up the motion of molecules, increasing the frequency and force with which they collide; it also moves atoms and bonds within the molecule slightly, helping them reach their transition state. For this reason, heating up a system will cause chemical reactants within that system to react more frequently. Increasing the pressure on a system has the same effect. Once reactants have absorbed enough heat energy from their surroundings to reach the transition state, the reaction will proceed.

The activation energy of a particular reaction determines the rate at which it will proceed. The higher the activation energy, the slower the chemical reaction will be. The example of iron rusting illustrates an inherently slow reaction. This reaction occurs slowly over time because of its high E_A. Additionally, the burning of many fuels, which is strongly exergonic, will take place at a negligible rate unless their activation energy is overcome by sufficient heat from a spark. Once they begin to burn, however, the chemical reactions release enough heat to continue the burning process, supplying the activation energy for surrounding fuel molecules. Like these reactions outside of cells, the activation energy for most cellular reactions is too high for heat energy to overcome at efficient rates. In other words, in order for important cellular reactions to occur at appreciable rates (number of reactions per unit time), their activation energies must be lowered (Figure 11.3.111.3.5); this is referred to as catalysis. This is a very good thing as far as living cells are concerned. Important macromolecules, such as proteins, DNA, and RNA, store considerable energy, and their breakdown is exergonic. If cellular temperatures alone provided enough heat energy for these exergonic reactions to overcome their activation barriers, the essential components of a cell would disintegrate.

Art Connection

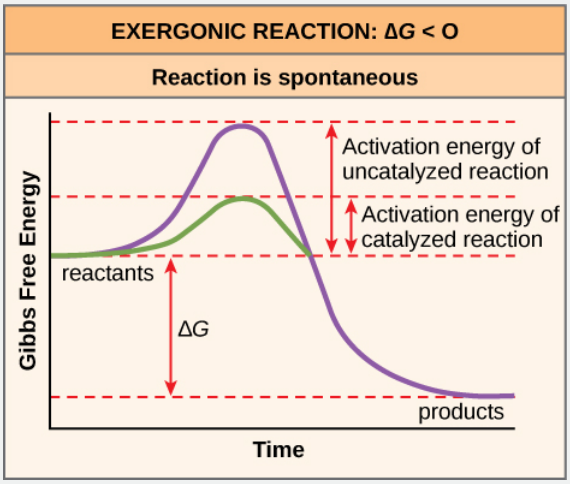


Figure 11.3.5: Activation energy is the energy required for a reaction to proceed, and it is lower if the reaction is catalyzed. The horizontal axis of this diagram describes the sequence of events in time.

If no activation energy were required to break down sucrose (table sugar), would you be able to store it in a sugar bowl?

Summary

Energy comes in many different forms. Objects in motion do physical work, and kinetic energy is the energy of objects in motion. Objects that are not in motion may have the potential to do work, and thus, have potential energy. Molecules also have potential energy because the breaking of molecular bonds has the potential to release energy. Living cells depend on the harvesting of potential energy from molecular bonds to perform work. Free energy is a measure of energy that is available to do work. The free energy of a system changes during energy transfers such as chemical reactions, and this change is referred to as ΔG.

The ΔG of a reaction can be negative or positive, meaning that the reaction releases energy or consumes energy, respectively. A reaction with a negative ΔG that gives off energy is called an exergonic reaction. One with a positive ΔG that requires energy input is called an endergonic reaction. Exergonic reactions are said to be spontaneous, because their products have less energy than their reactants. The products of endergonic reactions have a higher energy state than the reactants, and so these are nonspontaneous reactions. However, all reactions (including spontaneous -ΔG reactions) require an initial input of energy in order to reach the transition state, at which they'll proceed. This initial input of energy is called the activation energy.

Art Connections

Figure 11.3.3: Look at each of the processes shown, and decide if it is endergonic or exergonic. In each case, does enthalpy increase or decrease, and does entropy increase or decrease?

Answer

A compost pile decomposing is an exergonic process; enthalpy increases (energy is released) and entropy increases (large molecules are broken down into smaller ones). A baby developing from a fertilized egg is an endergonic process; enthalpy decreases (energy is absorbed) and entropy decreases. Sand art being destroyed is an exergonic process; there is no change in enthalpy, but entropy increases. A ball rolling downhill is an exergonic process; enthalpy decreases (energy is released), but there is no change in enthalpy.

Figure 11.3.5: If no activation energy were required to break down sucrose (table sugar), would you be able to store it in a sugar bowl?

Answer

No. We can store chemical energy because of the need to overcome the barrier to its breakdown.

Glossary

activation energy
energy necessary for reactions to occur

chemical energy
potential energy in chemical bonds that is released when those bonds are broken

endergonic
describes chemical reactions that require energy input

enthalpy
total energy of a system

exergonic
describes chemical reactions that release free energy

free energy
Gibbs free energy is the usable energy, or energy that is available to do work.

heat energy
total bond energy of reactants or products in a chemical reaction

kinetic energy
type of energy associated with objects or particles in motion

potential energy
type of energy that has the potential to do work; stored energy

transition state
high-energy, unstable state (an intermediate form between the substrate and the product) occurring during a chemical reaction

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11.4: The Laws of Thermodynamics

Skills to Develop

- Discuss the concept of entropy
- Explain the first and second laws of thermodynamics

Thermodynamics refers to the study of energy and energy transfer involving physical matter. The matter and its environment relevant to a particular case of energy transfer are classified as a system, and everything outside of that system is called the surroundings. For instance, when heating a pot of water on the stove, the system includes the stove, the pot, and the water. Energy is transferred within the system (between the stove, pot, and water). There are two types of systems: open and closed. An open system is one in which energy can be transferred between the system and its surroundings. The stovetop system is open because heat can be lost into the air. A closed system is one that cannot transfer energy to its surroundings.

Biological organisms are open systems. Energy is exchanged between them and their surroundings, as they consume energy-storing molecules and release energy to the environment by doing work. Like all things in the physical world, energy is subject to the laws of physics. The laws of thermodynamics govern the transfer of energy in and among all systems in the universe.

The First Law of Thermodynamics

The first law of thermodynamics deals with the total amount of energy in the universe. It states that this total amount of energy is constant. In other words, there has always been, and always will be, exactly the same amount of energy in the universe. Energy exists in many different forms. According to the first law of thermodynamics, energy may be transferred from place to place or transformed into different forms, but it cannot be created or destroyed. The transfers and transformations of energy take place around us all the time. Light bulbs transform electrical energy into light energy. Gas stoves transform chemical energy from natural gas into heat energy. Plants perform one of the most biologically useful energy transformations on earth: that of converting the energy of sunlight into the chemical energy stored within organic molecules (Figure 2.3.b.1). Some examples of energy transformations are shown in Figure 11.4.1.

The challenge for all living organisms is to obtain energy from their surroundings in forms that they can transfer or transform into usable energy to do work. Living cells have evolved to meet this challenge very well. Chemical energy stored within organic molecules such as sugars and fats is transformed through a series of cellular chemical reactions into energy within molecules of ATP. Energy in ATP molecules is easily accessible to do work. Examples of the types of work that cells need to do include building complex molecules, transporting materials, powering the beating motion of cilia or flagella, contracting muscle fibers to create movement, and reproduction.

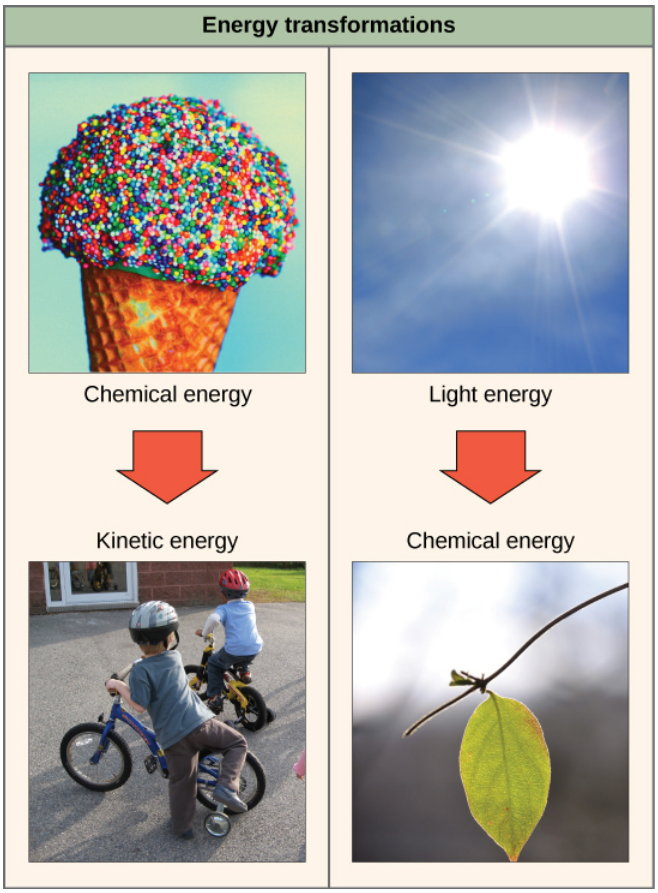


Figure 11.4.1: Shown are two examples of energy being transferred from one system to another and transformed from one form to another. Humans can convert the chemical energy in food, like this ice cream cone, into kinetic energy (the energy of movement to ride a bicycle). Plants can convert electromagnetic radiation (light energy) from the sun into chemical energy. (credit “ice cream”: modification of work by D. Sharon Pruitt; credit “kids on bikes”: modification of work by Michelle Riggen-Ransom; credit “leaf”: modification of work by Cory Zanker)

The Second Law of Thermodynamics

A living cell’s primary tasks of obtaining, transforming, and using energy to do work may seem simple. However, the second law of thermodynamics explains why these tasks are harder than they appear. None of the energy transfers we’ve discussed, along with all energy transfers and transformations in the universe, is completely efficient. In every energy transfer, some amount of energy is lost in a form that is unusable. In most cases, this form is heat energy. Thermodynamically, heat energy is defined as the energy transferred from one system to another that is not doing work. For example, when an airplane flies through the air, some of the energy of the flying plane is lost as heat energy due to friction with the surrounding air. This friction actually heats the air by temporarily increasing the speed of air molecules. Likewise, some energy is lost as heat energy during cellular metabolic reactions. This is good for warm-blooded creatures like us, because heat energy helps to maintain our body temperature. Strictly speaking, no energy transfer is completely efficient, because some energy is lost in an unusable form.

An important concept in physical systems is that of order and disorder (also known as randomness). The more energy that is lost by a system to its surroundings, the less ordered and more random the system is. Scientists refer to the measure of randomness or disorder within a system as entropy. High entropy means high disorder and low energy (Figure 11.4.2). To better understand entropy, think of a student’s bedroom. If no energy or work were put into it, the room would quickly become messy. It would exist in a very disordered state, one of high entropy. Energy must be put into the system, in the form of the student doing work and putting everything away, in order to bring the room back to a state of cleanliness and order. This state is one of low entropy. Similarly, a car or house must be constantly maintained with work in order to keep it in an ordered state. Left alone, the entropy of the house or car gradually increases through rust and degradation. Molecules and chemical reactions have varying amounts of entropy as well. For example, as chemical reactions reach a state of equilibrium, entropy increases, and as molecules at a high concentration in one place diffuse and spread out, entropy also increases.

Scientific Connection: Transfer of Energy and the Resulting Entropy

Set up a simple experiment to understand how energy is transferred and how a change in entropy results.

1. Take a block of ice. This is water in solid form, so it has a high structural order. This means that the molecules cannot move very much and are in a fixed position. The temperature of the ice is 0°C. As a result, the entropy of the system is low.
2. Allow the ice to melt at room temperature. What is the state of molecules in the liquid water now? How did the energy transfer take place? Is the entropy of the system higher or lower? Why?
3. Heat the water to its boiling point. What happens to the entropy of the system when the water is heated?

All physical systems can be thought of in this way: Living things are highly ordered, requiring constant energy input to be maintained in a state of low entropy. As living systems take in energy-storing molecules and transform them through chemical reactions, they lose some amount of usable energy in the process, because no reaction is completely efficient. They also produce waste and by-products that aren't useful energy sources. This process increases the entropy of the system's surroundings. Since all energy transfers result in the loss of some usable energy, the second law of thermodynamics states that every energy transfer or transformation increases the entropy of the universe. Even though living things are highly ordered and maintain a state of low entropy, the entropy of the universe in total is constantly increasing due to the loss of usable energy with each energy transfer that occurs. Essentially, living things are in a continuous uphill battle against this constant increase in universal entropy.

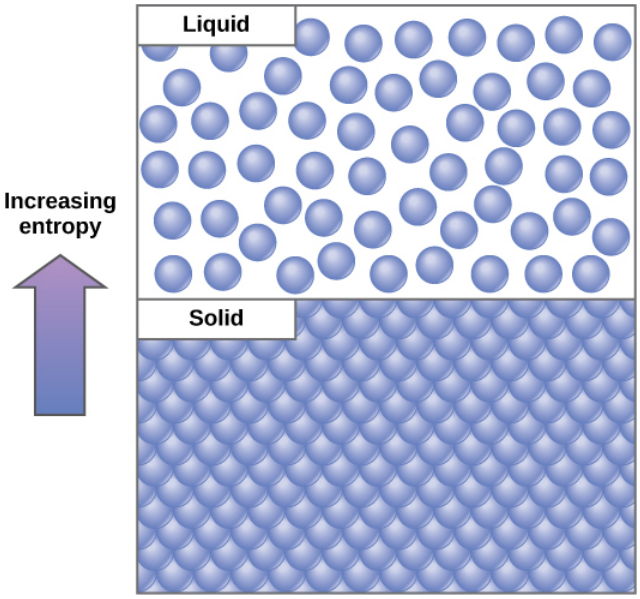


Figure 11.4.2: Entropy is a measure of randomness or disorder in a system. Gases have higher entropy than liquids, and liquids have higher entropy than solids.

Summary

In studying energy, scientists use the term "system" to refer to the matter and its environment involved in energy transfers. Everything outside of the system is called the surroundings. Single cells are biological systems. Systems can be thought of as having a certain amount of order. It takes energy to make a system more ordered. The more ordered a system is, the lower its entropy. Entropy is a measure of the disorder of a system. As a system becomes more disordered, the lower its energy and the higher its entropy become.

A series of laws, called the laws of thermodynamics, describe the properties and processes of energy transfer. The first law states that the total amount of energy in the universe is constant. This means that energy can't be created or destroyed, only transferred or transformed. The second law of thermodynamics states that every energy transfer involves some loss of energy in an unusable form, such as heat energy, resulting in a more disordered system. In other words, no energy transfer is completely efficient and tends toward disorder.

Glossary

entropy (S)
measure of randomness or disorder within a system

heat
energy energy transferred from one system to another that is not work (energy of the motion of molecules or particles)

thermodynamics
study of energy and energy transfer involving physical matter

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11.5: ATP- Adenosine Triphosphate

Skills to Develop

- Explain the role of ATP as the cellular energy currency
- Describe how energy is released through hydrolysis of ATP

Even exergonic, energy-releasing reactions require a small amount of activation energy in order to proceed. However, consider endergonic reactions, which require much more energy input, because their products have more free energy than their reactants. Within the cell, where does energy to power such reactions come from? The answer lies with an energy-supplying molecule called adenosine triphosphate, or ATP. ATP is a small, relatively simple molecule (Figure 11.5.1), but within some of its bonds, it contains the potential for a quick burst of energy that can be harnessed to perform cellular work. This molecule can be thought of as the primary energy currency of cells in much the same way that money is the currency that people exchange for things they need. ATP is used to power the majority of energy-requiring cellular reactions.

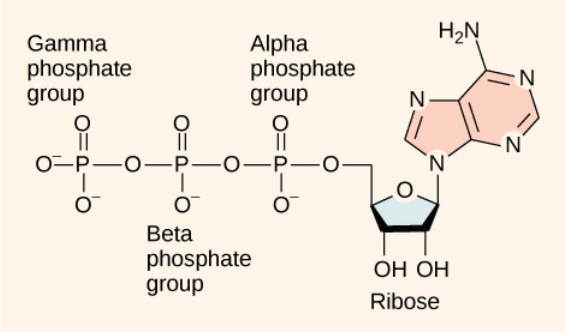


Figure 11.5.1: ATP is the primary energy currency of the cell. It has an adenosine backbone with three phosphate groups attached.

As its name suggests, adenosine triphosphate is comprised of adenosine bound to three phosphate groups (Figure 11.5.1). Adenosine is a nucleoside consisting of the nitrogenous base adenine and a five-carbon sugar, ribose. The three phosphate groups, in order of closest to furthest from the ribose sugar, are labeled alpha, beta, and gamma. Together, these chemical groups constitute an energy powerhouse. However, not all bonds within this molecule exist in a particularly high-energy state. Both bonds that link the phosphates are equally high-energy bonds (phosphoanhydride bonds) that, when broken, release sufficient energy to power a variety of cellular reactions and processes. These high-energy bonds are the bonds between the second and third (or beta and gamma) phosphate groups and between the first and second phosphate groups. The reason that these bonds are considered "high-energy" is because the products of such bond breaking—adenosine diphosphate (ADP) and one inorganic phosphate group (P_i)—have considerably lower free energy than the reactants: ATP and a water molecule. Because this reaction takes place with the use of a water molecule, it is considered a hydrolysis reaction. In other words, ATP is hydrolyzed into ADP in the following reaction:

$$\mathrm{ATP + H_2O \rightarrow ADP + P_i + free\ energy}$$

Like most chemical reactions, the hydrolysis of ATP to ADP is reversible. The reverse reaction regenerates ATP from ADP + P_i. Indeed, cells rely on the regeneration of ATP just as people rely on the regeneration of spent money through some sort of income. Since ATP hydrolysis releases energy, ATP regeneration must require an input of free energy. The formation of ATP is expressed in this equation:

$$\mathrm{ADP + P_i + free\ energy \rightarrow ATP + H_2O}$$

Two prominent questions remain with regard to the use of ATP as an energy source. Exactly how much free energy is released with the hydrolysis of ATP, and how is that free energy used to do cellular work? The calculated ΔG for the hydrolysis of one mole of ATP into ADP and P_i is −7.3 kcal/mole (−30.5 kJ/mol). Since this calculation is true under standard conditions, it would be expected that a different value exists under cellular conditions. In fact, the ΔG for the hydrolysis of one mole of ATP in a living cell is almost double the value at standard conditions: 14 kcal/mol (−57 kJ/mol).

ATP is a highly unstable molecule. Unless quickly used to perform work, ATP spontaneously dissociates into ADP + P_i, and the free energy released during this process is lost as heat. The second question posed above, that is, how the energy released by ATP

hydrolysis is used to perform work inside the cell, depends on a strategy called energy coupling. Cells couple the exergonic reaction of ATP hydrolysis with endergonic reactions, allowing them to proceed. One example of energy coupling using ATP involves a transmembrane ion pump that is extremely important for cellular function. This sodium-potassium pump (Na^+/K^+ pump) drives sodium out of the cell and potassium into the cell (Figure 11.5.2). A large percentage of a cell's ATP is spent powering this pump, because cellular processes bring a great deal of sodium into the cell and potassium out of the cell. The pump works constantly to stabilize cellular concentrations of sodium and potassium. In order for the pump to turn one cycle (exporting three Na^+ ions and importing two K^+ ions), one molecule of ATP must be hydrolyzed. When ATP is hydrolyzed, its gamma phosphate doesn't simply float away, but is actually transferred onto the pump protein. This process of a phosphate group binding to a molecule is called phosphorylation. As with most cases of ATP hydrolysis, a phosphate from ATP is transferred onto another molecule. In a phosphorylated state, the Na^+/K^+ pump has more free energy and is triggered to undergo a conformational change. This change allows it to release Na^+ to the outside of the cell. It then binds extracellular K^+, which, through another conformational change, causes the phosphate to detach from the pump. This release of phosphate triggers the K^+ to be released to the inside of the cell. Essentially, the energy released from the hydrolysis of ATP is coupled with the energy required to power the pump and transport Na^+ and K^+ ions. ATP performs cellular work using this basic form of energy coupling through phosphorylation.

Art Connection

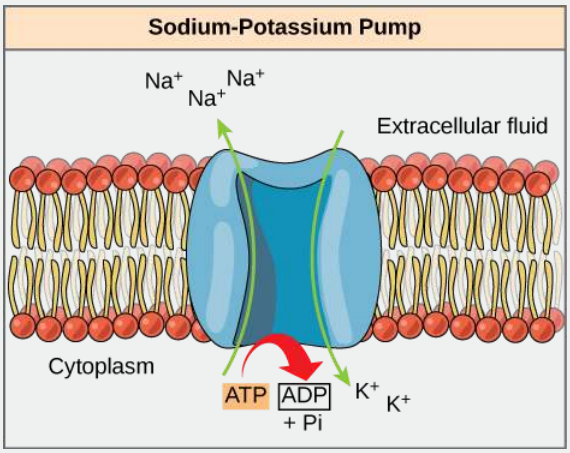


Figure 11.5.2: The sodium-potassium pump is an example of energy coupling. The energy derived from exergonic ATP hydrolysis is used to pump sodium and potassium ions across the cell membrane.

The hydrolysis of one ATP molecule releases 7.3 kcal/mol of energy ($\Delta G = -7.3$ kcal/mol of energy). If it takes 2.1 kcal/mol of energy to move one Na^+ across the membrane ($\Delta G = +2.1$ kcal/mol of energy), how many sodium ions could be moved by the hydrolysis of one ATP molecule?

Often during cellular metabolic reactions, such as the synthesis and breakdown of nutrients, certain molecules must be altered slightly in their conformation to become substrates for the next step in the reaction series. One example is during the very first steps of cellular respiration, when a molecule of the sugar glucose is broken down in the process of glycolysis. In the first step of this process, ATP is required for the phosphorylation of glucose, creating a high-energy but unstable intermediate. This phosphorylation reaction powers a conformational change that allows the phosphorylated glucose molecule to be converted to the phosphorylated sugar fructose. Fructose is a necessary intermediate for glycolysis to move forward. Here, the exergonic reaction of ATP hydrolysis is coupled with the endergonic reaction of converting glucose into a phosphorylated intermediate in the pathway. Once again, the energy released by breaking a phosphate bond within ATP was used for the phosphorylation of another molecule, creating an unstable intermediate and powering an important conformational change.

Link to Learning



See an interactive animation of the ATP-producing glycolysis process at this site.

Summary

ATP is the primary energy-supplying molecule for living cells. ATP is made up of a nucleotide, a five-carbon sugar, and three phosphate groups. The bonds that connect the phosphates (phosphoanhydride bonds) have high-energy content. The energy released from the hydrolysis of ATP into ADP + P_i is used to perform cellular work. Cells use ATP to perform work by coupling the exergonic reaction of ATP hydrolysis with endergonic reactions. ATP donates its phosphate group to another molecule via a process known as phosphorylation. The phosphorylated molecule is at a higher-energy state and is less stable than its unphosphorylated form, and this added energy from the addition of the phosphate allows the molecule to undergo its endergonic reaction.

Art Connections

Figure 11.5.2: The hydrolysis of one ATP molecule releases 7.3 kcal/mol of energy (ΔG = −7.3 kcal/mol of energy). If it takes 2.1 kcal/mol of energy to move one Na^+ across the membrane (ΔG = +2.1 kcal/mol of energy), how many sodium ions could be moved by the hydrolysis of one ATP molecule?

Answer

Three sodium ions could be moved by the hydrolysis of one ATP molecule. The ΔG of the coupled reaction must be negative. Movement of three sodium ions across the membrane will take 6.3 kcal of energy (2.1 kcal × 3 Na^+ ions = 6.3 kcal). Hydrolysis of ATP provides 7.3 kcal of energy, more than enough to power this reaction. Movement of four sodium ions across the membrane, however, would require 8.4 kcal of energy, more than one ATP molecule can provide.

Glossary

ATP

adenosine triphosphate, the cell’s energy currency

phosphoanhydride bond

bond that connects phosphates in an ATP molecule

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11.6: Enzymes

Skills to Develop

- Describe the role of enzymes in metabolic pathways
- Explain how enzymes function as molecular catalysts
- Discuss enzyme regulation by various factors

A substance that helps a chemical reaction to occur is a catalyst, and the special molecules that catalyze biochemical reactions are called enzymes. Almost all enzymes are proteins, made up of chains of amino acids, and they perform the critical task of lowering the activation energies of chemical reactions inside the cell. Enzymes do this by binding to the reactant molecules, and holding them in such a way as to make the chemical bond-breaking and bond-forming processes take place more readily. It is important to remember that enzymes don't change the ΔG of a reaction. In other words, they don't change whether a reaction is exergonic (spontaneous) or endergonic. This is because they don't change the free energy of the reactants or products. They only reduce the activation energy required to reach the transition state (Figure 11.6.1).

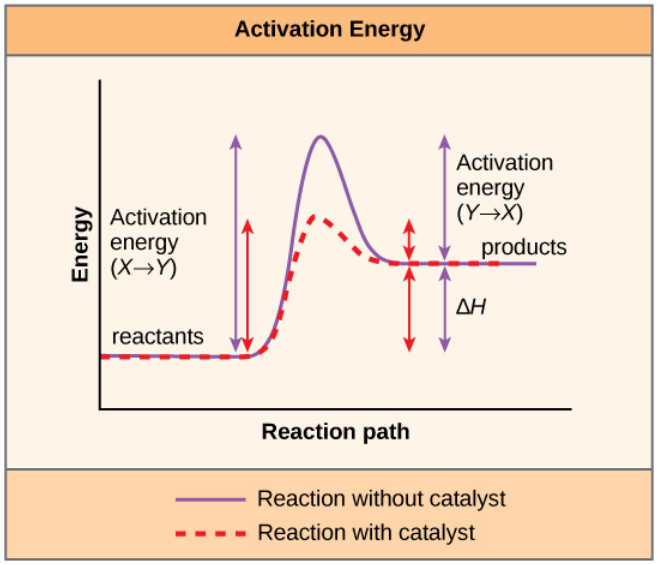


Figure 11.6.1: Enzymes lower the activation energy of the reaction but do not change the free energy of the reaction.

Enzyme Active Site and Substrate Specificity

The chemical reactants to which an enzyme binds are the enzyme's substrates. There may be one or more substrates, depending on the particular chemical reaction. In some reactions, a single-reactant substrate is broken down into multiple products. In others, two substrates may come together to create one larger molecule. Two reactants might also enter a reaction, both become modified, and leave the reaction as two products. The location within the enzyme where the substrate binds is called the enzyme's active site. The active site is where the "action" happens, so to speak. Since enzymes are proteins, there is a unique combination of amino acid residues (also called side chains, or R groups) within the active site. Each residue is characterized by different properties. Residues can be large or small, weakly acidic or basic, hydrophilic or hydrophobic, positively or negatively charged, or neutral. The unique combination of amino acid residues, their positions, sequences, structures, and properties, creates a very specific chemical environment within the active site. This specific environment is suited to bind, albeit briefly, to a specific chemical substrate (or substrates). Due to this jigsaw puzzle-like match between an enzyme and its substrates (which adapts to find the best fit between the transition state and the active site), enzymes are known for their specificity. The "best fit" results from the shape and the amino acid functional group's attraction to the substrate. There is a specifically matched enzyme for each substrate and, thus, for each chemical reaction; however, there is flexibility as well.

The fact that active sites are so perfectly suited to provide specific environmental conditions also means that they are subject to influences by the local environment. It is true that increasing the environmental temperature generally increases reaction rates, enzyme-catalyzed or otherwise. However, increasing or decreasing the temperature outside of an optimal range can affect chemical

bonds within the active site in such a way that they are less well suited to bind substrates. High temperatures will eventually cause enzymes, like other biological molecules, to denature, a process that changes the natural properties of a substance. Likewise, the pH of the local environment can also affect enzyme function. Active site amino acid residues have their own acidic or basic properties that are optimal for catalysis. These residues are sensitive to changes in pH that can impair the way substrate molecules bind. Enzymes are suited to function best within a certain pH range, and, as with temperature, extreme pH values (acidic or basic) of the environment can cause enzymes to denature.

Induced Fit and Enzyme Function

For many years, scientists thought that enzyme-substrate binding took place in a simple "lock-and-key" fashion. This model asserted that the enzyme and substrate fit together perfectly in one instantaneous step. However, current research supports a more refined view called induced fit (Figure 11.6.2). The induced-fit model expands upon the lock-and-key model by describing a more dynamic interaction between enzyme and substrate. As the enzyme and substrate come together, their interaction causes a mild shift in the enzyme's structure that confirms an ideal binding arrangement between the enzyme and the transition state of the substrate. This ideal binding maximizes the enzyme's ability to catalyze its reaction.

When an enzyme binds its substrate, an enzyme-substrate complex is formed. This complex lowers the activation energy of the reaction and promotes its rapid progression in one of many ways. On a basic level, enzymes promote chemical reactions that involve more than one substrate by bringing the substrates together in an optimal orientation. The appropriate region (atoms and bonds) of one molecule is juxtaposed to the appropriate region of the other molecule with which it must react. Another way in which enzymes promote the reaction of their substrates is by creating an optimal environment within the active site for the reaction to occur. Certain chemical reactions might proceed best in a slightly acidic or non-polar environment. The chemical properties that emerge from the particular arrangement of amino acid residues within an active site create the perfect environment for an enzyme's specific substrates to react.

You've learned that the activation energy required for many reactions includes the energy involved in manipulating or slightly contorting chemical bonds so that they can easily break and allow others to reform. Enzymatic action can aid this process. The enzyme-substrate complex can lower the activation energy by contorting substrate molecules in such a way as to facilitate bond-breaking, helping to reach the transition state. Finally, enzymes can also lower activation energies by taking part in the chemical reaction itself. The amino acid residues can provide certain ions or chemical groups that actually form covalent bonds with substrate molecules as a necessary step of the reaction process. In these cases, it is important to remember that the enzyme will always return to its original state at the completion of the reaction. One of the hallmark properties of enzymes is that they remain ultimately unchanged by the reactions they catalyze. After an enzyme is done catalyzing a reaction, it releases its product(s).

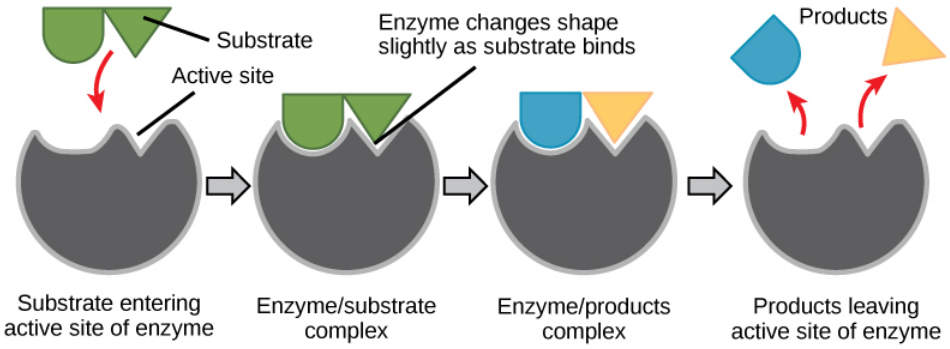


Figure 11.6.2: According to the induced-fit model, both enzyme and substrate undergo dynamic conformational changes upon binding. The enzyme contorts the substrate into its transition state, thereby increasing the rate of the reaction.

Control of Metabolism Through Enzyme Regulation

It would seem ideal to have a scenario in which all of the enzymes encoded in an organism's genome existed in abundant supply and functioned optimally under all cellular conditions, in all cells, at all times. In reality, this is far from the case. A variety of mechanisms ensure that this does not happen. Cellular needs and conditions vary from cell to cell, and change within individual cells over time. The required enzymes and energetic demands of stomach cells are different from those of fat storage cells, skin

cells, blood cells, and nerve cells. Furthermore, a digestive cell works much harder to process and break down nutrients during the time that closely follows a meal compared with many hours after a meal. As these cellular demands and conditions vary, so do the amounts and functionality of different enzymes.

Since the rates of biochemical reactions are controlled by activation energy, and enzymes lower and determine activation energies for chemical reactions, the relative amounts and functioning of the variety of enzymes within a cell ultimately determine which reactions will proceed and at which rates. This determination is tightly controlled. In certain cellular environments, enzyme activity is partly controlled by environmental factors, like pH and temperature. There are other mechanisms through which cells control the activity of enzymes and determine the rates at which various biochemical reactions will occur.

Regulation of Enzymes by Molecules

Enzymes can be regulated in ways that either promote or reduce their activity. There are many different kinds of molecules that inhibit or promote enzyme function, and various mechanisms exist for doing so. In some cases of enzyme inhibition, for example, an inhibitor molecule is similar enough to a substrate that it can bind to the active site and simply block the substrate from binding. When this happens, the enzyme is inhibited through competitive inhibition, because an inhibitor molecule competes with the substrate for active site binding (Figure 11.6.3). On the other hand, in noncompetitive inhibition, an inhibitor molecule binds to the enzyme in a location other than an allosteric site and still manages to block substrate binding to the active site.

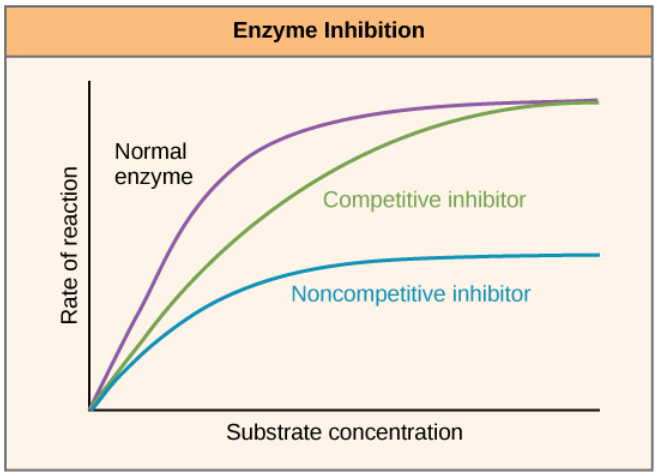


Figure 11.6.3: Competitive and noncompetitive inhibition affect the rate of reaction differently. Competitive inhibitors affect the initial rate but do not affect the maximal rate, whereas noncompetitive inhibitors affect the maximal rate.

Some inhibitor molecules bind to enzymes in a location where their binding induces a conformational change that reduces the affinity of the enzyme for its substrate. This type of inhibition is called allosteric inhibition (Figure 11.6.4). Most allosterically regulated enzymes are made up of more than one polypeptide, meaning that they have more than one protein subunit. When an allosteric inhibitor binds to an enzyme, all active sites on the protein subunits are changed slightly such that they bind their substrates with less efficiency. There are allosteric activators as well as inhibitors. Allosteric activators bind to locations on an enzyme away from the active site, inducing a conformational change that increases the affinity of the enzyme's active site(s) for its substrate(s).

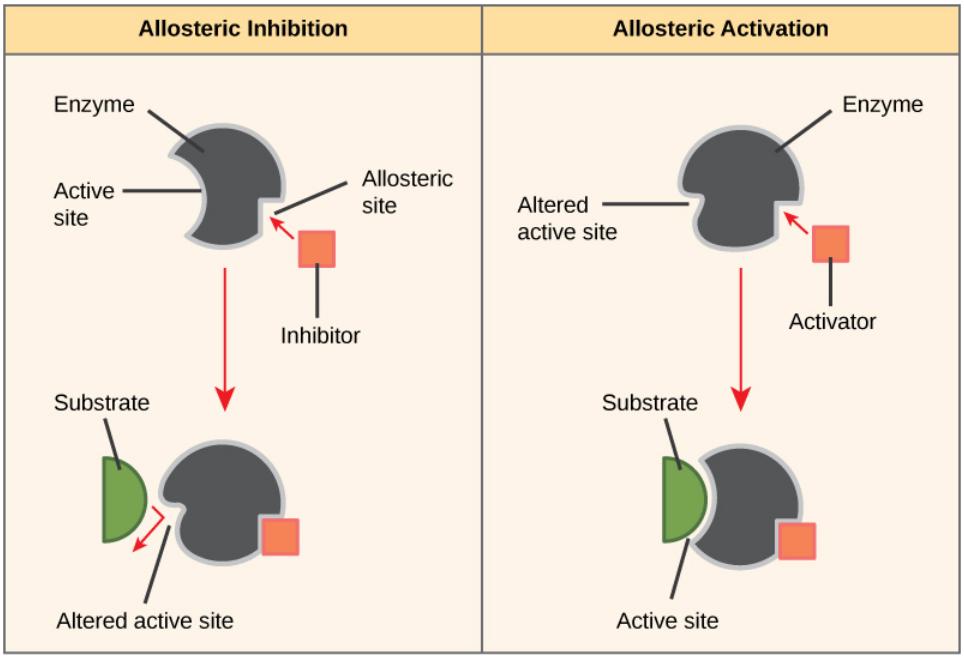


Figure 11.6.4: Allosteric inhibitors modify the active site of the enzyme so that substrate binding is reduced or prevented. In contrast, allosteric activators modify the active site of the enzyme so that the affinity for the substrate increases.

Everyday Connection: Drug Discovery by Looking for Inhibitors of Key Enzymes in Specific Pathways



Figure 11.6.5: Have you ever wondered how pharmaceutical drugs are developed? (credit: Deborah Austin)

Enzymes are key components of metabolic pathways. Understanding how enzymes work and how they can be regulated is a key principle behind the development of many of the pharmaceutical drugs (Figure 11.6.5) on the market today. Biologists working in this field collaborate with other scientists, usually chemists, to design drugs.

Consider statins for example—which is the name given to the class of drugs that reduces cholesterol levels. These compounds are essentially inhibitors of the enzyme HMG-CoA reductase. HMG-CoA reductase is the enzyme that synthesizes cholesterol from lipids in the body. By inhibiting this enzyme, the levels of cholesterol synthesized in the body can be reduced. Similarly, acetaminophen, popularly marketed under the brand name Tylenol, is an inhibitor of the enzyme cyclooxygenase. While it is effective in providing relief from fever and inflammation (pain), its mechanism of action is still not completely understood.

How are drugs developed? One of the first challenges in drug development is identifying the specific molecule that the drug is intended to target. In the case of statins, HMG-CoA reductase is the drug target. Drug targets are identified through painstaking research in the laboratory. Identifying the target alone is not sufficient; scientists also need to know how the target acts inside the cell and which reactions go awry in the case of disease. Once the target and the pathway are identified, then the actual process of drug design begins. During this stage, chemists and biologists work together to design and synthesize molecules that can either block or activate a particular reaction. However, this is only the beginning: both if and when a drug prototype is

successful in performing its function, then it must undergo many tests from in vitro experiments to clinical trials before it can get FDA approval to be on the market.

Many enzymes don't work optimally, or even at all, unless bound to other specific non-protein helper molecules, either temporarily through ionic or hydrogen bonds or permanently through stronger covalent bonds. Two types of helper molecules are cofactors and coenzymes. Binding to these molecules promotes optimal conformation and function for their respective enzymes. Cofactors are inorganic ions such as iron (Fe++) and magnesium (Mg++). One example of an enzyme that requires a metal ion as a cofactor is the enzyme that builds DNA molecules, DNA polymerase, which requires bound zinc ion (Zn++) to function. Coenzymes are organic helper molecules, with a basic atomic structure made up of carbon and hydrogen, which are required for enzyme action. The most common sources of coenzymes are dietary vitamins (Figure 11.6.6). Some vitamins are precursors to coenzymes and others act directly as coenzymes. Vitamin C is a coenzyme for multiple enzymes that take part in building the important connective tissue component, collagen. An important step in the breakdown of glucose to yield energy is catalysis by a multi-enzyme complex called pyruvate dehydrogenase. Pyruvate dehydrogenase is a complex of several enzymes that actually requires one cofactor (a magnesium ion) and five different organic coenzymes to catalyze its specific chemical reaction. Therefore, enzyme function is, in part, regulated by an abundance of various cofactors and coenzymes, which are supplied primarily by the diets of most organisms.

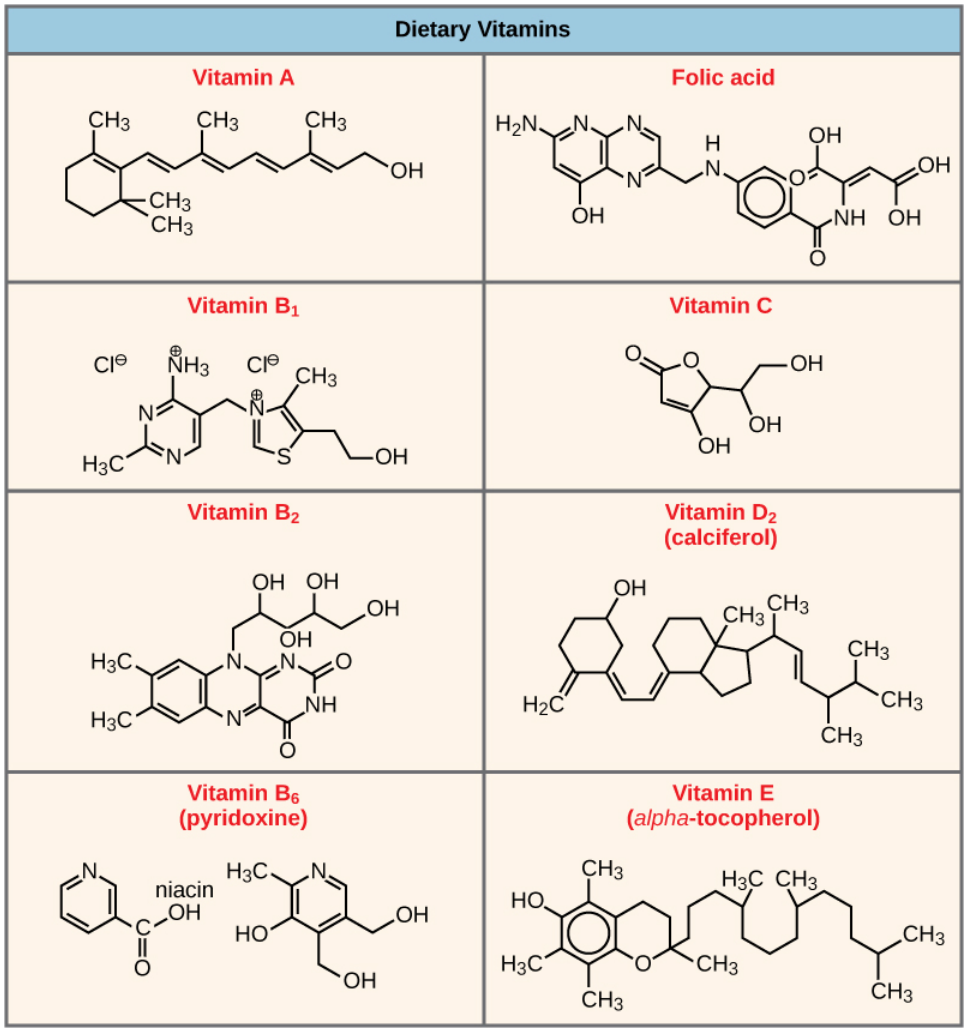


Figure 11.6.6: Vitamins are important coenzymes or precursors of coenzymes, and are required for enzymes to function properly. Multivitamin capsules usually contain mixtures of all the vitamins at different percentages.

Enzyme Compartmentalization

In eukaryotic cells, molecules such as enzymes are usually compartmentalized into different organelles. This allows for yet another level of regulation of enzyme activity. Enzymes required only for certain cellular processes can be housed separately along with

their substrates, allowing for more efficient chemical reactions. Examples of this sort of enzyme regulation based on location and proximity include the enzymes involved in the latter stages of cellular respiration, which take place exclusively in the mitochondria, and the enzymes involved in the digestion of cellular debris and foreign materials, located within lysosomes.

Feedback Inhibition in Metabolic Pathways

Molecules can regulate enzyme function in many ways. A major question remains, however: What are these molecules and where do they come from? Some are cofactors and coenzymes, ions, and organic molecules, as you've learned. What other molecules in the cell provide enzymatic regulation, such as allosteric modulation, and competitive and noncompetitive inhibition? The answer is that a wide variety of molecules can perform these roles. Some of these molecules include pharmaceutical and non-pharmaceutical drugs, toxins, and poisons from the environment. Perhaps the most relevant sources of enzyme regulatory molecules, with respect to cellular metabolism, are the products of the cellular metabolic reactions themselves. In a most efficient and elegant way, cells have evolved to use the products of their own reactions for feedback inhibition of enzyme activity. Feedback inhibition involves the use of a reaction product to regulate its own further production (Figure 11.6.7). The cell responds to the abundance of specific products by slowing down production during anabolic or catabolic reactions. Such reaction products may inhibit the enzymes that catalyzed their production through the mechanisms described above.

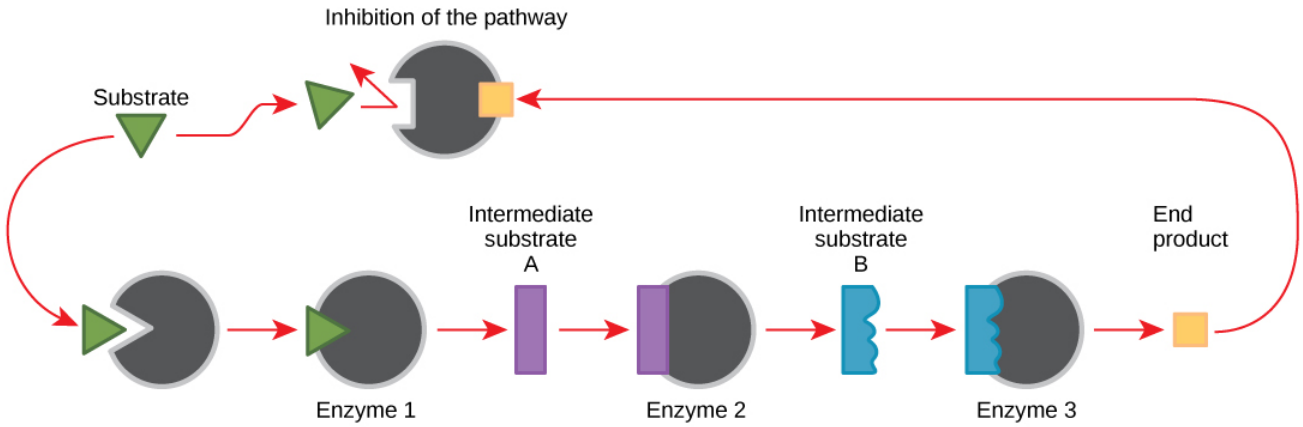


Figure 11.6.7: Metabolic pathways are a series of reactions catalyzed by multiple enzymes. Feedback inhibition, where the end product of the pathway inhibits an upstream step, is an important regulatory mechanism in cells.

The production of both amino acids and nucleotides is controlled through feedback inhibition. Additionally, ATP is an allosteric regulator of some of the enzymes involved in the catabolic breakdown of sugar, the process that produces ATP. In this way, when ATP is abundant, the cell can prevent its further production. Remember that ATP is an unstable molecule that can spontaneously dissociate into ADP. If too much ATP were present in a cell, much of it would go to waste. On the other hand, ADP serves as a positive allosteric regulator (an allosteric activator) for some of the same enzymes that are inhibited by ATP. Thus, when relative levels of ADP are high compared to ATP, the cell is triggered to produce more ATP through the catabolism of sugar.

Summary

Enzymes are chemical catalysts that accelerate chemical reactions at physiological temperatures by lowering their activation energy. Enzymes are usually proteins consisting of one or more polypeptide chains. Enzymes have an active site that provides a unique chemical environment, made up of certain amino acid R groups (residues). This unique environment is perfectly suited to convert particular chemical reactants for that enzyme, called substrates, into unstable intermediates called transition states. Enzymes and substrates are thought to bind with an induced fit, which means that enzymes undergo slight conformational adjustments upon substrate contact, leading to full, optimal binding. Enzymes bind to substrates and catalyze reactions in four different ways: bringing substrates together in an optimal orientation, compromising the bond structures of substrates so that bonds can be more easily broken, providing optimal environmental conditions for a reaction to occur, or participating directly in their chemical reaction by forming transient covalent bonds with the substrates.

Enzyme action must be regulated so that in a given cell at a given time, the desired reactions are being catalyzed and the undesired reactions are not. Enzymes are regulated by cellular conditions, such as temperature and pH. They are also regulated through their

location within a cell, sometimes being compartmentalized so that they can only catalyze reactions under certain circumstances. Inhibition and activation of enzymes via other molecules are other important ways that enzymes are regulated. Inhibitors can act competitively, noncompetitively, or allosterically; noncompetitive inhibitors are usually allosteric. Activators can also enhance the function of enzymes allosterically. The most common method by which cells regulate the enzymes in metabolic pathways is through feedback inhibition. During feedback inhibition, the products of a metabolic pathway serve as inhibitors (usually allosteric) of one or more of the enzymes (usually the first committed enzyme of the pathway) involved in the pathway that produces them.

Glossary

active site
specific region of the enzyme to which the substrate binds

allosteric inhibition
inhibition by a binding event at a site different from the active site, which induces a conformational change and reduces the affinity of the enzyme for its substrate

coenzyme
small organic molecule, such as a vitamin or its derivative, which is required to enhance the activity of an enzyme

cofactor
inorganic ion, such as iron and magnesium ions, required for optimal regulation of enzyme activity

competitive inhibition
type of inhibition in which the inhibitor competes with the substrate molecule by binding to the active site of the enzyme

denature
process that changes the natural properties of a substance

feedback inhibition
effect of a product of a reaction sequence to decrease its further production by inhibiting the activity of the first enzyme in the pathway that produces it

induced fit
dynamic fit between the enzyme and its substrate, in which both components modify their structures to allow for ideal binding

substrate
molecule on which the enzyme acts

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11.E: Metabolism (Exercises)

6.1: Energy and Metabolism

Multiple Choice

Energy is stored long-term in the bonds of _____ and used short-term to perform work from a(n) _____ molecule.

A. ATP : glucose
B. an anabolic molecule : catabolic molecule
C. glucose : ATP
D. a catabolic molecule : anabolic molecule

Answer

C

DNA replication involves unwinding two strands of parent DNA, copying each strand to synthesize complementary strands, and releasing the parent and daughter DNA. Which of the following accurately describes this process?

A. This is an anabolic process
B. This is a catabolic process
C. This is both anabolic and catabolic
D. This is a metabolic process but is neither anabolic nor catabolic

Answer

A

Free Response

Does physical exercise involve anabolic and/or catabolic processes? Give evidence for your answer.

Answer

Physical exercise involves both anabolic and catabolic processes. Body cells break down sugars to provide ATP to do the work necessary for exercise, such as muscle contractions. This is catabolism. Muscle cells also must repair muscle tissue damaged by exercise by building new muscle. This is anabolism.

Name two different cellular functions that require energy that parallel human energy-requiring functions.

Answer

Energy is required for cellular motion, through beating of cilia or flagella, as well as human motion, produced by muscle contraction. Cells also need energy to perform digestion, as humans require energy to digest food.

6.2: Potential, Kinetic, Free, and Activation Energy

Review Questions

Consider a pendulum swinging. Which type(s) of energy is/are associated with the pendulum in the following instances: i. the moment at which it completes one cycle, just before it begins to fall back towards the other end, ii. the moment that it is in the middle between the two ends, iii. just before it reaches the end of one cycle (just before instant i.).

A. i. potential and kinetic, ii. potential and kinetic, iii. kinetic
B. i. potential, ii. potential and kinetic, iii. potential and kinetic

C. i. potential, ii. kinetic, iii. potential and kinetic
D. i. potential and kinetic, ii. kinetic iii. kinetic

Answer

C

Which of the following comparisons or contrasts between endergonic and exergonic reactions is false?

A. Endergonic reactions have a positive ΔG and exergonic reactions have a negative ΔG
B. Endergonic reactions consume energy and exergonic reactions release energy
C. Both endergonic and exergonic reactions require a small amount of energy to overcome an activation barrier
D. Endergonic reactions take place slowly and exergonic reactions take place quickly

Answer

D

Which of the following is the best way to judge the relative activation energies between two given chemical reactions?

A. Compare the ΔG values between the two reactions
B. Compare their reaction rates
C. Compare their ideal environmental conditions
D. Compare the spontaneity between the two reactions

Answer

B

Free Response

Explain in your own words the difference between a spontaneous reaction and one that occurs instantaneously, and what causes this difference.

Answer

A spontaneous reaction is one that has a negative ΔG and thus releases energy. However, a spontaneous reaction need not occur quickly or suddenly like an instantaneous reaction. It may occur over long periods due to a large energy of activation, which prevents the reaction from occurring quickly.

Describe the position of the transition state on a vertical energy scale, from low to high, relative to the position of the reactants and products, for both endergonic and exergonic reactions.

Answer

The transition state is always higher in energy than the reactants and the products of a reaction (therefore, above), regardless of whether the reaction is endergonic or exergonic.

6.3: The Laws of Thermodynamics

Review Questions

Which of the following is not an example of an energy transformation?

A. Turning on a light switch
B. Solar panels at work
C. Formation of static electricity

D. None of the above

Answer

A

Label each of the following systems as high or low entropy: i. the instant that a perfume bottle is sprayed compared with 30 seconds later, ii. an old 1950s car compared with a brand new car, and iii. a living cell compared with a dead cell.

A. i. low, ii. high, iii. low
B. i. low, ii. high, iii. high
C. i. high, ii. low, iii. high
D. i. high, ii. low, iii. Low

Answer

A

Free Response

Imagine an elaborate ant farm with tunnels and passageways through the sand where ants live in a large community. Now imagine that an earthquake shook the ground and demolished the ant farm. In which of these two scenarios, before or after the earthquake, was the ant farm system in a state of higher or lower entropy?

Answer

The ant farm had lower entropy before the earthquake because it was a highly ordered system. After the earthquake, the system became much more disordered and had higher entropy.

Energy transfers take place constantly in everyday activities. Think of two scenarios: cooking on a stove and driving. Explain how the second law of thermodynamics applies to these two scenarios.

Answer

While cooking, food is heating up on the stove, but not all of the heat goes to cooking the food, some of it is lost as heat energy to the surrounding air, increasing entropy. While driving, cars burn gasoline to run the engine and move the car. This reaction is not completely efficient, as some energy during this process is lost as heat energy, which is why the hood and the components underneath it heat up while the engine is turned on. The tires also heat up because of friction with the pavement, which is additional energy loss. This energy transfer, like all others, also increases entropy.

6.4: ATP: Adenosine Triphosphate

Review Questions

The energy released by the hydrolysis of ATP is

A. primarily stored between the alpha and beta phosphates
B. equal to −57 kcal/mol
C. harnessed as heat energy by the cell to perform work
D. providing energy to coupled reactions

Answer

D

Which of the following molecules is likely to have the most potential energy?

A. sucrose
B. ATP
C. glucose
D. ADP

Answer

A

Free Response

Do you think that the E_A for ATP hydrolysis is relatively low or high? Explain your reasoning.

Answer

The activation energy for hydrolysis is very low. Not only is ATP hydrolysis an exergonic process with a large $-\Delta G$, but ATP is also a very unstable molecule that rapidly breaks down into ADP + P_i if not utilized quickly. This suggests a very low E_A since it hydrolyzes so quickly.

6.5: Enzymes

Review Questions

Which of the following is not true about enzymes:

A. They increase ΔG of reactions
B. They are usually made of amino acids
C. They lower the activation energy of chemical reactions
D. Each one is specific to the particular substrate(s) to which it binds

Answer

A

An allosteric inhibitor does which of the following?

A. Binds to an enzyme away from the active site and changes the conformation of the active site, increasing its affinity for substrate binding
B. Binds to the active site and blocks it from binding substrate
C. Binds to an enzyme away from the active site and changes the conformation of the active site, decreasing its affinity for the substrate
D. Binds directly to the active site and mimics the substrate

Answer

C

Which of the following analogies best describe the induced-fit model of enzyme-substrate binding?

A. A hug between two people
B. A key fitting into a lock
C. A square peg fitting through the square hole and a round peg fitting through the round hole of a children's toy
D. The fitting together of two jigsaw puzzle pieces.

Answer

A

Free Response

With regard to enzymes, why are vitamins necessary for good health? Give examples.

Answer

Most vitamins and minerals act as coenzymes and cofactors for enzyme action. Many enzymes require the binding of certain cofactors or coenzymes to be able to catalyze their reactions. Since enzymes catalyze many important reactions, it is critical to obtain sufficient vitamins and minerals from the diet and from supplements. Vitamin C (ascorbic acid) is a coenzyme necessary for the action of enzymes that build collagen, an important protein component of connective tissue throughout the body. Magnesium ion (Mg^{++}) is an important cofactor that is necessary for the enzyme pyruvate dehydrogenase to catalyze part of the pathway that breaks down sugar to produce energy. Vitamins cannot be produced in the human body and therefore must be obtained in the diet.

Explain in your own words how enzyme feedback inhibition benefits a cell.

Answer

Feedback inhibition allows cells to control the amounts of metabolic products produced. If there is too much of a particular product relative to what the cell's needs, feedback inhibition effectively causes the cell to decrease production of that particular product. In general, this reduces the production of superfluous products and conserves energy, maximizing energy efficiency.

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CHAPTER OVERVIEW

12: Cellular Respiration

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12.E: Cellular Respiration (Exercises)

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12.1: Prelude to Cellular Respiration



Figure 12.1.1: This geothermal energy plant transforms thermal energy from deep in the ground into electrical energy, which can be easily used. (credit: modification of work by the U.S. Department of Defense)

The electrical energy plant in Figure 12.1.1 converts energy from one form to another form that can be more easily used. This type of generating plant starts with underground thermal energy (heat) and transforms it into electrical energy that will be transported to homes and factories. Like a generating plant, plants and animals also must take in energy from the environment and convert it into a form that their cells can use. Energy enters an organism's body in one form and is converted into another form that can fuel the organism's life functions. In the process of photosynthesis, plants and other photosynthetic producers take in energy in the form of light (solar energy) and convert it into chemical energy, glucose, which stores this energy in its chemical bonds. Then, a series of metabolic pathways, collectively called cellular respiration, extracts the energy from the bonds in glucose and converts it into a form that all living things can use—both producers, such as plants, and consumers, such as animals.

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12.2: Energy in Living Systems

Skills to Develop

- Discuss the importance of electrons in the transfer of energy in living systems
- Explain how ATP is used by the cell as an energy source

Energy production within a cell involves many coordinated chemical pathways. Most of these pathways are combinations of oxidation and reduction reactions. Oxidation and reduction occur in tandem. An oxidation reaction strips an electron from an atom in a compound, and the addition of this electron to another compound is a reduction reaction. Because oxidation and reduction usually occur together, these pairs of reactions are called oxidation reduction reactions, or redox reactions.

Electrons and Energy

The removal of an electron from a molecule, oxidizing it, results in a decrease in potential energy in the oxidized compound. The electron (sometimes as part of a hydrogen atom), does not remain unbonded, however, in the cytoplasm of a cell. Rather, the electron is shifted to a second compound, reducing the second compound. The shift of an electron from one compound to another removes some potential energy from the first compound (the oxidized compound) and increases the potential energy of the second compound (the reduced compound). The transfer of electrons between molecules is important because most of the energy stored in atoms and used to fuel cell functions is in the form of high-energy electrons. The transfer of energy in the form of electrons allows the cell to transfer and use energy in an incremental fashion—in small packages rather than in a single, destructive burst. This chapter focuses on the extraction of energy from food; you will see that as you track the path of the transfers, you are tracking the path of electrons moving through metabolic pathways.

Electron Carriers

In living systems, a small class of compounds functions as electron shuttles: They bind and carry high-energy electrons between compounds in pathways. The principal electron carriers we will consider are derived from the B vitamin group and are derivatives of nucleotides. These compounds can be easily reduced (that is, they accept electrons) or oxidized (they lose electrons). Nicotinamide adenine dinucleotide (NAD) (Figure 12.2.1) is derived from vitamin B_3, niacin. NAD^+ is the oxidized form of the molecule; NADH is the reduced form of the molecule after it has accepted two electrons and a proton (which together are the equivalent of a hydrogen atom with an extra electron).

NAD^+ can accept electrons from an organic molecule according to the general equation:

$$\underset{\text{reducing agent}}{RH} + \underset{\text{oxidizing agent}}{NAD^+} \rightarrow \underset{\text{reduced}}{NADH} + \underset{\text{oxidized}}{R^+}$$

When electrons are added to a compound, they are reduced. A compound that reduces another is called a reducing agent. In the above equation, RH is a reducing agent, and NAD^+ is reduced to NADH. When electrons are removed from compound, it oxidized. A compound that oxidizes another is called an oxidizing agent. In the above equation, NAD^+ is an oxidizing agent, and RH is oxidized to R.

Similarly, flavin adenine dinucleotide (FAD^+) is derived from vitamin B_2, also called riboflavin. Its reduced form is $FADH_2$. A second variation of NAD, NADP, contains an extra phosphate group. Both NAD^+ and FAD^+ are extensively used in energy extraction from sugars, and NADP plays an important role in anabolic reactions and photosynthesis.

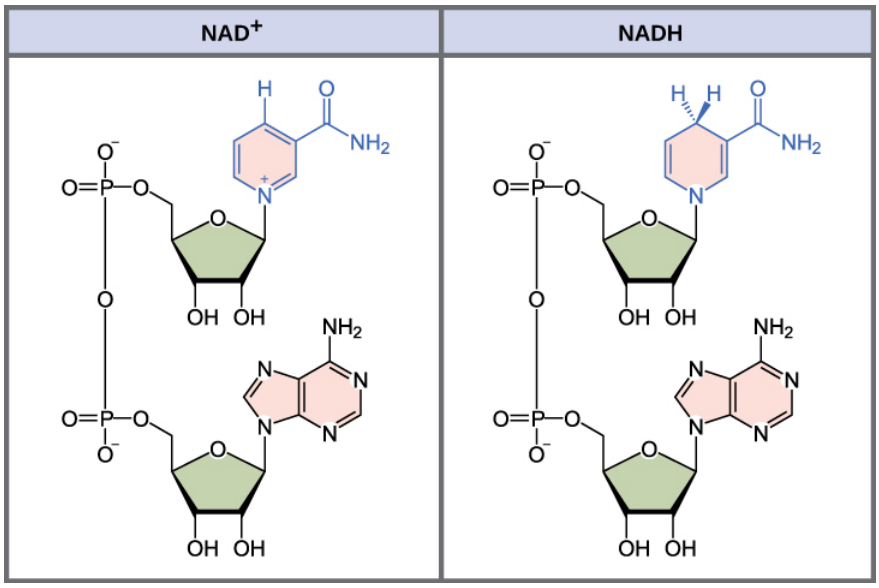


Figure 12.2.1: The oxidized form of the electron carrier (NAD^+) is shown on the left and the reduced form (NADH) is shown on the right. The nitrogenous base in NADH has one more hydrogen ion and two more electrons than in NAD^+.

ATP in Living Systems

A living cell cannot store significant amounts of free energy. Excess free energy would result in an increase of heat in the cell, which would result in excessive thermal motion that could damage and then destroy the cell. Rather, a cell must be able to handle that energy in a way that enables the cell to store energy safely and release it for use only as needed. Living cells accomplish this by using the compound adenosine triphosphate (ATP). ATP is often called the "energy currency" of the cell, and, like currency, this versatile compound can be used to fill any energy need of the cell. How? It functions similarly to a rechargeable battery.

When ATP is broken down, usually by the removal of its terminal phosphate group, energy is released. The energy is used to do work by the cell, usually by the released phosphate binding to another molecule, activating it. For example, in the mechanical work of muscle contraction, ATP supplies the energy to move the contractile muscle proteins. Recall the active transport work of the sodium-potassium pump in cell membranes. ATP alters the structure of the integral protein that functions as the pump, changing its affinity for sodium and potassium. In this way, the cell performs work, pumping ions against their electrochemical gradients.

ATP Structure and Function

At the heart of ATP is a molecule of adenosine monophosphate (AMP), which is composed of an adenine molecule bonded to a ribose molecule and to a single phosphate group (Figure 12.2.2). Ribose is a five-carbon sugar found in RNA, and AMP is one of the nucleotides in RNA. The addition of a second phosphate group to this core molecule results in the formation of adenosine diphosphate (ADP); the addition of a third phosphate group forms adenosine triphosphate (ATP).

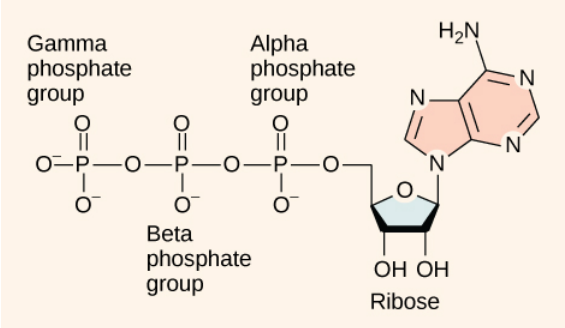


Figure 12.2.2: ATP (adenosine triphosphate) has three phosphate groups that can be removed by hydrolysis to form ADP (adenosine diphosphate) or AMP (adenosine monophosphate).The negative charges on the phosphate group naturally repel each other, requiring energy to bond them together and releasing energy when these bonds are broken.

The addition of a phosphate group to a molecule requires energy. Phosphate groups are negatively charged and thus repel one another when they are arranged in series, as they are in ADP and ATP. This repulsion makes the ADP and ATP molecules inherently unstable. The release of one or two phosphate groups from ATP, a process called dephosphorylation, releases energy.

Energy from ATP

Hydrolysis is the process of breaking complex macromolecules apart. During hydrolysis, water is split, or lysed, and the resulting hydrogen atom (H^+) and a hydroxyl group (OH^-) are added to the larger molecule. The hydrolysis of ATP produces ADP, together with an inorganic phosphate ion (P_i), and the release of free energy. To carry out life processes, ATP is continuously broken down into ADP, and like a rechargeable battery, ADP is continuously regenerated into ATP by the reattachment of a third phosphate group. Water, which was broken down into its hydrogen atom and hydroxyl group during ATP hydrolysis, is regenerated when a third phosphate is added to the ADP molecule, reforming ATP.

Obviously, energy must be infused into the system to regenerate ATP. Where does this energy come from? In nearly every living thing on earth, the energy comes from the metabolism of glucose. In this way, ATP is a direct link between the limited set of exergonic pathways of glucose catabolism and the multitude of endergonic pathways that power living cells.

Phosphorylation

Recall that, in some chemical reactions, enzymes may bind to several substrates that react with each other on the enzyme, forming an intermediate complex. An intermediate complex is a temporary structure, and it allows one of the substrates (such as ATP) and reactants to more readily react with each other; in reactions involving ATP, ATP is one of the substrates and ADP is a product. During an endergonic chemical reaction, ATP forms an intermediate complex with the substrate and enzyme in the reaction. This intermediate complex allows the ATP to transfer its third phosphate group, with its energy, to the substrate, a process called phosphorylation. Phosphorylation refers to the addition of the phosphate (~P). This is illustrated by the following generic reaction:

$$\mathrm{A + enzyme + ATP \rightarrow [A - enzyme - {\sim}P] \rightarrow B + enzyme + ADP + phosphate\ ion}$$

When the intermediate complex breaks apart, the energy is used to modify the substrate and convert it into a product of the reaction. The ADP molecule and a free phosphate ion are released into the medium and are available for recycling through cell metabolism.

Substrate Phosphorylation

ATP is generated through two mechanisms during the breakdown of glucose. A few ATP molecules are generated (that is, regenerated from ADP) as a direct result of the chemical reactions that occur in the catabolic pathways. A phosphate group is removed from an intermediate reactant in the pathway, and the free energy of the reaction is used to add the third phosphate to an available ADP molecule, producing ATP (Figure 12.2.3). This very direct method of phosphorylation is called substrate-level phosphorylation.

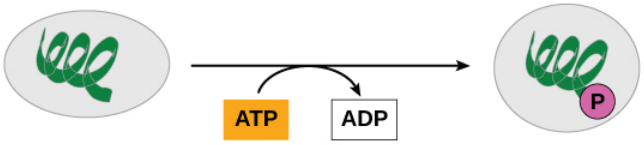


Figure 12.2.3: In phosphorylation reactions, the gamma phosphate of ATP is attached to a protein.

Oxidative Phosphorylation

Most of the ATP generated during glucose catabolism, however, is derived from a much more complex process, chemiosmosis, which takes place in mitochondria (Figure 12.2.4) within a eukaryotic cell or the plasma membrane of a prokaryotic cell. Chemiosmosis, a process of ATP production in cellular metabolism, is used to generate 90 percent of the ATP made during glucose catabolism and is also the method used in the light reactions of photosynthesis to harness the energy of sunlight. The production of ATP using the process of chemiosmosis is called oxidative phosphorylation because of the involvement of oxygen in the process.

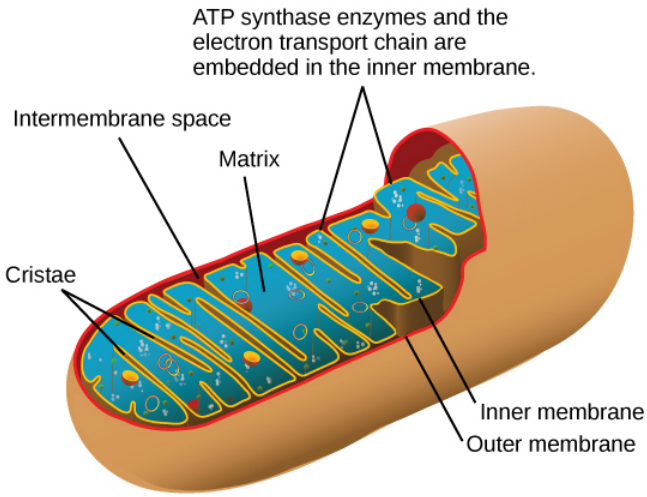


Figure 12.2.4: In eukaryotes, oxidative phosphorylation takes place in mitochondria. In prokaryotes, this process takes place in the plasma membrane. (Credit: modification of work by Mariana Ruiz Villareal)

Career Connections: Mitochondrial Disease Physician

What happens when the critical reactions of cellular respiration do not proceed correctly? Mitochondrial diseases are genetic disorders of metabolism. Mitochondrial disorders can arise from mutations in nuclear or mitochondrial DNA, and they result in the production of less energy than is normal in body cells. In type 2 diabetes, for instance, the oxidation efficiency of NADH is reduced, impacting oxidative phosphorylation but not the other steps of respiration. Symptoms of mitochondrial diseases can include muscle weakness, lack of coordination, stroke-like episodes, and loss of vision and hearing. Most affected people are diagnosed in childhood, although there are some adult-onset diseases. Identifying and treating mitochondrial disorders is a specialized medical field. The educational preparation for this profession requires a college education, followed by medical school with a specialization in medical genetics. Medical geneticists can be board certified by the American Board of Medical Genetics and go on to become associated with professional organizations devoted to the study of mitochondrial diseases, such as the Mitochondrial Medicine Society and the Society for Inherited Metabolic Disease.

Summary

ATP functions as the energy currency for cells. It allows the cell to store energy briefly and transport it within the cell to support endergonic chemical reactions. The structure of ATP is that of an RNA nucleotide with three phosphates attached. As ATP is used for energy, a phosphate group or two are detached, and either ADP or AMP is produced. Energy derived from glucose catabolism is used to convert ADP into ATP. When ATP is used in a reaction, the third phosphate is temporarily attached to a substrate in a process called phosphorylation. The two processes of ATP regeneration that are used in conjunction with glucose catabolism are substrate-level phosphorylation and oxidative phosphorylation through the process of chemiosmosis.

Glossary

chemiosmosis
process in which there is a production of adenosine triphosphate (ATP) in cellular metabolism by the involvement of a proton gradient across a membrane

dephosphorylation
removal of a phosphate group from a molecule

oxidative phosphorylation
production of ATP using the process of chemiosmosis and oxygen

phosphorylation
addition of a high-energy phosphate to a compound, usually a metabolic intermediate, a protein, or ADP

redox reaction

chemical reaction that consists of the coupling of an oxidation reaction and a reduction reaction

substrate-level phosphorylation

production of ATP from ADP using the excess energy from a chemical reaction and a phosphate group from a reactant

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12.3: Glycolysis

Skills to Develop

- Describe the overall result in terms of molecules produced in the breakdown of glucose by glycolysis
- Compare the output of glycolysis in terms of ATP molecules and NADH molecules produced

You have read that nearly all of the energy used by living cells comes to them in the bonds of the sugar, glucose. Glycolysis is the first step in the breakdown of glucose to extract energy for cellular metabolism. Nearly all living organisms carry out glycolysis as part of their metabolism. The process does not use oxygen and is therefore anaerobic. Glycolysis takes place in the cytoplasm of both prokaryotic and eukaryotic cells. Glucose enters heterotrophic cells in two ways. One method is through secondary active transport in which the transport takes place against the glucose concentration gradient. The other mechanism uses a group of integral proteins called GLUT proteins, also known as glucose transporter proteins. These transporters assist in the facilitated diffusion of glucose.

Glycolysis begins with the six carbon ring-shaped structure of a single glucose molecule and ends with two molecules of a three-carbon sugar called pyruvate. Glycolysis consists of two distinct phases. The first part of the glycolysis pathway traps the glucose molecule in the cell and uses energy to modify it so that the six-carbon sugar molecule can be split evenly into the two three-carbon molecules. The second part of glycolysis extracts energy from the molecules and stores it in the form of ATP and NADH, the reduced form of NAD.

First Half of Glycolysis (Energy-Requiring Steps)

Step 1. The first step in glycolysis (Figure 12.3.1) is catalyzed by hexokinase, an enzyme with broad specificity that catalyzes the phosphorylation of six-carbon sugars. Hexokinase phosphorylates glucose using ATP as the source of the phosphate, producing glucose-6-phosphate, a more reactive form of glucose. This reaction prevents the phosphorylated glucose molecule from continuing to interact with the GLUT proteins, and it can no longer leave the cell because the negatively charged phosphate will not allow it to cross the hydrophobic interior of the plasma membrane.

Step 2. In the second step of glycolysis, an isomerase converts glucose-6-phosphate into one of its isomers, fructose-6-phosphate. An isomerase is an enzyme that catalyzes the conversion of a molecule into one of its isomers. (This change from phosphoglucose to phosphofructose allows the eventual split of the sugar into two three-carbon molecules.).

Step 3. The third step is the phosphorylation of fructose-6-phosphate, catalyzed by the enzyme phosphofructokinase. A second ATP molecule donates a high-energy phosphate to fructose-6-phosphate, producing fructose-1,6-bisphosphate. In this pathway, phosphofructokinase is a rate-limiting enzyme. It is active when the concentration of ADP is high; it is less active when ADP levels are low and the concentration of ATP is high. Thus, if there is “sufficient” ATP in the system, the pathway slows down. This is a type of end product inhibition, since ATP is the end product of glucose catabolism.

Step 4. The newly added high-energy phosphates further destabilize fructose-1,6-bisphosphate. The fourth step in glycolysis employs an enzyme, aldolase, to cleave 1,6-bisphosphate into two three-carbon isomers: dihydroxyacetone-phosphate and glyceraldehyde-3-phosphate.

Step 5. In the fifth step, an isomerase transforms the dihydroxyacetone-phosphate into its isomer, glyceraldehyde-3-phosphate. Thus, the pathway will continue with two molecules of a single isomer. At this point in the pathway, there is a net investment of energy from two ATP molecules in the breakdown of one glucose molecule.

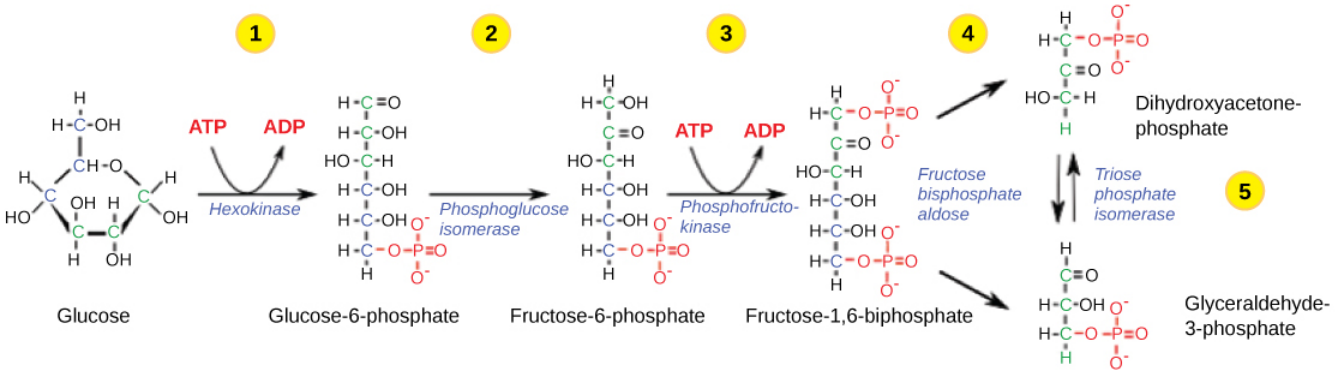


Figure 12.3.1: The first half of glycolysis uses two ATP molecules in the phosphorylation of glucose, which is then split into two three-carbon molecules.

Second Half of Glycolysis (Energy-Releasing Steps)

So far, glycolysis has cost the cell two ATP molecules and produced two small, three-carbon sugar molecules. Both of these molecules will proceed through the second half of the pathway, and sufficient energy will be extracted to pay back the two ATP molecules used as an initial investment and produce a profit for the cell of two additional ATP molecules and two even higher-energy NADH molecules.

Step 6. The sixth step in glycolysis (Figure 12.3.2) oxidizes the sugar (glyceraldehyde-3-phosphate), extracting high-energy electrons, which are picked up by the electron carrier NAD^+, producing NADH. The sugar is then phosphorylated by the addition of a second phosphate group, producing 1,3-bisphosphoglycerate. Note that the second phosphate group does not require another ATP molecule.

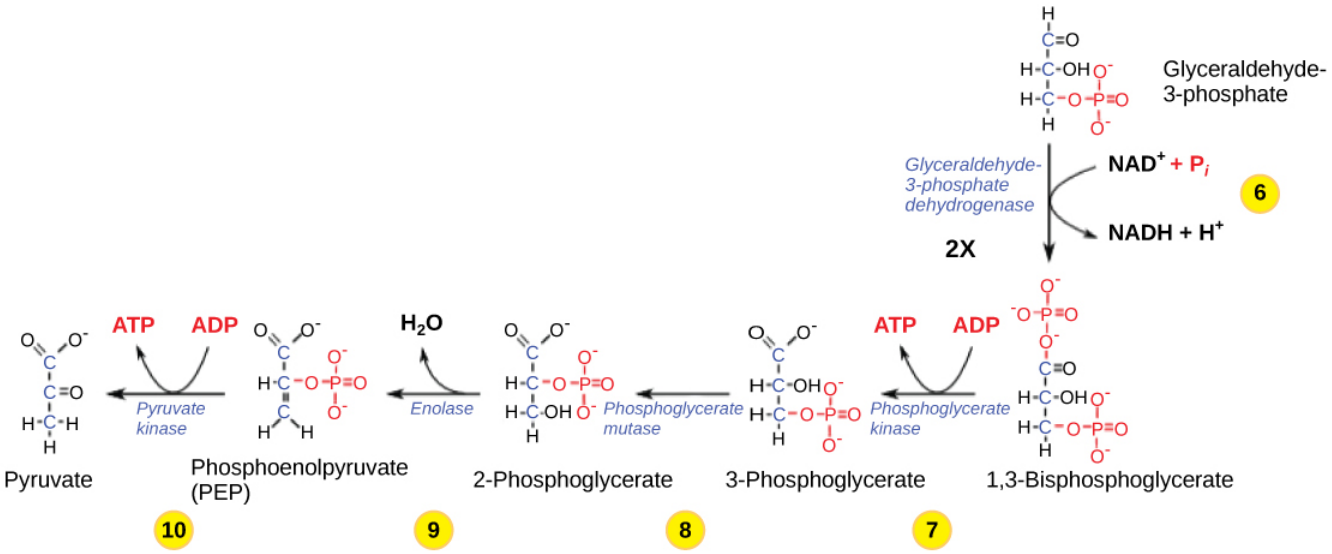


Figure 12.3.2: The second half of glycolysis involves phosphorylation without ATP investment (step 6) and produces two NADH and four ATP molecules per glucose.

Here again is a potential limiting factor for this pathway. The continuation of the reaction depends upon the availability of the oxidized form of the electron carrier, NAD^+. Thus, NADH must be continuously oxidized back into NAD^+ in order to keep this step going. If NAD^+ is not available, the second half of glycolysis slows down or stops. If oxygen is available in the system, the NADH will be oxidized readily, though indirectly, and the high-energy electrons from the hydrogen released in this process will be used to produce ATP. In an environment without oxygen, an alternate pathway (fermentation) can provide the oxidation of NADH to NAD^+.

Step 7. In the seventh step, catalyzed by phosphoglycerate kinase (an enzyme named for the reverse reaction), 1,3-bisphosphoglycerate donates a high-energy phosphate to ADP, forming one molecule of ATP. (This is an example of substrate-level

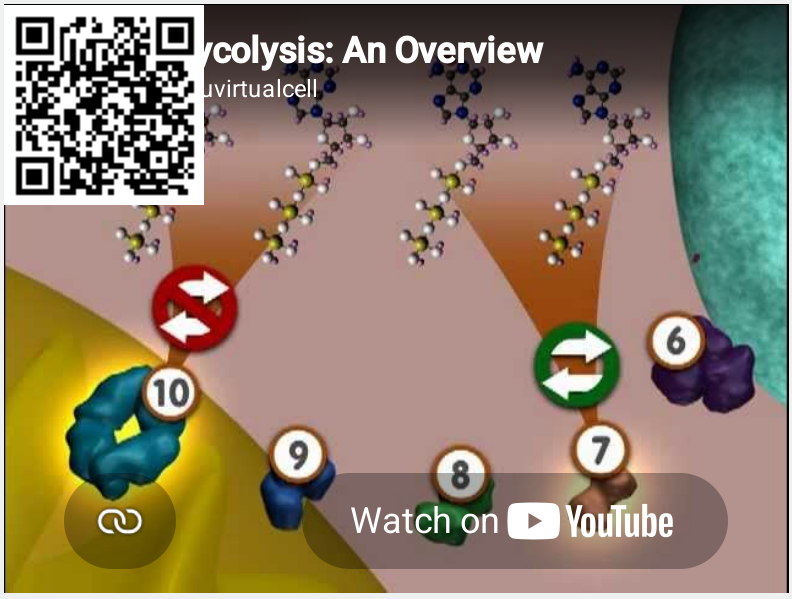
phosphorylation.) A carbonyl group on the 1,3-bisphosphoglycerate is oxidized to a carboxyl group, and 3-phosphoglycerate is formed.

Step 8. In the eighth step, the remaining phosphate group in 3-phosphoglycerate moves from the third carbon to the second carbon, producing 2-phosphoglycerate (an isomer of 3-phosphoglycerate). The enzyme catalyzing this step is a mutase (isomerase).

Step 9. Enolase catalyzes the ninth step. This enzyme causes 2-phosphoglycerate to lose water from its structure; this is a dehydration reaction, resulting in the formation of a double bond that increases the potential energy in the remaining phosphate bond and produces phosphoenolpyruvate (PEP).

Step 10. The last step in glycolysis is catalyzed by the enzyme pyruvate kinase (the enzyme in this case is named for the reverse reaction of pyruvate's conversion into PEP) and results in the production of a second ATP molecule by substrate-level phosphorylation and the compound pyruvic acid (or its salt form, pyruvate). Many enzymes in enzymatic pathways are named for the reverse reactions, since the enzyme can catalyze both forward and reverse reactions (these may have been described initially by the reverse reaction that takes place in vitro, under non-physiological conditions).

Link to Learning



Gain a better understanding of the breakdown of glucose by glycolysis by visiting this site to see the process in action.

Outcomes of Glycolysis

Glycolysis starts with glucose and ends with two pyruvate molecules, a total of four ATP molecules and two molecules of NADH. Two ATP molecules were used in the first half of the pathway to prepare the six-carbon ring for cleavage, so the cell has a net gain of two ATP molecules and 2 NADH molecules for its use. If the cell cannot catabolize the pyruvate molecules further, it will harvest only two ATP molecules from one molecule of glucose. Mature mammalian red blood cells are not capable of aerobic respiration—the process in which organisms convert energy in the presence of oxygen—and glycolysis is their sole source of ATP. If glycolysis is interrupted, these cells lose their ability to maintain their sodium-potassium pumps, and eventually, they die.

The last step in glycolysis will not occur if pyruvate kinase, the enzyme that catalyzes the formation of pyruvate, is not available in sufficient quantities. In this situation, the entire glycolysis pathway will proceed, but only two ATP molecules will be made in the second half. Thus, pyruvate kinase is a rate-limiting enzyme for glycolysis.

Summary

Glycolysis is the first pathway used in the breakdown of glucose to extract energy. It was probably one of the earliest metabolic pathways to evolve and is used by nearly all of the organisms on earth. Glycolysis consists of two parts: The first part prepares the six-carbon ring of glucose for cleavage into two three-carbon sugars. ATP is invested in the process during this half to energize the

separation. The second half of glycolysis extracts ATP and high-energy electrons from hydrogen atoms and attaches them to NAD^+. Two ATP molecules are invested in the first half and four ATP molecules are formed by substrate phosphorylation during the second half. This produces a net gain of two ATP and two NADH molecules for the cell.

Glossary

aerobic respiration
process in which organisms convert energy in the presence of oxygen

anaerobic
process that does not use oxygen

glycolysis
process of breaking glucose into two three-carbon molecules with the production of ATP and NADH

isomerase
enzyme that converts a molecule into its isomer

pyruvate
three-carbon sugar that can be decarboxylated and oxidized to make acetyl CoA, which enters the citric acid cycle under aerobic conditions; the end product of glycolysis

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12.4: Oxidation of Pyruvate and the Citric Acid Cycle

Skills to Develop

- Explain how a circular pathway, such as the citric acid cycle, fundamentally differs from a linear pathway, such as glycolysis
- Describe how pyruvate, the product of glycolysis, is prepared for entry into the citric acid cycle

If oxygen is available, aerobic respiration will go forward. In eukaryotic cells, the pyruvate molecules produced at the end of glycolysis are transported into mitochondria, which are the sites of cellular respiration. There, pyruvate will be transformed into an acetyl group that will be picked up and activated by a carrier compound called coenzyme A (CoA). The resulting compound is called acetyl CoA. CoA is made from vitamin B5, pantothenic acid. Acetyl CoA can be used in a variety of ways by the cell, but its major function is to deliver the acetyl group derived from pyruvate to the next stage of the pathway in glucose catabolism.

Breakdown of Pyruvate

In order for pyruvate, the product of glycolysis, to enter the next pathway, it must undergo several changes. The conversion is a three-step process (Figure 12.4.1).

Step 1. A carboxyl group is removed from pyruvate, releasing a molecule of carbon dioxide into the surrounding medium. The result of this step is a two-carbon hydroxyethyl group bound to the enzyme (pyruvate dehydrogenase). This is the first of the six carbons from the original glucose molecule to be removed. This step proceeds twice (remember: there are *two* pyruvate molecules produced at the end of glycolsis) for every molecule of glucose metabolized; thus, two of the six carbons will have been removed at the end of both steps.

Step 2. The hydroxyethyl group is oxidized to an acetyl group, and the electrons are picked up by NAD^+, forming NADH. The high-energy electrons from NADH will be used later to generate ATP.

Step 3. The enzyme-bound acetyl group is transferred to CoA, producing a molecule of acetyl CoA.

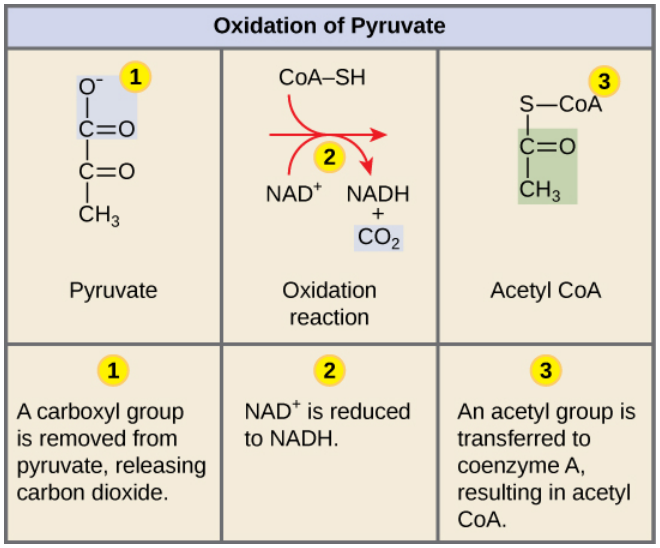


Figure 12.4.1: Upon entering the mitochondrial matrix, a multi-enzyme complex converts pyruvate into acetyl CoA. In the process, carbon dioxide is released and one molecule of NADH is formed.

Note that during the second stage of glucose metabolism, whenever a carbon atom is removed, it is bound to two oxygen atoms, producing carbon dioxide, one of the major end products of cellular respiration.

Acetyl CoA to CO_2

In the presence of oxygen, acetyl CoA delivers its acetyl group to a four-carbon molecule, oxaloacetate, to form citrate, a six-carbon molecule with three carboxyl groups; this pathway will harvest the remainder of the extractable energy from what began as

a glucose molecule. This single pathway is called by different names: the citric acid cycle (for the first intermediate formed—citric acid, or citrate—when acetate joins to the oxaloacetate), the TCA cycle (since citric acid or citrate and isocitrate are tricarboxylic acids), and the Krebs cycle, after Hans Krebs, who first identified the steps in the pathway in the 1930s in pigeon flight muscles.

Citric Acid Cycle

Like the conversion of pyruvate to acetyl CoA, the citric acid cycle takes place in the matrix of mitochondria. Almost all of the enzymes of the citric acid cycle are soluble, with the single exception of the enzyme succinate dehydrogenase, which is embedded in the inner membrane of the mitochondrion. Unlike glycolysis, the citric acid cycle is a closed loop: The last part of the pathway regenerates the compound used in the first step. The eight steps of the cycle are a series of redox, dehydration, hydration, and decarboxylation reactions that produce two carbon dioxide molecules, one GTP/ATP, and reduced forms of NADH and $FADH_2$ (Figure 12.4.2). This is considered an aerobic pathway because the NADH and $FADH_2$ produced must transfer their electrons to the next pathway in the system, which will use oxygen. If this transfer does not occur, the oxidation steps of the citric acid cycle also do not occur. Note that the citric acid cycle produces very little ATP directly and does not directly consume oxygen.

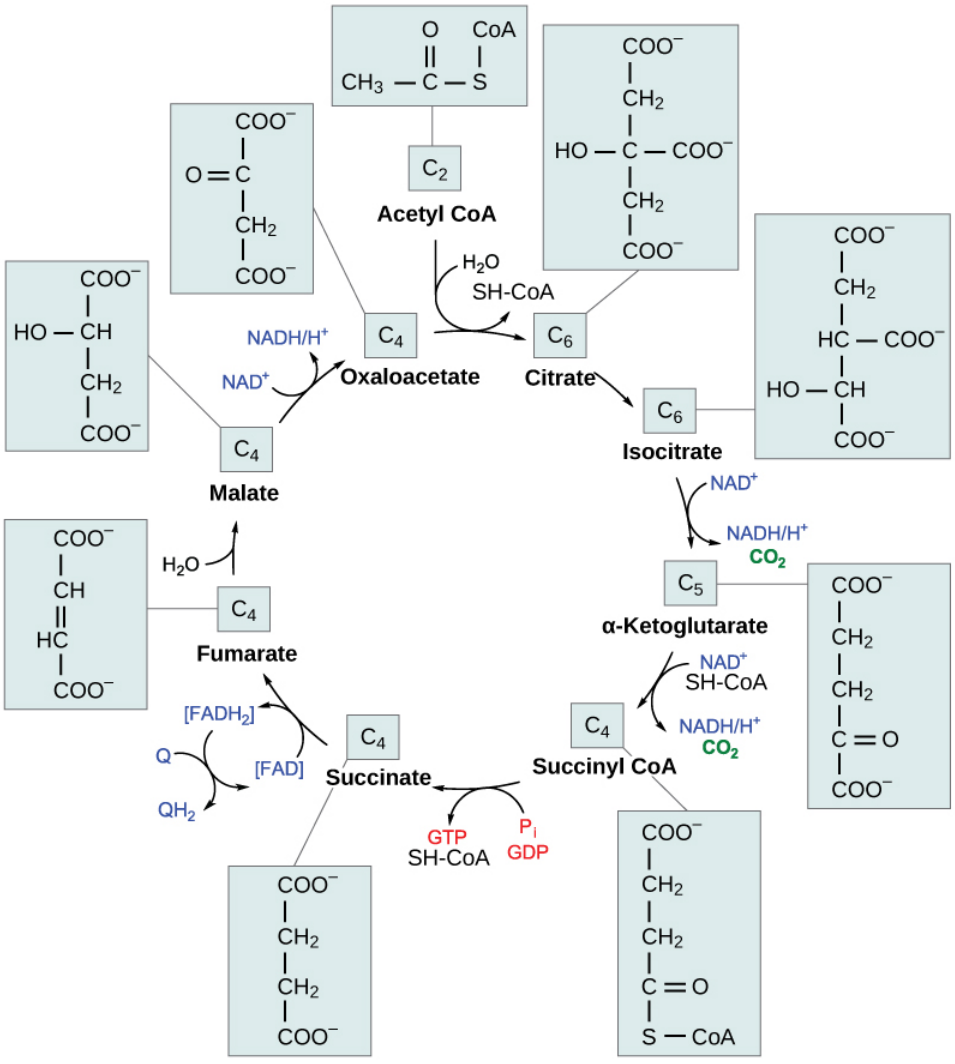


Figure 12.4.2: In the citric acid cycle, the acetyl group from acetyl CoA is attached to a four-carbon oxaloacetate molecule to form a six-carbon citrate molecule. Through a series of steps, citrate is oxidized, releasing two carbon dioxide molecules for each acetyl group fed into the cycle. In the process, three NAD^+ molecules are reduced to NADH, one FAD molecule is reduced to $FADH_2$, and one ATP or GTP (depending on the cell type) is produced (by substrate-level phosphorylation). Because the final product of the citric acid cycle is also the first reactant, the cycle runs continuously in the presence of sufficient reactants. (credit: modification of work by "Yikrazuul"/Wikimedia Commons)

Steps in the Citric Acid Cycle

Step 1. Prior to the start of the first step, a transitional phase occurs during which pyruvic acid is converted to acetyl CoA. Then, the first step of the cycle begins: This is a condensation step, combining the two-carbon acetyl group with a four-carbon oxaloacetate molecule to form a six-carbon molecule of citrate. CoA is bound to a sulfhydryl group (-SH) and diffuses away to eventually combine with another acetyl group. This step is irreversible because it is highly exergonic. The rate of this reaction is controlled by negative feedback and the amount of ATP available. If ATP levels increase, the rate of this reaction decreases. If ATP is in short supply, the rate increases.

Step 2. In step two, citrate loses one water molecule and gains another as citrate is converted into its isomer, isocitrate.

Step 3. In step three, isocitrate is oxidized, producing a five-carbon molecule, α-ketoglutarate, together with a molecule of CO_2 and two electrons, which reduce NAD^+ to NADH. This step is also regulated by negative feedback from ATP and NADH, and a positive effect of ADP.

Steps 3 and 4. Steps three and four are both oxidation and decarboxylation steps, which release electrons that reduce NAD^+ to NADH and release carboxyl groups that form CO_2 molecules. α-Ketoglutarate is the product of step three, and a succinyl group is the product of step four. CoA binds the succinyl group to form succinyl CoA. The enzyme that catalyzes step four is regulated by feedback inhibition of ATP, succinyl CoA, and NADH.

Step 5. In step five, a phosphate group is substituted for coenzyme A, and a high-energy bond is formed. This energy is used in substrate-level phosphorylation (during the conversion of the succinyl group to succinate) to form either guanine triphosphate (GTP) or ATP. There are two forms of the enzyme, called isoenzymes, for this step, depending upon the type of animal tissue in which they are found. One form is found in tissues that use large amounts of ATP, such as heart and skeletal muscle. This form produces ATP. The second form of the enzyme is found in tissues that have a high number of anabolic pathways, such as liver. This form produces GTP. GTP is energetically equivalent to ATP; however, its use is more restricted. In particular, protein synthesis primarily uses GTP.

Step 6. Step six is a dehydration process that converts succinate into fumarate. Two hydrogen atoms are transferred to FAD, producing $FADH_2$. The energy contained in the electrons of these atoms is insufficient to reduce NAD^+ but adequate to reduce FAD. Unlike NADH, this carrier remains attached to the enzyme and transfers the electrons to the electron transport chain directly. This process is made possible by the localization of the enzyme catalyzing this step inside the inner membrane of the mitochondrion.

Step 7. Water is added to fumarate during step seven, and malate is produced. The last step in the citric acid cycle regenerates oxaloacetate by oxidizing malate. Another molecule of NADH is produced in the process.

Link to Learning

Click through each step of the citric acid cycle here.

Products of the Citric Acid Cycle

Two carbon atoms come into the citric acid cycle from each acetyl group, representing four out of the six carbons of one glucose molecule. Two carbon dioxide molecules are released on each turn of the cycle; however, these do not necessarily contain the most recently added carbon atoms. The two acetyl carbon atoms will eventually be released on later turns of the cycle; thus, all six carbon atoms from the original glucose molecule are eventually incorporated into carbon dioxide. Each turn of the cycle forms three NADH molecules and one $FADH_2$ molecule. These carriers will connect with the last portion of aerobic respiration to

produce ATP molecules. One GTP or ATP is also made in each cycle. Several of the intermediate compounds in the citric acid cycle can be used in synthesizing non-essential amino acids; therefore, the cycle is amphibolic (both catabolic and anabolic).

Summary

In the presence of oxygen, pyruvate is transformed into an acetyl group attached to a carrier molecule of coenzyme A. The resulting acetyl CoA can enter several pathways, but most often, the acetyl group is delivered to the citric acid cycle for further catabolism. During the conversion of pyruvate into the acetyl group, a molecule of carbon dioxide and two high-energy electrons are removed. The carbon dioxide accounts for two (conversion of two pyruvate molecules) of the six carbons of the original glucose molecule. The electrons are picked up by NAD^+, and the NADH carries the electrons to a later pathway for ATP production. At this point, the glucose molecule that originally entered cellular respiration has been completely oxidized. Chemical potential energy stored within the glucose molecule has been transferred to electron carriers or has been used to synthesize a few ATPs.

The citric acid cycle is a series of redox and decarboxylation reactions that remove high-energy electrons and carbon dioxide. The electrons temporarily stored in molecules of NADH and $FADH_2$ are used to generate ATP in a subsequent pathway. One molecule of either GTP or ATP is produced by substrate-level phosphorylation on each turn of the cycle. There is no comparison of the cyclic pathway with a linear one.

Glossary

acetyl CoA

combination of an acetyl group derived from pyruvic acid and coenzyme A, which is made from pantothenic acid (a B-group vitamin)

citric acid cycle

(also, Krebs cycle) series of enzyme-catalyzed chemical reactions of central importance in all living cells

Krebs cycle

(also, citric acid cycle) alternate name for the citric acid cycle, named after Hans Krebs who first identified the steps in the pathway in the 1930s in pigeon flight muscles; see citric acid cycle

TCA cycle

(also, citric acid cycle) alternate name for the citric acid cycle, named after the group name for citric acid, tricarboxylic acid (TCA); see citric acid cycle

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12.5: Oxidative Phosphorylation

Skills to Develop

- Describe how electrons move through the electron transport chain and what happens to their energy levels
- Explain how a proton (H^+) gradient is established and maintained by the electron transport chain

You have just read about two pathways in glucose catabolism—glycolysis and the citric acid cycle—that generate ATP. Most of the ATP generated during the aerobic catabolism of glucose, however, is not generated directly from these pathways. Rather, it is derived from a process that begins with moving electrons through a series of electron transporters that undergo redox reactions. This causes hydrogen ions to accumulate within the matrix space. Therefore, a concentration gradient forms in which hydrogen ions diffuse out of the matrix space by passing through ATP synthase. The current of hydrogen ions powers the catalytic action of ATP synthase, which phosphorylates ADP, producing ATP.

Electron Transport Chain

The electron transport chain (Figure 12.5.1) is the last component of aerobic respiration and is the only part of glucose metabolism that uses atmospheric oxygen. Oxygen continuously diffuses into plants; in animals, it enters the body through the respiratory system. Electron transport is a series of redox reactions that resemble a relay race or bucket brigade in that electrons are passed rapidly from one component to the next, to the endpoint of the chain where the electrons reduce molecular oxygen, producing water. There are four complexes composed of proteins, labeled I through IV in Figure 12.5.1, and the aggregation of these four complexes, together with associated mobile, accessory electron carriers, is called the electron transport chain. The electron transport chain is present in multiple copies in the inner mitochondrial membrane of eukaryotes and the plasma membrane of prokaryotes.

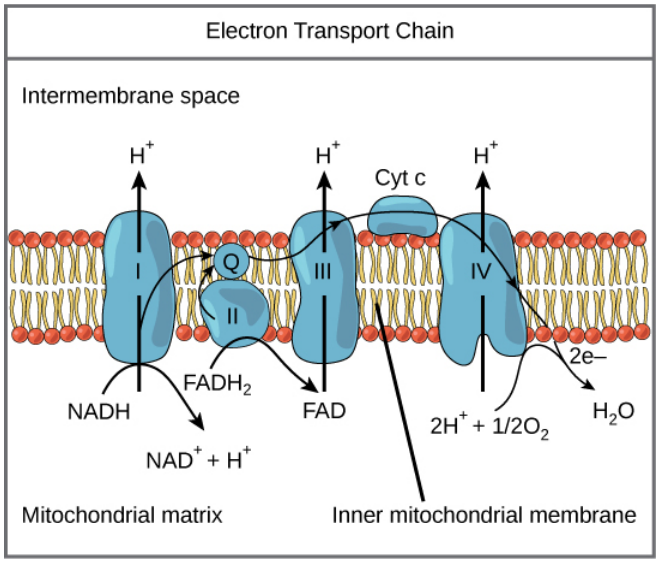


Figure 12.5.1: The electron transport chain is a series of electron transporters embedded in the inner mitochondrial membrane that shuttles electrons from NADH and $FADH_2$ to molecular oxygen. In the process, protons are pumped from the mitochondrial matrix to the intermembrane space, and oxygen is reduced to form water.

Complex I

To start, two electrons are carried to the first complex aboard NADH. This complex, labeled I, is composed of flavin mononucleotide (FMN) and an iron-sulfur (Fe-S)-containing protein. FMN, which is derived from vitamin B_2, also called riboflavin, is one of several prosthetic groups or co-factors in the electron transport chain. A prosthetic group is a non-protein molecule required for the activity of a protein. Prosthetic groups are organic or inorganic, non-peptide molecules bound to a protein that facilitate its function; prosthetic groups include co-enzymes, which are the prosthetic groups of enzymes. The enzyme in complex I is NADH dehydrogenase and is a very large protein, containing 45 amino acid chains. Complex I can pump four

hydrogen ions across the membrane from the matrix into the intermembrane space, and it is in this way that the hydrogen ion gradient is established and maintained between the two compartments separated by the inner mitochondrial membrane.

Q and Complex II

Complex II directly receives $FADH_2$, which does not pass through complex I. The compound connecting the first and second complexes to the third is ubiquinone (Q). The Q molecule is lipid soluble and freely moves through the hydrophobic core of the membrane. Once it is reduced, (QH_2), ubiquinone delivers its electrons to the next complex in the electron transport chain. Q receives the electrons derived from NADH from complex I and the electrons derived from $FADH_2$ from complex II, including succinate dehydrogenase. This enzyme and $FADH_2$ form a small complex that delivers electrons directly to the electron transport chain, bypassing the first complex. Since these electrons bypass and thus do not energize the proton pump in the first complex, fewer ATP molecules are made from the $FADH_2$ electrons. The number of ATP molecules ultimately obtained is directly proportional to the number of protons pumped across the inner mitochondrial membrane.

Complex III

The third complex is composed of cytochrome b, another Fe-S protein, Rieske center (2Fe-2S center), and cytochrome c proteins; this complex is also called cytochrome oxidoreductase. Cytochrome proteins have a prosthetic group of heme. The heme molecule is similar to the heme in hemoglobin, but it carries electrons, not oxygen. As a result, the iron ion at its core is reduced and oxidized as it passes the electrons, fluctuating between different oxidation states: Fe^{++} (reduced) and Fe^{+++} (oxidized). The heme molecules in the cytochromes have slightly different characteristics due to the effects of the different proteins binding them, giving slightly different characteristics to each complex. Complex III pumps protons through the membrane and passes its electrons to cytochrome c for transport to the fourth complex of proteins and enzymes (cytochrome c is the acceptor of electrons from Q; however, whereas Q carries pairs of electrons, cytochrome c can accept only one at a time).

Complex IV

The fourth complex is composed of cytochrome proteins c, a, and a_3. This complex contains two heme groups (one in each of the two cytochromes, a, and a_3) and three copper ions (a pair of Cu_A and one Cu_B in cytochrome a_3). The cytochromes hold an oxygen molecule very tightly between the iron and copper ions until the oxygen is completely reduced. The reduced oxygen then picks up two hydrogen ions from the surrounding medium to make water (H_2O). The removal of the hydrogen ions from the system contributes to the ion gradient used in the process of chemiosmosis.

Chemiosmosis

In chemiosmosis, the free energy from the series of redox reactions just described is used to pump hydrogen ions (protons) across the membrane. The uneven distribution of H^+ ions across the membrane establishes both concentration and electrical gradients (thus, an electrochemical gradient), owing to the hydrogen ions' positive charge and their aggregation on one side of the membrane.

If the membrane were open to diffusion by the hydrogen ions, the ions would tend to diffuse back across into the matrix, driven by their electrochemical gradient. Recall that many ions cannot diffuse through the nonpolar regions of phospholipid membranes without the aid of ion channels. Similarly, hydrogen ions in the matrix space can only pass through the inner mitochondrial membrane through an integral membrane protein called ATP synthase (Figure 12.5.2). This complex protein acts as a tiny generator, turned by the force of the hydrogen ions diffusing through it, down their electrochemical gradient. The turning of parts of this molecular machine facilitates the addition of a phosphate to ADP, forming ATP, using the potential energy of the hydrogen ion gradient.

Art Connection

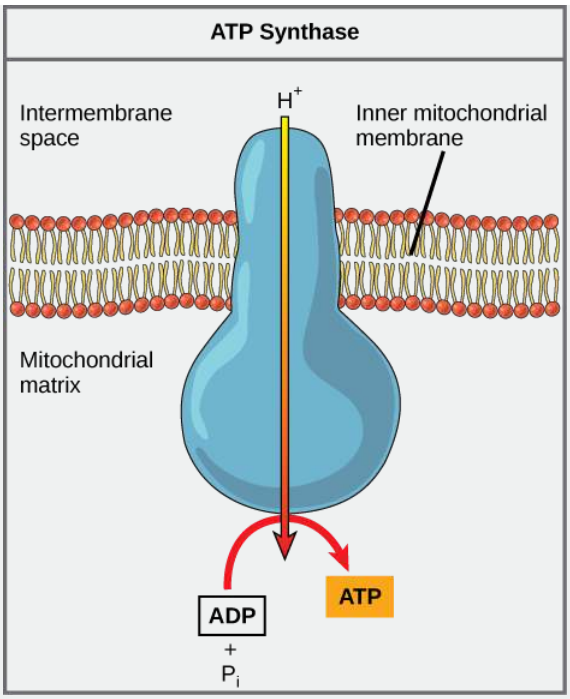


Figure 12.5.2: ATP synthase is a complex, molecular machine that uses a proton (H^+) gradient to form ATP from ADP and inorganic phosphate (Pi). (Credit: modification of work by Klaus Hoffmeier)

Dinitrophenol (DNP) is an uncoupler that makes the inner mitochondrial membrane leaky to protons. It was used until 1938 as a weight-loss drug. What effect would you expect DNP to have on the change in pH across the inner mitochondrial membrane? Why do you think this might be an effective weight-loss drug?

Chemiosmosis (Figure 12.5.3) is used to generate 90 percent of the ATP made during aerobic glucose catabolism; it is also the method used in the light reactions of photosynthesis to harness the energy of sunlight in the process of photophosphorylation. Recall that the production of ATP using the process of chemiosmosis in mitochondria is called oxidative phosphorylation. The overall result of these reactions is the production of ATP from the energy of the electrons removed from hydrogen atoms. These atoms were originally part of a glucose molecule. At the end of the pathway, the electrons are used to reduce an oxygen molecule to oxygen ions. The extra electrons on the oxygen attract hydrogen ions (protons) from the surrounding medium, and water is formed.

Art Connection

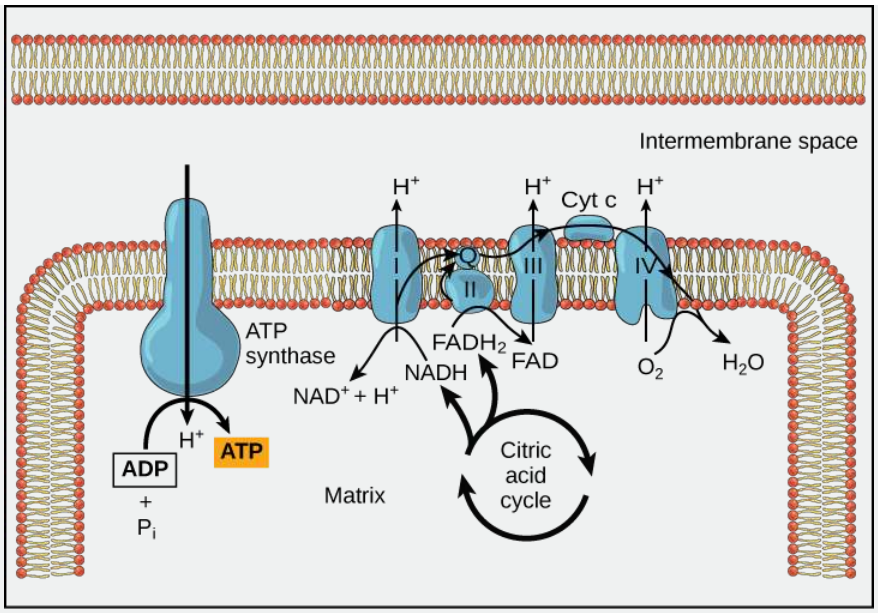


Figure 12.5.3: In oxidative phosphorylation, the pH gradient formed by the electron transport chain is used by ATP synthase to form ATP.

Cyanide inhibits cytochrome c oxidase, a component of the electron transport chain. If cyanide poisoning occurs, would you expect the pH of the intermembrane space to increase or decrease? What effect would cyanide have on ATP synthesis?

ATP Yield

The number of ATP molecules generated from the catabolism of glucose varies. For example, the number of hydrogen ions that the electron transport chain complexes can pump through the membrane varies between species. Another source of variance stems from the shuttle of electrons across the membranes of the mitochondria. (The NADH generated from glycolysis cannot easily enter mitochondria.) Thus, electrons are picked up on the inside of mitochondria by either NAD^+ or FAD^+. As you have learned earlier, these FAD^+ molecules can transport fewer ions; consequently, fewer ATP molecules are generated when FAD^+ acts as a carrier. NAD^+ is used as the electron transporter in the liver and FAD^+ acts in the brain.

Another factor that affects the yield of ATP molecules generated from glucose is the fact that intermediate compounds in these pathways are used for other purposes. Glucose catabolism connects with the pathways that build or break down all other biochemical compounds in cells, and the result is somewhat messier than the ideal situations described thus far. For example, sugars other than glucose are fed into the glycolytic pathway for energy extraction. Moreover, the five-carbon sugars that form nucleic acids are made from intermediates in glycolysis. Certain nonessential amino acids can be made from intermediates of both glycolysis and the citric acid cycle. Lipids, such as cholesterol and triglycerides, are also made from intermediates in these pathways, and both amino acids and triglycerides are broken down for energy through these pathways. Overall, in living systems, these pathways of glucose catabolism extract about 34 percent of the energy contained in glucose.

Summary

The electron transport chain is the portion of aerobic respiration that uses free oxygen as the final electron acceptor of the electrons removed from the intermediate compounds in glucose catabolism. The electron transport chain is composed of four large, multiprotein complexes embedded in the inner mitochondrial membrane and two small diffusible electron carriers shuttling electrons between them. The electrons are passed through a series of redox reactions, with a small amount of free energy used at three points to transport hydrogen ions across a membrane. This process contributes to the gradient used in chemiosmosis. The electrons passing through the electron transport chain gradually lose energy, High-energy electrons donated to the chain by either NADH or $FADH_2$ complete the chain, as low-energy electrons reduce oxygen molecules and form water. The level of free energy of the electrons drops from about 60 kcal/mol in NADH or 45 kcal/mol in $FADH_2$ to about 0 kcal/mol in water. The end products of the electron transport chain are water and ATP. A number of intermediate compounds of the citric acid cycle can be diverted into

the anabolism of other biochemical molecules, such as nonessential amino acids, sugars, and lipids. These same molecules can serve as energy sources for the glucose pathways.

Art Connections

Figure 12.5.2: Dinitrophenol (DNP) is an uncoupler that makes the inner mitochondrial membrane leaky to protons. It was used until 1938 as a weight-loss drug. What effect would you expect DNP to have on the change in pH across the inner mitochondrial membrane? Why do you think this might be an effective weight-loss drug?

Answer

After DNP poisoning, the electron transport chain can no longer form a proton gradient, and ATP synthase can no longer make ATP. DNP is an effective diet drug because it uncouples ATP synthesis; in other words, after taking it, a person obtains less energy out of the food he or she eats. Interestingly, one of the worst side effects of this drug is hyperthermia, or overheating of the body. Since ATP cannot be formed, the energy from electron transport is lost as heat.

Figure 12.5.3: Cyanide inhibits cytochrome c oxidase, a component of the electron transport chain. If cyanide poisoning occurs, would you expect the pH of the intermembrane space to increase or decrease? What effect would cyanide have on ATP synthesis?

Answer

After cyanide poisoning, the electron transport chain can no longer pump electrons into the intermembrane space. The pH of the intermembrane space would increase, the pH gradient would decrease, and ATP synthesis would stop.

Glossary

ATP synthase
(also, F1F0 ATP synthase) membrane-embedded protein complex that adds a phosphate to ADP with energy from protons diffusing through it

prosthetic group
(also, prosthetic cofactor) molecule bound to a protein that facilitates the function of the protein

ubiquinone
soluble electron transporter in the electron transport chain that connects the first or second complex to the third

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12.6: Metabolism without Oxygen

Skills to Develop

- Discuss the fundamental difference between anaerobic cellular respiration and fermentation
- Describe the type of fermentation that readily occurs in animal cells and the conditions that initiate that fermentation

In aerobic respiration, the final electron acceptor is an oxygen molecule, O_2. If aerobic respiration occurs, then ATP will be produced using the energy of high-energy electrons carried by NADH or $FADH_2$ to the electron transport chain. If aerobic respiration does not occur, NADH must be reoxidized to NAD^+ for reuse as an electron carrier for the glycolytic pathway to continue. How is this done? Some living systems use an organic molecule as the final electron acceptor. Processes that use an organic molecule to regenerate NAD^+ from NADH are collectively referred to as fermentation. In contrast, some living systems use an inorganic molecule as a final electron acceptor. Both methods are called anaerobic cellular respiration in which organisms convert energy for their use in the absence of oxygen.

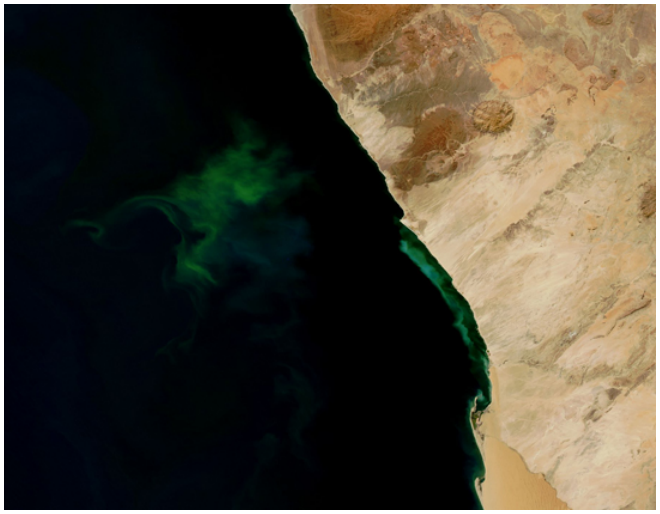


Figure 12.6.1: The green color seen in these coastal waters is from an eruption of hydrogen sulfide-producing bacteria. These anaerobic, sulfate-reducing bacteria release hydrogen sulfide gas as they decompose algae in the water. (credit: modification of work by NASA/Jeff Schmaltz, MODIS Land Rapid Response Team at NASA GSFC, Visible Earth Catalog of NASA images)

Anaerobic Cellular Respiration

Certain prokaryotes, including some species of bacteria and Archaea, use anaerobic respiration. For example, the group of Archaea called methanogens reduces carbon dioxide to methane to oxidize NADH. These microorganisms are found in soil and in the digestive tracts of ruminants, such as cows and sheep. Similarly, sulfate-reducing bacteria and Archaea, most of which are anaerobic (Figure 12.6.1), reduce sulfate to hydrogen sulfide to regenerate NAD^+ from NADH.

Link to Learning



Video 12.6.1: Watch this video to see anaerobic cellular respiration in action.

Lactic Acid Fermentation

The fermentation method used by animals and certain bacteria, like those in yogurt, is lactic acid fermentation (Figure 12.6.2). This type of fermentation is used routinely in mammalian red blood cells and in skeletal muscle that has an insufficient oxygen supply to allow aerobic respiration to continue (that is, in muscles used to the point of fatigue). In muscles, lactic acid accumulation must be removed by the blood circulation and the lactate brought to the liver for further metabolism. The chemical reactions of lactic acid fermentation are the following:

$$\text{Pyruvic acid} + \text{NADH} \leftrightarrow \text{lactic acid} + \text{NAD}^+$$

The enzyme used in this reaction is lactate dehydrogenase (LDH). The reaction can proceed in either direction, but the reaction from left to right is inhibited by acidic conditions. Such lactic acid accumulation was once believed to cause muscle stiffness, fatigue, and soreness, although more recent research disputes this hypothesis. Once the lactic acid has been removed from the muscle and circulated to the liver, it can be reconverted into pyruvic acid and further catabolized for energy.

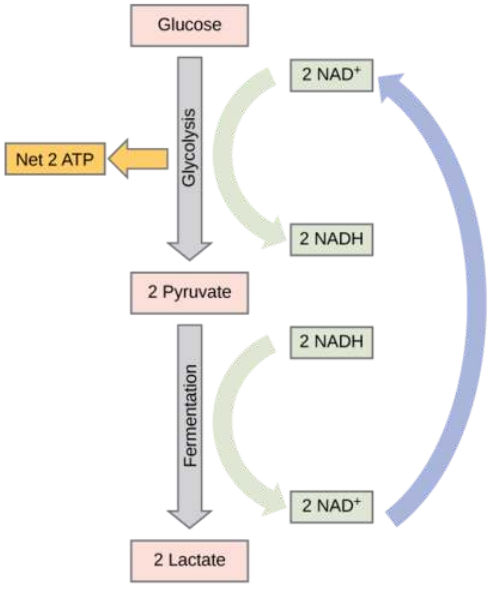


Figure 12.6.2: Lactic acid fermentation is common in muscle cells that have run out of oxygen.

Exercise 12.6.1

Tremetol, a metabolic poison found in the white snake root plant, prevents the metabolism of lactate. When cows eat this plant, it is concentrated in the milk they produce. Humans who consume the milk become ill. Symptoms of this disease, which include vomiting, abdominal pain, and tremors, become worse after exercise. Why do you think this is the case?

Answer

The illness is caused by lactate accumulation. Lactate levels rise after exercise, making the symptoms worse. Milk sickness is rare today, but was common in the Midwestern United States in the early 1800s.

Alcohol Fermentation

Another familiar fermentation process is alcohol fermentation (Figure 12.6.3) that produces ethanol, an alcohol. The first chemical reaction of alcohol fermentation is the following (CO_2 does not participate in the second reaction):

$$\text{Pyruvic acid} \rightarrow CO_2 + \text{acetaldehyde} + \text{NADH} \rightarrow \text{ethanol} + NAD^+$$

The first reaction is catalyzed by pyruvate decarboxylase, a cytoplasmic enzyme, with a coenzyme of thiamine pyrophosphate (TPP, derived from vitamin B_1 and also called thiamine). A carboxyl group is removed from pyruvic acid, releasing carbon dioxide as a gas. The loss of carbon dioxide reduces the size of the molecule by one carbon, making acetaldehyde. The second reaction is catalyzed by alcohol dehydrogenase to oxidize NADH to NAD^+ and reduce acetaldehyde to ethanol. The fermentation of pyruvic acid by yeast produces the ethanol found in alcoholic beverages. Ethanol tolerance of yeast is variable, ranging from about 5 percent to 21 percent, depending on the yeast strain and environmental conditions.



Figure 12.6.3: Fermentation of grape juice into wine produces CO_2 as a byproduct. Fermentation tanks have valves so that the pressure inside the tanks created by the carbon dioxide produced can be released.

Other Types of Fermentation

Other fermentation methods occur in bacteria. Many prokaryotes are facultatively anaerobic. This means that they can switch between aerobic respiration and fermentation, depending on the availability of oxygen. Certain prokaryotes, like *Clostridia*, are obligate anaerobes. Obligate anaerobes live and grow in the absence of molecular oxygen. Oxygen is a poison to these microorganisms and kills them on exposure. It should be noted that all forms of fermentation, except lactic acid fermentation, produce gas. The production of particular types of gas is used as an indicator of the fermentation of specific carbohydrates, which plays a role in the laboratory identification of the bacteria. Various methods of fermentation are used by assorted organisms to ensure an adequate supply of NAD^+ for the sixth step in glycolysis. Without these pathways, that step would not occur and no ATP would be harvested from the breakdown of glucose.

Summary

If NADH cannot be oxidized through aerobic respiration, another electron acceptor is used. Most organisms will use some form of fermentation to accomplish the regeneration of NAD^+, ensuring the continuation of glycolysis. The regeneration of NAD^+ in fermentation is not accompanied by ATP production; therefore, the potential of NADH to produce ATP using an electron transport chain is not utilized.

anaerobic cellular respiration

process in which organisms convert energy for their use in the absence of oxygen

fermentation

process of regenerating NAD^+ with either an inorganic or organic compound serving as the final electron acceptor, occurs in the absence; occurs in the absence of oxygen

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12.7: Connections of Carbohydrate, Protein, and Lipid Metabolic Pathways

Skills to Develop

- Discuss the ways in which carbohydrate metabolic pathways, glycolysis, and the citric acid cycle interrelate with protein and lipid metabolic pathways
- Explain why metabolic pathways are not considered closed systems

You have learned about the catabolism of glucose, which provides energy to living cells. But living things consume more than glucose for food. How does a turkey sandwich end up as ATP in your cells? This happens because all of the catabolic pathways for carbohydrates, proteins, and lipids eventually connect into glycolysis and the citric acid cycle pathways (see Figure 12.7.2). Metabolic pathways should be thought of as porous—that is, substances enter from other pathways, and intermediates leave for other pathways. These pathways are not closed systems. Many of the substrates, intermediates, and products in a particular pathway are reactants in other pathways.

Connections of Other Sugars to Glucose Metabolism

Glycogen, a polymer of glucose, is an energy storage molecule in animals. When there is adequate ATP present, excess glucose is shunted into glycogen for storage. Glycogen is made and stored in both liver and muscle. The glycogen will be hydrolyzed into glucose monomers (G-1-P) if blood sugar levels drop. The presence of glycogen as a source of glucose allows ATP to be produced for a longer period of time during exercise. Glycogen is broken down into G-1-P and converted into G-6-P in both muscle and liver cells, and this product enters the glycolytic pathway.

Sucrose is a disaccharide with a molecule of glucose and a molecule of fructose bonded together with a glycosidic linkage. Fructose is one of the three dietary monosaccharides, along with glucose and galactose (which is part of the milk sugar, the disaccharide lactose), which are absorbed directly into the bloodstream during digestion. The catabolism of both fructose and galactose produces the same number of ATP molecules as glucose.

Connections of Proteins to Glucose Metabolism

Proteins are hydrolyzed by a variety of enzymes in cells. Most of the time, the amino acids are recycled into the synthesis of new proteins. If there are excess amino acids, however, or if the body is in a state of starvation, some amino acids will be shunted into the pathways of glucose catabolism (Figure 12.7.1). Each amino acid must have its amino group removed prior to entry into these pathways. The amino group is converted into ammonia. In mammals, the liver synthesizes urea from two ammonia molecules and a carbon dioxide molecule. Thus, urea is the principal waste product in mammals produced from the nitrogen originating in amino acids, and it leaves the body in urine.

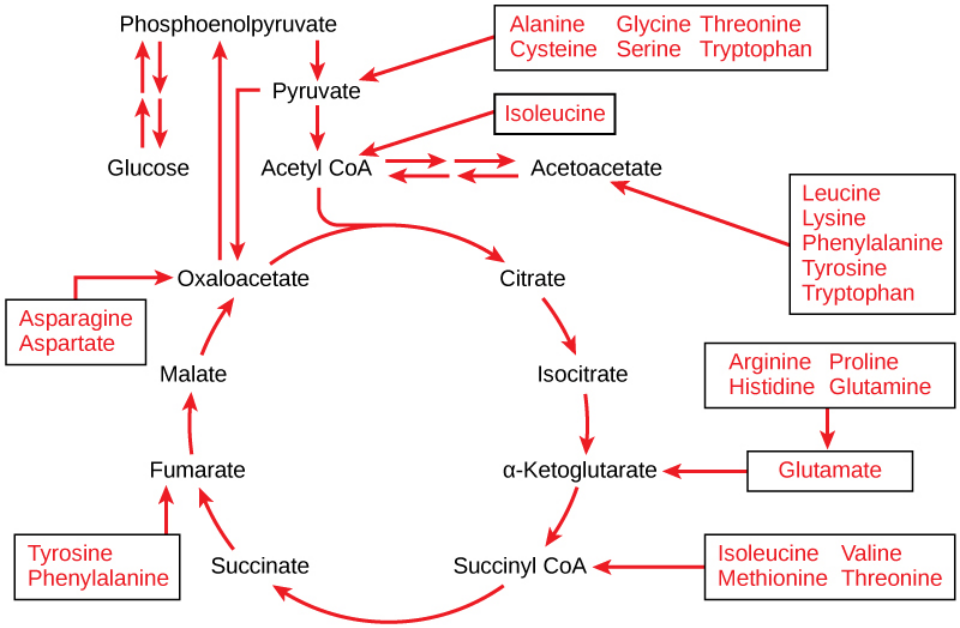


Figure 12.7.1: The carbon skeletons of certain amino acids (indicated in boxes) derived from proteins can feed into the citric acid cycle. (credit: modification of work by Mikael Häggström)

Connections of Lipid and Glucose Metabolisms

The lipids that are connected to the glucose pathways are cholesterol and triglycerides. Cholesterol is a lipid that contributes to cell membrane flexibility and is a precursor of steroid hormones. The synthesis of cholesterol starts with acetyl groups and proceeds in only one direction. The process cannot be reversed.

Triglycerides are a form of long-term energy storage in animals. Triglycerides are made of glycerol and three fatty acids. Animals can make most of the fatty acids they need. Triglycerides can be both made and broken down through parts of the glucose catabolism pathways. Glycerol can be phosphorylated to glycerol-3-phosphate, which continues through glycolysis. Fatty acids are catabolized in a process called beta-oxidation that takes place in the matrix of the mitochondria and converts their fatty acid chains into two carbon units of acetyl groups. The acetyl groups are picked up by CoA to form acetyl CoA that proceeds into the citric acid cycle.

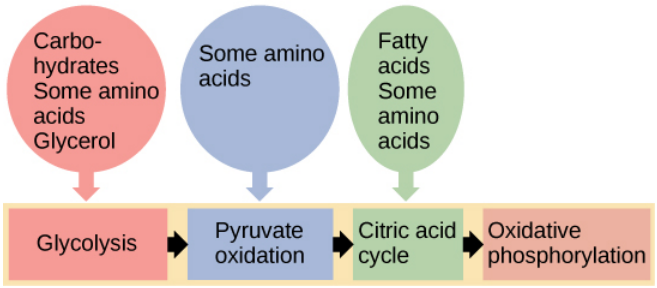


Figure 12.7.2: Glycogen from the liver and muscles, hydrolyzed into glucose-1-phosphate, together with fats and proteins, can feed into the catabolic pathways for carbohydrates.

Evolution Connection: Pathways of Photosynthesis and Cellular Metabolism

The processes of photosynthesis and cellular metabolism consist of several very complex pathways. It is generally thought that the first cells arose in an aqueous environment—a “soup” of nutrients—probably on the surface of some porous clays. If these cells reproduced successfully and their numbers climbed steadily, it follows that the cells would begin to deplete the nutrients from the medium in which they lived as they shifted the nutrients into the components of their own bodies. This hypothetical situation would have resulted in natural selection favoring those organisms that could exist by using the nutrients that remained in their environment and by manipulating these nutrients into materials upon which they could survive. Selection would favor those organisms that could extract maximal value from the nutrients to which they had access.

An early form of photosynthesis developed that harnessed the sun's energy using water as a source of hydrogen atoms, but this pathway did not produce free oxygen (anoxygenic photosynthesis). (Early photosynthesis did not produce free oxygen because it did not use water as the source of hydrogen ions; instead, it used materials like hydrogen sulfide and consequently produced sulfur). It is thought that glycolysis developed at this time and could take advantage of the simple sugars being produced, but these reactions were unable to fully extract the energy stored in the carbohydrates. The development of glycolysis probably predated the evolution of photosynthesis, as it was well suited to extract energy from materials spontaneously accumulating in the "primeval soup." A later form of photosynthesis used water as a source of electrons and hydrogen, and generated free oxygen. Over time, the atmosphere became oxygenated, but not before the oxygen released oxidized metals in the ocean and created a "rust" layer in the sediment, permitting the dating of the rise of the first oxygenic photosynthesizers. Living things adapted to exploit this new atmosphere that allowed aerobic respiration as we know it to evolve. When the full process of oxygenic photosynthesis developed and the atmosphere became oxygenated, cells were finally able to use the oxygen expelled by photosynthesis to extract considerably more energy from the sugar molecules using the citric acid cycle and oxidative phosphorylation.

Summary

The breakdown and synthesis of carbohydrates, proteins, and lipids connect with the pathways of glucose catabolism. The simple sugars are galactose, fructose, glycogen, and pentose. These are catabolized during glycolysis. The amino acids from proteins connect with glucose catabolism through pyruvate, acetyl CoA, and components of the citric acid cycle. Cholesterol synthesis starts with acetyl groups, and the components of triglycerides come from glycerol-3-phosphate from glycolysis and acetyl groups produced in the mitochondria from pyruvate.

Contributors and Attributions

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12.8: Regulation of Cellular Respiration

Skills to Develop

- Describe how feedback inhibition would affect the production of an intermediate or product in a pathway
- Identify the mechanism that controls the rate of the transport of electrons through the electron transport chain

Cellular respiration must be regulated in order to provide balanced amounts of energy in the form of ATP. The cell also must generate a number of intermediate compounds that are used in the anabolism and catabolism of macromolecules. Without controls, metabolic reactions would quickly come to a stand still as the forward and backward reactions reached a state of equilibrium. Resources would be used inappropriately. A cell does not need the maximum amount of ATP that it can make all the time: At times, the cell needs to shunt some of the intermediates to pathways for amino acid, protein, glycogen, lipid, and nucleic acid production. In short, the cell needs to control its metabolism.

Regulatory Mechanisms

A variety of mechanisms is used to control cellular respiration. Some type of control exists at each stage of glucose metabolism. Access of glucose to the cell can be regulated using the GLUT proteins that transport glucose (Figure 12.8.1). Different forms of the GLUT protein control passage of glucose into the cells of specific tissues.

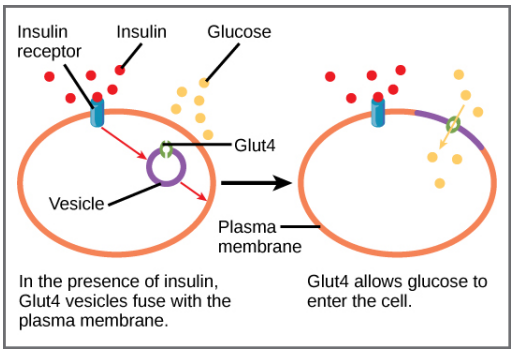


Figure 12.8.1: GLUT4 is a glucose transporter that is stored in vesicles. A cascade of events that occurs upon insulin binding to a receptor in the plasma membrane causes GLUT4-containing vesicles to fuse with the plasma membrane so that glucose may be transported into the cell.

Some reactions are controlled by having two different enzymes—one each for the two directions of a reversible reaction. Reactions that are catalyzed by only one enzyme can go to equilibrium, stalling the reaction. In contrast, if two different enzymes (each specific for a given direction) are necessary for a reversible reaction, the opportunity to control the rate of the reaction increases, and equilibrium is not reached.

A number of enzymes involved in each of the pathways—in particular, the enzyme catalyzing the first committed reaction of the pathway—are controlled by attachment of a molecule to an allosteric site on the protein. The molecules most commonly used in this capacity are the nucleotides ATP, ADP, AMP, NAD^+, and NADH. These regulators, allosteric effectors, may increase or decrease enzyme activity, depending on the prevailing conditions. The allosteric effector alters the steric structure of the enzyme, usually affecting the configuration of the active site. This alteration of the protein's (the enzyme's) structure either increases or decreases its affinity for its substrate, with the effect of increasing or decreasing the rate of the reaction. The attachment signals to the enzyme. This binding can increase or decrease the enzyme's activity, providing feedback. This feedback type of control is effective as long as the chemical affecting it is attached to the enzyme. Once the overall concentration of the chemical decreases, it will diffuse away from the protein, and the control is relaxed.

Control of Catabolic Pathways

Enzymes, proteins, electron carriers, and pumps that play roles in glycolysis, the citric acid cycle, and the electron transport chain tend to catalyze non-reversible reactions. In other words, if the initial reaction takes place, the pathway is committed to proceeding with the remaining reactions. Whether a particular enzyme activity is released depends upon the energy needs of the cell (as reflected by the levels of ATP, ADP, and AMP).

Glycolysis

The control of glycolysis begins with the first enzyme in the pathway, hexokinase (Figure 12.8.2). This enzyme catalyzes the phosphorylation of glucose, which helps to prepare the compound for cleavage in a later step. The presence of the negatively charged phosphate in the molecule also prevents the sugar from leaving the cell. When hexokinase is inhibited, glucose diffuses out of the cell and does not become a substrate for the respiration pathways in that tissue. The product of the hexokinase reaction is glucose-6-phosphate, which accumulates when a later enzyme, phosphofructokinase, is inhibited.

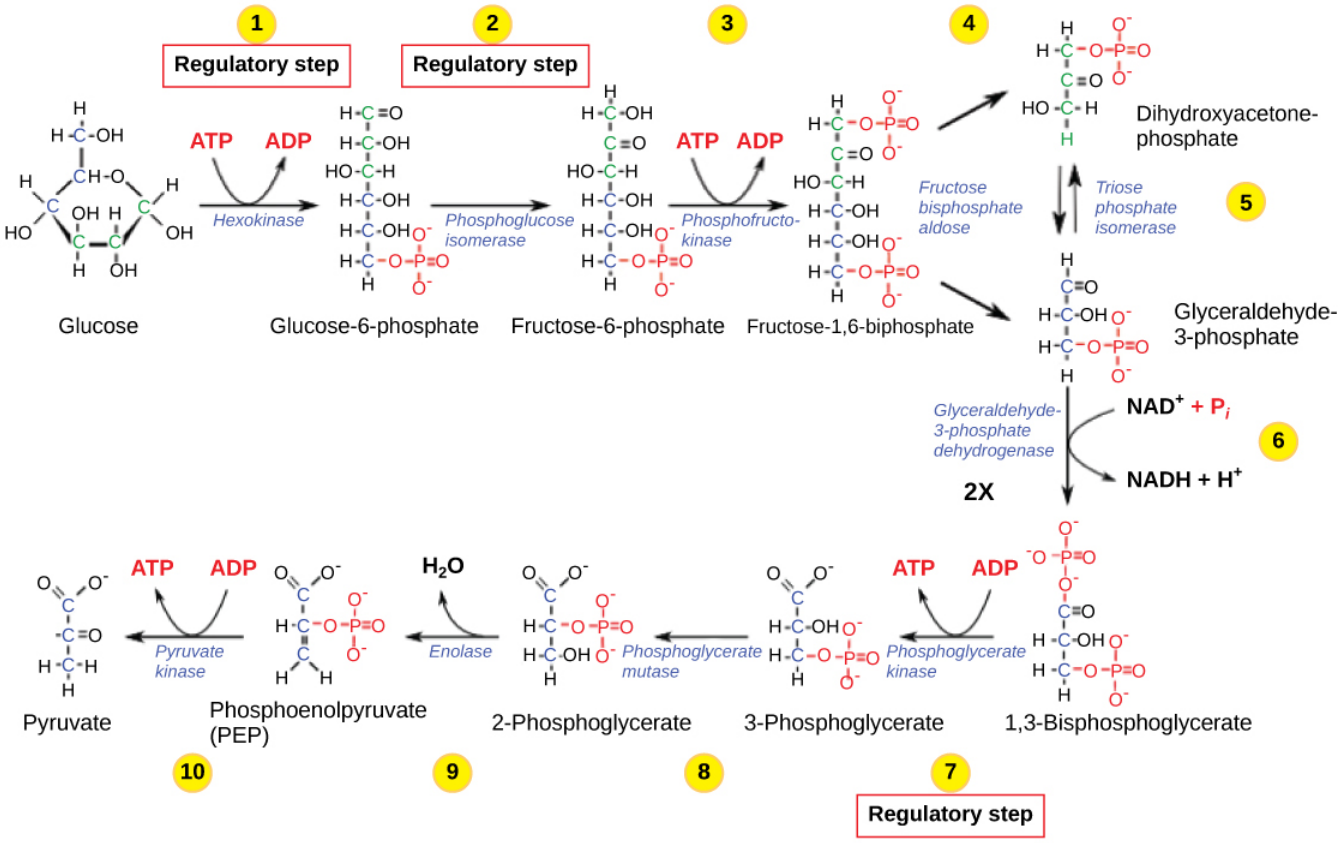


Figure 12.8.2: The glycolysis pathway is primarily regulated at the three key enzymatic steps (1, 2, and 7) as indicated. Note that the first two steps that are regulated occur early in the pathway and involve hydrolysis of ATP.

Phosphofructokinase is the main enzyme controlled in glycolysis. High levels of ATP, citrate, or a lower, more acidic pH decrease the enzyme's activity. An increase in citrate concentration can occur because of a blockage in the citric acid cycle. Fermentation, with its production of organic acids like lactic acid, frequently accounts for the increased acidity in a cell; however, the products of fermentation do not typically accumulate in cells.

The last step in glycolysis is catalyzed by pyruvate kinase. The pyruvate produced can proceed to be catabolized or converted into the amino acid alanine. If no more energy is needed and alanine is in adequate supply, the enzyme is inhibited. The enzyme's activity is increased when fructose-1,6-bisphosphate levels increase. (Recall that fructose-1,6-bisphosphate is an intermediate in the first half of glycolysis.) The regulation of pyruvate kinase involves phosphorylation by a kinase (pyruvate kinase kinase), resulting in a less-active enzyme. Dephosphorylation by a phosphatase reactivates it. Pyruvate kinase is also regulated by ATP (a negative allosteric effect).

If more energy is needed, more pyruvate will be converted into acetyl CoA through the action of pyruvate dehydrogenase. If either acetyl groups or NADH accumulate, there is less need for the reaction and the rate decreases. Pyruvate dehydrogenase is also regulated by phosphorylation: A kinase phosphorylates it to form an inactive enzyme, and a phosphatase reactivates it. The kinase and the phosphatase are also regulated.

Citric Acid Cycle

The citric acid cycle is controlled through the enzymes that catalyze the reactions that make the first two molecules of NADH. These enzymes are isocitrate dehydrogenase and α-ketoglutarate dehydrogenase. When adequate ATP and NADH levels are available, the rates of these reactions decrease. When more ATP is needed, as reflected in rising ADP levels, the rate increases. α-Ketoglutarate dehydrogenase will also be affected by the levels of succinyl CoA—a subsequent intermediate in the cycle—causing a decrease in activity. A decrease in the rate of operation of the pathway at this point is not necessarily negative, as the increased levels of the α-ketoglutarate not used by the citric acid cycle can be used by the cell for amino acid (glutamate) synthesis.

Electron Transport Chain

Specific enzymes of the electron transport chain are unaffected by feedback inhibition, but the rate of electron transport through the pathway is affected by the levels of ADP and ATP. Greater ATP consumption by a cell is indicated by a buildup of ADP. As ATP usage decreases, the concentration of ADP decreases, and now, ATP begins to build up in the cell. This change is the relative concentration of ADP to ATP triggers the cell to slow down the electron transport chain.

Link to Learning



Visit this site to see an animation of the electron transport chain and ATP synthesis.

For a summary of feedback controls in cellular respiration, see Table 12.8.1.

Table 12.8.1: Feedback Controls in Cellular Respiration.

Pathway	Enzyme affected	Elevated levels of effector	Effect on pathway activity
glycolysis	hexokinase	glucose-6-phosphate	decrease
	phosphofructokinase	low-energy charge (ATP, AMP), fructose-6-phosphate via fructose-2,6-bisphosphate	increase
		high-energy charge (ATP, AMP), citrate, acidic pH	decrease
	pyruvate kinase	fructose-1,6-bisphosphate	increase
		high-energy charge (ATP, AMP), alanine	decrease
pyruvate to acetyl CoA conversion	pyruvate dehydrogenase	ADP, pyruvate	increase
		acetyl CoA, ATP, NADH	decrease
citric acid cycle	isocitrate dehydrogenase	ADP	increase
		ATP, NADH	decrease
	α-ketoglutarate dehydrogenase	Calcium ions, ADP	increase
		ATP, NADH, succinyl CoA	decrease
electron transport chain		ADP	increase
		ATP	decrease

Summary

Cellular respiration is controlled by a variety of means. The entry of glucose into a cell is controlled by the transport proteins that aid glucose passage through the cell membrane. Most of the control of the respiration processes is accomplished through the control of specific enzymes in the pathways. This is a type of negative feedback, turning the enzymes off. The enzymes respond most often to the levels of the available nucleosides ATP, ADP, AMP, NAD^+, and FAD. Other intermediates of the pathway also affect certain enzymes in the systems.

Glossary

GLUT protein

integral membrane protein that transports glucose

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12.E: Cellular Respiration (Exercises)

7.1: Energy in Living Systems

Energy production within a cell involves many coordinated chemical pathways. Most of these pathways are combinations of oxidation and reduction reactions. Oxidation and reduction occur in tandem. An oxidation reaction strips an electron from an atom in a compound, and the addition of this electron to another compound is a reduction reaction. Because oxidation and reduction usually occur together, these pairs of reactions are called oxidation reduction reactions, or redox reactions.

Review Questions

The energy currency used by cells is _____.

A. ATP
B. ADP
C. AMP
D. adenosine

Answer

A

A reducing chemical reaction _____.

A. reduces the compound to a simpler form
B. adds an electron to the substrate
C. removes a hydrogen atom from the substrate
D. is a catabolic reaction

Answer

B

Free Response

Why is it beneficial for cells to use ATP rather than energy directly from the bonds of carbohydrates? What are the greatest drawbacks to harnessing energy directly from the bonds of several different compounds?

Answer

ATP provides the cell with a way to handle energy in an efficient manner. The molecule can be charged, stored, and used as needed. Moreover, the energy from hydrolyzing ATP is delivered as a consistent amount. Harvesting energy from the bonds of several different compounds would result in energy deliveries of different quantities.

7.2: Glycolysis

Glycolysis is the first step in the breakdown of glucose to extract energy for cellular metabolism. Nearly all living organisms carry out glycolysis as part of their metabolism. The process does not use oxygen and is therefore anaerobic. Glycolysis takes place in the cytoplasm of both prokaryotic and eukaryotic cells.

Review Questions

During the second half of glycolysis, what occurs?

A. ATP is used up.
B. Fructose is split in two.
C. ATP is made.

D. Glucose becomes fructose.

Answer

C

Free Response

Nearly all organisms on earth carry out some form of glycolysis. How does that fact support or not support the assertion that glycolysis is one of the oldest metabolic pathways?

Answer

If glycolysis evolved relatively late, it likely would not be as universal in organisms as it is. It probably evolved in very primitive organisms and persisted, with the addition of other pathways of carbohydrate metabolism that evolved later.

Red blood cells do not perform aerobic respiration, but they do perform glycolysis. Why do all cells need an energy source, and what would happen if glycolysis were blocked in a red blood cell?

Answer

All cells must consume energy to carry out basic functions, such as pumping ions across membranes. A red blood cell would lose its membrane potential if glycolysis were blocked, and it would eventually die.

7.3: Oxidation of Pyruvate and the Citric Acid Cycle

If oxygen is available, aerobic respiration will go forward. In eukaryotic cells, the pyruvate molecules produced at the end of glycolysis are transported into mitochondria, which are the sites of cellular respiration. There, pyruvate will be transformed into an acetyl group that will be picked up and activated by a carrier compound called coenzyme A (CoA). The resulting compound is called acetyl CoA. CoA is made from vitamin B5, pantothenic acid.

Review Questions

What is removed from pyruvate during its conversion into an acetyl group?

A. oxygen
B. ATP
C. B vitamin
D. carbon dioxide

Answer

D

What do the electrons added to NAD^+ do?

A. They become part of a fermentation pathway.
B. They go to another pathway for ATP production.
C. They energize the entry of the acetyl group into the citric acid cycle.
D. They are converted to NADP.

Answer

B

GTP or ATP is produced during the conversion of _____.

A. isocitrate into α-ketoglutarate
B. succinyl CoA into succinate
C. fumarate into malate
D. malate into oxaloacetate

Answer

B

How many NADH molecules are produced on each turn of the citric acid cycle?

A. one
B. two
C. three
D. four

Answer

C

Free Response

What is the primary difference between a circular pathway and a linear pathway?

Answer

In a circular pathway, the final product of the reaction is also the initial reactant. The pathway is self-perpetuating, as long as any of the intermediates of the pathway are supplied. Circular pathways are able to accommodate multiple entry and exit points, thus being particularly well suited for amphibolic pathways. In a linear pathway, one trip through the pathway completes the pathway, and a second trip would be an independent event.

7.4: Oxidative Phosphorylation

You have just read about two pathways in glucose catabolism—glycolysis and the citric acid cycle—that generate ATP. Most of the ATP generated during the aerobic catabolism of glucose, however, is not generated directly from these pathways. Rather, it is derived from a process that begins with moving electrons through a series of electron transporters that undergo redox reactions. This causes hydrogen ions to accumulate within the matrix space.

Review Questions

What compound receives electrons from NADH?

A. FMN
B. ubiquinone
C. cytochrome c_1
D. oxygen

Answer

A

Chemiosmosis involves _____.

A. the movement of electrons across the cell membrane
B. the movement of hydrogen atoms across a mitochondrial membrane
C. the movement of hydrogen ions across a mitochondrial membrane
D. the movement of glucose through the cell membrane

Answer

C

Free Response

How do the roles of ubiquinone and cytochrome c differ from the other components of the electron transport chain?

Answer

Q and cytochrome c are transport molecules. Their function does not result directly in ATP synthesis in that they are not pumps. Moreover, Q is the only component of the electron transport chain that is not a protein. Ubiquinone and cytochrome c are small, mobile, electron carriers, whereas the other components of the electron transport chain are large complexes anchored in the inner mitochondrial membrane.

What accounts for the different number of ATP molecules that are formed through cellular respiration?

Answer

Few tissues except muscle produce the maximum possible amount of ATP from nutrients. The intermediates are used to produce needed amino acids, fatty acids, cholesterol, and sugars for nucleic acids. When NADH is transported from the cytoplasm to the mitochondria, an active transport mechanism is used, which decreases the amount of ATP that can be made. The electron transport chain differs in composition between species, so different organisms will make different amounts of ATP using their electron transport chains.

7.5: Metabolism without Oxygen

In aerobic respiration, the final electron acceptor is an oxygen molecule, O2. If aerobic respiration occurs, then ATP will be produced using the energy of high-energy electrons carried by NADH or FADH2 to the electron transport chain. If aerobic respiration does not occur, NADH must be reoxidized to NAD+ for reuse as an electron carrier for the glycolytic pathway to continue.

Review Questions

Which of the following fermentation methods can occur in animal skeletal muscles?

A. lactic acid fermentation
B. alcohol fermentation
C. mixed acid fermentation
D. propionic fermentation

Answer

A

Free Response

What is the primary difference between fermentation and anaerobic respiration?

Answer

Fermentation uses glycolysis only. Anaerobic respiration uses all three parts of cellular respiration, including the parts in the mitochondria like the citric acid cycle and electron transport; it also uses a different final electron acceptor instead of oxygen gas.

7.6: Connections of Carbohydrate, Protein, and Lipid Metabolic Pathways

All of the catabolic pathways for carbohydrates, proteins, and lipids eventually connect into glycolysis and the citric acid cycle pathways. Metabolic pathways should be thought of as porous—that is, substances enter from other pathways, and intermediates leave for other pathways. These pathways are not closed systems. Many of the substrates, intermediates, and products in a particular pathway are reactants in other pathways.

Review Questions

A major connection for sugars in glycolysis is _____.

A. glucose-6-phosphate
B. fructose-1,6-bisphosphate
C. dihydroxyacetone phosphate
D. phosphoenolpyruvate

Answer

A

Beta-oxidation is _____.

A. the breakdown of sugars
B. the assembly of sugars
C. the breakdown of fatty acids
D. the removal of amino groups from amino acids

Answer

C

Free Response

Would you describe metabolic pathways as inherently wasteful or inherently economical, and why?

Answer

They are very economical. The substrates, intermediates, and products move between pathways and do so in response to finely tuned feedback inhibition loops that keep metabolism balanced overall. Intermediates in one pathway may occur in another, and they can move from one pathway to another fluidly in response to the needs of the cell.

7.7: Regulation of Cellular Respiration

Cellular respiration must be regulated in order to provide balanced amounts of energy in the form of ATP. The cell also must generate a number of intermediate compounds that are used in the anabolism and catabolism of macromolecules. Without controls, metabolic reactions would quickly come to a stand still as the forward and backward reactions reached a state of equilibrium. Resources would be used inappropriately.

Review Questions

The effect of high levels of ADP is to _____.

A. increase the activity of the enzyme
B. decrease the activity of the enzyme
C. have no effect on the activity of the enzyme
D. slow down the pathway

Answer

A

The control of which enzyme exerts the most control on glycolysis?

A. hexokinase
B. phosphofructokinase
C. glucose-6-phosphatase
D. aldolase

Answer

B

Free Response

How does citrate from the citric acid cycle affect glycolysis?

Answer

Citrate can inhibit phosphofructokinase by feedback regulation.

Why might negative feedback mechanisms be more common than positive feedback mechanisms in living cells?

Answer

Negative feedback mechanisms actually control a process; it can turn it off, whereas positive feedback accelerates the process, allowing the cell no control over it. Negative feedback naturally maintains homeostasis, whereas positive feedback drives the system away from equilibrium.

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CHAPTER OVERVIEW

13: DNA and Protein Synthesis

13.1: DNA and RNA

13.2: Protein Synthesis

13.3: Genetic Code

13.4: Mutations

13.5: Regulation of Gene Expression

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13.1: DNA AND RNA

WHAT MAKES YOU...YOU?

This person has naturally red hair. Why is this hair red instead of some other color? And, in general, what causes specific traits to occur? There is a molecule in human beings and most other living things that is largely responsible for their traits. The molecule is large and has a spiral structure in eukaryotes. What molecule is it? With these hints, you probably know that the molecule is DNA.



Figure **13.1.1**: Red hair

INTRODUCING DNA

Today, it is commonly known that DNA is the genetic material that is passed from parents to offspring and determines our traits. For a long time, scientists knew such molecules existed, that is, they were aware that genetic information is contained within biochemical molecules. However, they didn't know which molecules play this role. In fact, for many decades, scientists thought that proteins were the molecules that contain genetic information.

DISCOVERY THAT DNA IS THE GENETIC MATERIAL

Determining that DNA is the genetic material was an important milestone in biology. It took many scientists undertaking creative experiments over several decades to show with certainty that DNA is the molecule that determines the traits of organisms. This research began in the early part of the 20th century.

GRIFFITH'S EXPERIMENTS WITH MICE

The first important discovery was made in the 1920s. An American scientist named Frederick Griffith was studying mice and two different strains of a bacterium called R (rough) strain and S (smooth) strain. He injected the two bacterial strains into mice. The S strain was virulent and killed the mice, whereas the R strain was not virulent and did not kill the mice. You can see these details in Figure **13.1.2**. Griffith also injected mice with S-strain bacteria that had been killed by heat. As expected, the dead bacteria did not harm the mice. However, when the dead S-strain bacteria were mixed with live R-strain bacteria and injected, the mice died.

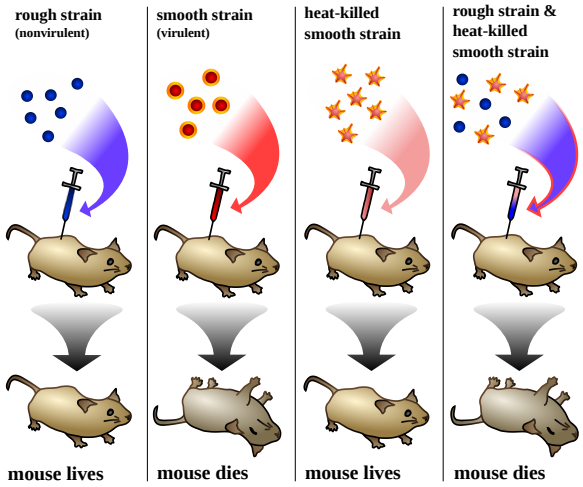


Figure **13.1.2**: Griffith's experiment discovering a "transforming principle" in heat-killed virulent smooth *pneumococcus* that enables the transformation of rough non-virulent rough pneumococcal bacteria.

Based on his observations, Griffith deduced that something in the dead S-strain was transferred to the previously harmless R-strain, making the R-strain deadly. What was this "something?" What type of substance could change the characteristics of the organism that received it?

AVERY AND HIS COLLEAGUES MAKE A MAJOR CONTRIBUTION

In the early 1940s, a team of scientists led by Oswald Avery tried to answer the question raised by Griffith's research results. First, they inactivated various substances in the S-strain bacteria. Then they killed the S-strain bacteria and mixed the remains with live R-strain bacteria. (Keep in mind that the R-strain bacteria normally did not harm the mice.) When they inactivated proteins, the R-strain was deadly to the injected mice. This ruled out proteins as genetic material. Why? Even without the S-strain proteins, the R-strain was changed or transformed into a deadly strain. However, when the researchers inactivated DNA in the S-strain, the R-strain remained harmless. This led to the conclusion that DNA — and not protein — is the substance that controls the characteristics of organisms. In other words, DNA is the genetic material.

HERSHEY AND CHASE CONFIRM THE RESULTS

The conclusion that DNA is the genetic material was not widely accepted until it was confirmed by additional research. In the 1950s, Alfred Hershey and Martha Chase did experiments with viruses and bacteria. Viruses are not cells. Instead, they are basically DNA (or RNA) inside a protein coat. To reproduce, a virus must insert its own genetic material into a cell (such as a bacterium). Then it uses the cell's machinery to make more viruses. The researchers used different radioactive elements to label the DNA and proteins in DNA viruses. This allowed them to identify which molecule the viruses

inserted into bacterial cells. DNA was the molecule they identified. This confirmed that DNA is the genetic material.

CHARGAFF FOCUSES ON DNA BASES

Erwin Chargaff (1905-2002), an Austrian-American biochemist from Columbia University, analyzed the base composition of the DNA of various species. This led him to propose two main rules that have been appropriately named **Chargaff's rules**.

RULE 1

Chargaff determined that in DNA, the amount of one base, a purine, always approximately equals the amount of a particular second base, a pyrimidine. Specifically, in any double-stranded DNA, the number of guanine units equals approximately the number of cytosine units and the number of adenine units equals approximately the number of thymine units.

Human DNA is 30.9% A and 29.4% T, 19.9% G and 19.8% C. The rule constitutes the basis of **base pairs** in the DNA double helix: A always pairs with T, and G always pairs with C. He also demonstrated that the number of purines (A+G) always approximates the number of pyrimidines (T+C), an obvious consequence of the base-pairing nature of the DNA double helix.

RULE 2

In 1947 Chargaff showed that the composition of DNA, in terms of the relative amounts of the A, C, G, and T bases, varied from one species to another. This molecular diversity added to the evidence that DNA could be the genetic material.

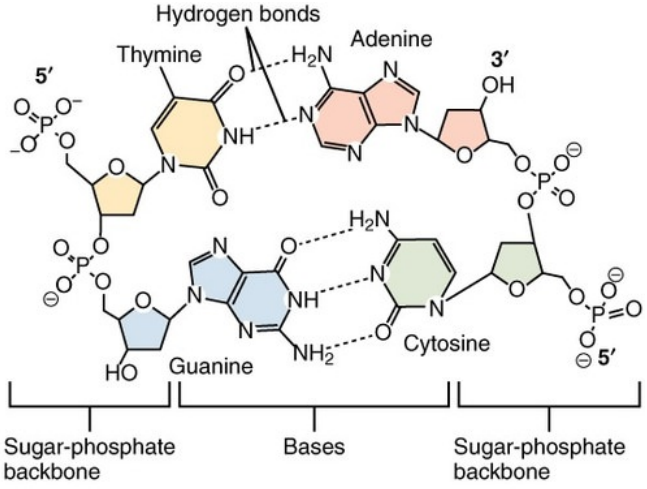


Figure **13.1.3**: Chemical structure of the four nitrogenous bases in the two strands of DNA. Notice how the purines (A and G) are composed of two ring structures, whereas the pyrimidines (T and C) are composed of one ring structure. The DNA of all species has the same four nitrogen bases. The figure also illustrates that Adenine pairs with Thymine and Guanine pairs with cytosine.

DISCOVERY OF THE DOUBLE HELIX

After DNA was shown to be the genetic material, scientists wanted to learn more about it, including its structure. James Watson and Francis Crick are usually given credit for discovering that DNA has a double-helix shape like a spiral staircase, as shown in Figure **13.1.4**. In fact, Watson and Crick's discovery of the double helix depended heavily on the prior work of Rosalind Franklin and other scientists, who had used X-rays to learn more about DNA's structure. Unfortunately, Franklin and these other scientists have not usually been given credit for their important contributions to the discovery of the double helix.

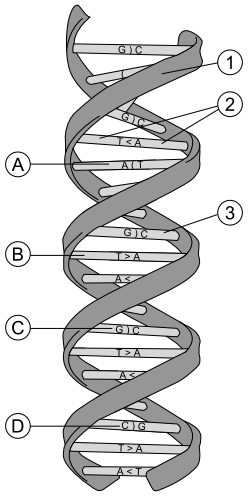


Figure **13.1.4**: Double helix structure of DNA resembles a twisted staircase. In this image A. Adenine B. Thymine C. Guanine D. Cytosine 1. Sugar, Phosphate, Backbone 2. Base pair 3. Nitrogenous base. This image also shows the application of 2 rules of Chargaff.

The double-helix shape of DNA, together with Chargaff's rules, led to a better understanding of DNA. As a nucleic acid, DNA is made from nucleotide monomers. Long chains of nucleotides form polynucleotides, and the DNA double helix consists of two polynucleotide chains. Each nucleotide consists of a sugar (deoxyribose), a phosphate group, and one of the four bases (adenine, cytosine, guanine, or thymine). The sugar and phosphate molecules in adjacent nucleotides bond together and form the "backbone" of each polynucleotide chain.

Scientists concluded that bonds between the bases hold together the two polynucleotide chains of DNA. Moreover, adenine always bonds with thymine, and cytosine always bonds with guanine. That's why these pairs of bases are called **complementary base pairs.** If you look at the nitrogen bases in Figure **13.1.3**, you will see why the bases bond together only in these pairings. Adenine and guanine have a two-ring structure, whereas cytosine and thymine have just one ring. If adenine were to bond with guanine as well as thymine, for example, the distance between the two DNA chains would be variable. However, when a one-ring molecule (such as thymine) always bonds with a two-ring molecule (such as adenine), the distance between the two chains remains constant. This maintains the uniform shape of the DNA double helix. The bonded base pairs (A-T and G-C) stick into the middle of the double helix, forming, in essence, the steps of the spiral staircase.

DNA REPLICATION

Knowledge of DNA's structure helped scientists understand how DNA replicates. **DNA replication** is the process in which DNA is copied. It occurs during the synthesis (S) phase of the eukaryotic cell

cycle. DNA must be copied so that, after cell division occurs, each daughter cell will have a complete set of chromosomes.

DNA replication begins when an enzyme breaks the bonds between complementary bases in the molecule. This exposes the bases inside the molecule so they can be “read” by another enzyme and used to build two new DNA strands with complementary bases. The two daughter molecules that result each contain one strand from the parent molecule and one new strand that is complementary to it. As a result, the two daughter molecules are both identical to the parent molecule. This is a semi-conservative process (see Figure **13.1.5**.)

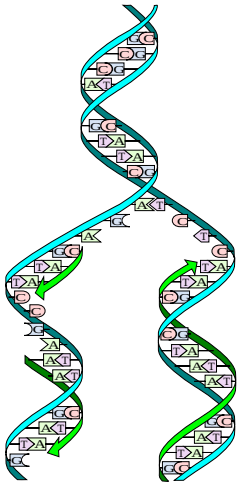


Figure **13.1.5**: DNA Replication. DNA replication is a semi-conservative process. Half of the parent DNA molecule is conserved in each of the two daughter DNA molecules. The blue strand belongs to the parent cell, and the green DNA strand represents a brand new DNA strand.

HELICASE AND POLYMERASE

DNA replication begins as an enzyme, **DNA helicase**, breaks the hydrogen bonds holding the two strands together and forms a **replication fork** (see Figure **13.1.6**. The resulting structure has two branching strands of DNA backbone with exposed bases. These exposed bases allow the DNA to be “read” by another enzyme, **DNA polymerase**, which then builds the complementary DNA strand. As DNA helicase continues to open the double helix, the replication fork grows.

LEADING AND LAGGING STRANDS

Two DNA polymerase enzymes work at a Replication fork. This enzyme can only build new DNA in the 5' → 3' direction. It also needs a **primer** built by **primase** to start building DNA. Therefore, the two new strands, the l**eading strand** and the **lagging strand**, of DNA are “built” in opposite directions. The leading strand is the DNA strand that DNA polymerase constructs in the 5' → 3' direction. This strand of DNA is made in a continuous manner, moving as the replication fork grows. The "lagging” strand is synthesized in short segments known as **Okazaki fragments**. On the lagging strand, **primase** builds a short RNA primer. DNA polymerase is then able to use the free 3'-OH group on the RNA primer to make DNA in the 5' → 3' direction till it reaches to end of the template strand. DNA polymerase of the lagging strand then jumps to go further into the replication fork to make another Okazaki fragment. The RNA fragments are then degraded and new DNA nucleotides are added to fill the gaps where the RNA was present. Another enzyme, **DNA ligase**, is then able to attach (ligate) the DNA nucleotides together, completing the synthesis of the lagging strand (Figure **13.1.6**).

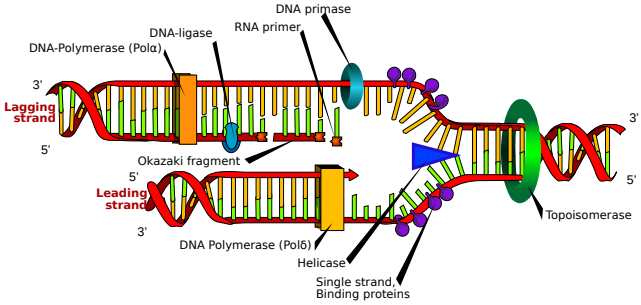


Figure **13.1.6**: DNA replication. The two DNA strands are opened by helicase. The strands are held open by a single strand of binding proteins, preventing premature reannealing. Topoisomerase solves the problem caused by the tension generated by the winding/unwinding of DNA. This enzyme wraps around DNA and makes a cut permitting the helix to spin and relax. Once DNA is relaxed, topoisomerase reconnects broken strands. DNA primase synthesizes a short RNA primer that initiates the Okazaki fragment and leading strand. DNA polymerase synthesizes the leading strand and Okazaki fragments. Okazaki fragments are attached by DNA ligase after the primers are removed.

WHAT IS RNA?

RNA structure differs from the DNA structure in three specific ways. Both are nucleic acids and made out of **nucleotides**; however, RNA is single-stranded while DNA is double-stranded. RNA nucleotides, like those from DNA, have three parts: a 5-carbon sugar, a phosphate group, and a base. RNA contains the 5-carbon sugar **ribose**, whereas, in DNA, the sugar is **deoxyribose**. The difference between ribose and deoxyribose is the lack of a hydroxyl group attached to the pentose ring in the 2' position of deoxyribose (see figure Figure **13.1.7**.

Table **13.1.1**: comparison of RNA and DNA

	RNA	DNA
Strands	single stranded	double stranded
Specific Base	contains uracil	contains thymine
Sugar	ribose	deoxyribose
Size	relatively small	big (chromosomes)
Location	moves to cytoplasm	stays in nucleus
Types	3 types: mRNA, tRNA, rRNA	generally 1 type

Though both RNA and DNA contain the nitrogenous bases adenine, guanine, and cytosine, RNA contains the nitrogenous base **uracil** instead of thymine. Uracil pairs with adenine in RNA, just as thymine pairs with adenine in DNA. Uracil and thymine have very similar structures; uracil is an unmethylated form of thymine.

The nucleotide sequence of RNA, which is complementary to the DNA sequence, allows RNA to encode genetic information. RNA

though carries the genetic information of just one gene. Hence, compared to DNA, RNA molecules are relatively small.

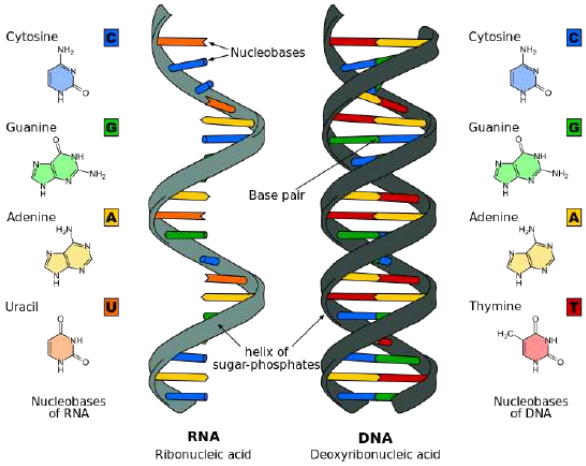


Figure **13.1.7**. Comparison of a single-stranded RNA and a double-stranded DNA with their corresponding nucleobases. Also, refer to Table **13.1.1** as your read this image.

REVIEW

1. Outline the discoveries that led to the determination that DNA, and not protein, is the biochemical molecule that contains genetic information.
2. State Chargaff's rules. Explain how the rules are related to the structure of the DNA molecule.
3. Explain how the structure of a DNA molecule is like a spiral staircase. Which parts of the staircase represent the various parts of the molecule?
4. Describe the process of DNA replication.
5. When does DNA replication occur, and why is the process said to be semi-conservative?
6. Why do you think dead S strain bacteria injected into mice does not harm the mice but kills them when mixed with living (and normally harmless) R strain bacteria?
7. In Griffith's experiment, do you think the heat treatment that killed the bacteria also inactivated the bacterial DNA? Why or why not?
8. Give one example of a specific piece of evidence that helped rule out proteins as the genetic material.
9. *True or False.* Two-ring bases always bind to each other.
10. *True or False.* DNA replication involves the breaking of one of the polynucleotide chains into individual nucleotides.
11. *True or False.* In DNA, each nucleotide has a sugar.
12. What would the complementary strand of this stretch of DNA bases be? GTTAC
13. Which scientists detected labeled DNA that was transferred from one organism to another?

    A. Hershey and Chase
    B. Chargaff
    C. Avery
    D. Griffith

14. Which enzyme break the bonds between complementary bases and add new complementary nucleotides to the parental strands during DNA replication?

    A. Phosphates
    B. Enzymes
    C. Viruses
    D. RNA molecules

15. Describe the differences between DNA and RNA.
16. How is DNA replicated? Why is DNA replication called a "semi-conservative" process?
17. What are the roles of the following enzymes?

    A. DNA polymerase
    B. DNA helicase
    C. DNA ligase
    D. primase

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13.2: PROTEIN SYNTHESIS

THE CENTRAL DOGMA OF BIOLOGY

Your **DNA**, or deoxyribonucleic acid, contains the genes that determine who you are. How can this organic molecule control your characteristics? DNA contains instructions for all the proteins your body makes. **Proteins**, in turn, determine the structure and function of all your cells. What determines a **protein**'s structure? It begins with the sequence of **amino acids** that make up the protein. Instructions for making proteins with the correct sequence of amino acids are encoded in DNA.



Figure **13.2.1**: Transcription and translation (Protein synthesis) in a cell.

DNA is found in chromosomes. In eukaryotic cells, chromosomes always remain in the nucleus, but proteins are made at ribosomes in the cytoplasm or on the rough endoplasmic reticulum (RER). How do the instructions in DNA get to the site of protein synthesis outside the nucleus? Another type of nucleic acid is responsible. This nucleic acid is **RNA** or ribonucleic acid. RNA is a small molecule that can squeeze through pores in the nuclear membrane. It carries the information from DNA in the nucleus to a ribosome in the cytoplasm and then helps assemble the protein. In short:

DNA → RNA → Protein

Discovering this sequence of events was a major milestone in molecular biology. It is called the **central dogma of biology**. The two processes involved in the central dogma are **transcription** and **translation.**

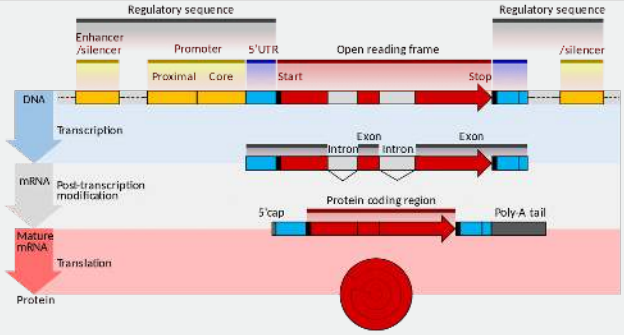


Figure **13.2.2**: An overview of transcription and translation. The top panel shows a gene. A gene is composed of the open reading frame (aka coding sequence) that is flanked by regulatory sequences. At the beginning of the gene, the regulatory sequence contains a promoter where RNA polymerase attaches and starts transcription. At the end of the open reading frame, the regulatory sequence contains a terminator (not shown.)The middle panel shows a pre mRNA which is modified by excising introns and keeping exons. This is called post transcription modification. A mature mRNA contains a 5' cap and poly-A tail. The bottom panel shows a synthesis of protein via translation.

TRANSCRIPTION

Transcription is the first part of the central dogma of molecular biology: **DNA → RNA**. It is the transfer of genetic instructions in DNA to mRNA. Transcription happens in the nucleus of the cell. During transcription, a strand of mRNA is made that is complementary to a strand of DNA called a gene. A gene can easily be identified from the DNA sequence. A gene contains the basic three regions, promoter, coding sequence (reading frame), and terminator. There are more parts of a gene which are illustrated in Figure **13.2.3**.

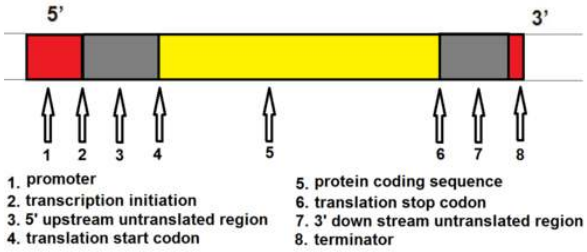


Figure **13.2.3**: The major components of a gene. 1. promoter, 2. transcription initiation, 3. 5' upstream untranslated region, 4. translation start codon site, 5. protein-coding sequence, 6. translation stop codon region, 7. 3' downstream untranslated region, and 8. terminator.

STEPS OF TRANSCRIPTION

Transcription takes place in three steps, called initiation, elongation, and termination. The steps are illustrated in Figure **13.2.4**.

1. Initiation is the beginning of transcription. It occurs when the enzyme RNA polymerase binds to a region of a gene called the **promoter**. This signals the DNA to unwind so the enzyme can "read" the bases in one of the DNA strands. The enzyme is ready

to make a strand of mRNA with a complementary sequence of bases. The promoter is not part of the resulting mRNA

2. Elongation is the addition of nucleotides to the mRNA strand.
3. Termination is the ending of transcription. As RNA polymerase transcribes the terminator, it detaches from DNA. The mRNA strand is complete after this step.

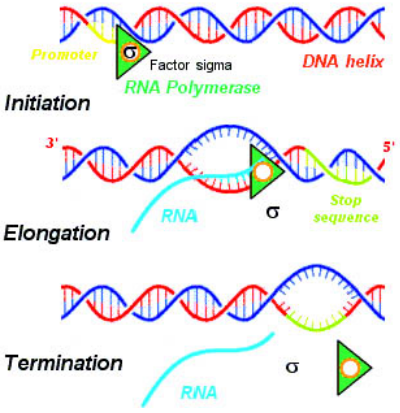


Figure **13.2.4**: Transcription occurs in the three steps - initiation, elongation, and termination

PROCESSING MRNA

In eukaryotes, the new mRNA is not yet ready for translation. At this stage, it is called pre-mRNA, and it must go through more processing before it leaves the nucleus as mature mRNA. The processing may include the addition of a 5' cap, splicing, editing, and 3' polyadenylation (poly-A) tail. These processes modify the mRNA in various ways. Such modifications allow a single gene to be used to make more than one protein. See Figure **13.2.5** as you read below:

- 5' cap protects mRNA in the cytoplasm and helps in the attachment of mRNA with the ribosome for translation.
- Splicing removes introns from the protein-coding sequence of mRNA. **Introns** are regions that do not code for the protein. The remaining mRNA consists only of regions called **exons** that do code for the protein.
- Editing changes some of the nucleotides in mRNA. For example, a human protein called APOB, which helps transport lipids in the blood, has two different forms because of editing. One form is smaller than the other because editing adds an earlier stop signal in mRNA.
- Polyadenylation adds a “tail” to the mRNA. The tail consists of a string of As (adenine bases). It signals the end of mRNA. It is also involved in exporting mRNA from the nucleus, and it protects mRNA from enzymes that might break it down.

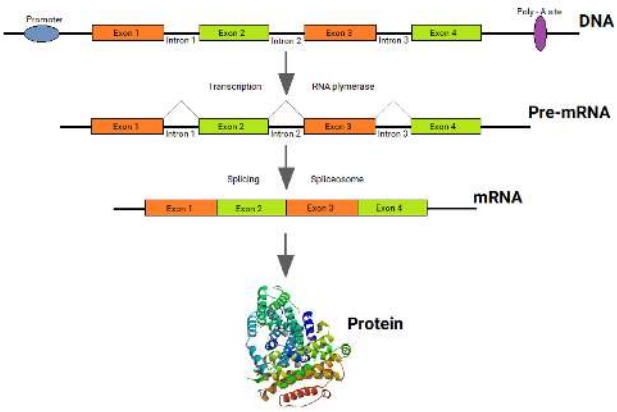


Figure **13.2.5**: Splicing removes introns from mRNA. Mature mRNA is translated to protein.

TRANSLATION

The translation is the second part of the central dogma of molecular biology: **RNA --> Protein**. It is the process in which the genetic code in mRNA is read to make a protein. The translation is illustrated in Figure **13.2.6**. After mRNA leaves the nucleus, it moves to a ribosome, which consists of rRNA and proteins. Translation happens on the ribosomes floating in the cytosol, or on the ribosomes attached to the rough endoplasmic reticulum. The ribosome reads the sequence of codons in mRNA, and molecules of tRNA bring amino acids to the ribosome in the correct sequence.

To understand the role of tRNA, you need to know more about its structure. Each tRNA molecule has an anticodon for the amino acid it carries. An **anticodon** is complementary to the codon for an amino acid. For example, the amino acid lysine has the codon AAG, so the anticodon is UUC. Therefore, lysine would be carried by a tRNA molecule with the anticodon UUC. Wherever the codon AAG appears in mRNA, a UUC anticodon of tRNA temporarily binds. While bound to mRNA, tRNA gives up its amino acid. With the help of rRNA, bonds form between the amino acids as they are brought one by one to the ribosome, creating a polypeptide chain. The chain of amino acids keeps growing until a stop codon is reached.

Ribosomes, which are just made out of rRNA (ribosomal RNA) and protein, have been classified as ribozymes because the rRNA has enzymatic activity. The rRNA is important for the peptidyl transferase activity that bonds amino acids. Ribosomes have two subunits of rRNA and protein. The large subunit has three active sites called E, P, and A sites. These sites are important in the catalytic activity of ribosomes.

Just as with mRNA synthesis, protein synthesis can be divided into three phases: initiation, elongation, and termination. In addition to the mRNA template, many other molecules contribute to the process of translation, such as ribosomes, tRNAs, and various enzymatic factors

Translation Initiation: The small subunit binds to a site upstream (on the 5' side) of the start of the mRNA. It proceeds to scan the mRNA in the 5'-->3' direction until it encounters the START codon

(AUG). The large subunit attaches and the initiator tRNA, which carries methionine (Met), binds to the P site on the ribosome.

Translation Elongation: The ribosome shifts one codon at a time, catalyzing each process that occurs in the three sites. With each step, a charged tRNA enters the complex, the polypeptide becomes one amino acid longer, and an uncharged tRNA departs. The energy for each bond between amino acids is derived from GTP, a molecule similar to ATP. Briefly, the ribosomes interact with other RNA molecules to make chains of amino acids called polypeptide chains, due to the peptide bond that forms between individual amino acids. Inside the ribosome, three sites participate in the translation process, the A, P, and E sites. Amazingly, the E. coli translation apparatus takes only 0.05 seconds to add each amino acid, meaning that a 200-amino acid polypeptide could be translated in just 10 seconds.

Translation Termination: Termination of translation occurs when a stop codon (UAA, UAG, or UGA) is encountered (see Figure **13.2.7**. When the ribosome encounters the stop codon, the growing polypeptide is released with the help of various releasing factors and the ribosome subunits dissociate and leave the mRNA. After many ribosomes have completed translation, the mRNA is degraded so the nucleotides can be reused in another transcription reaction.

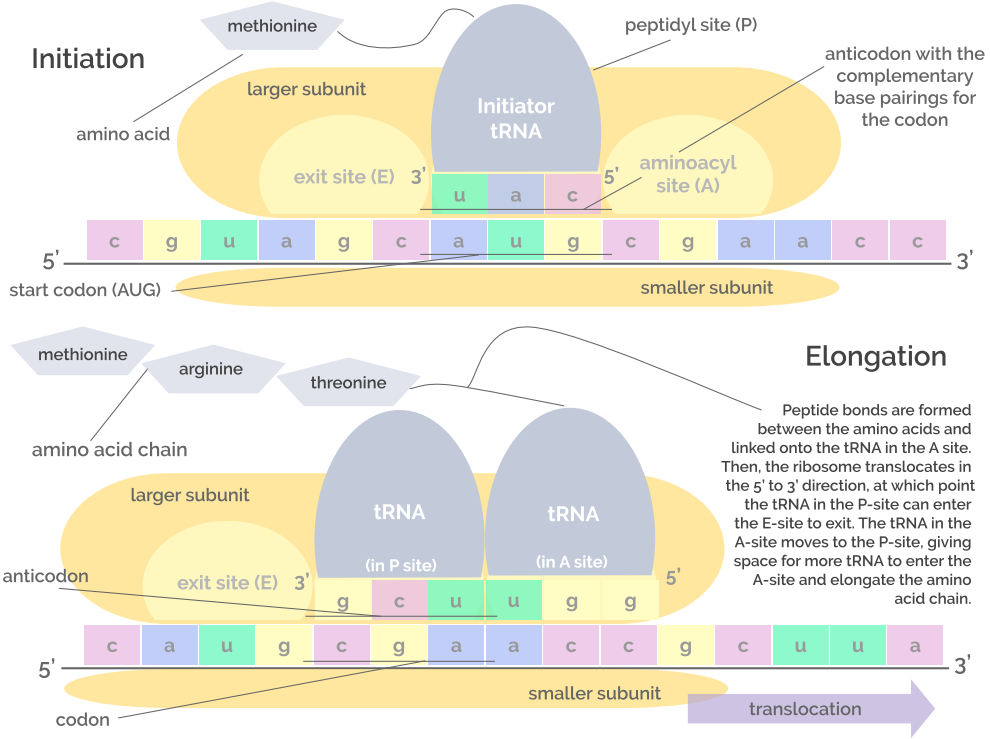


Figure **13.2.6**: At the initiation phase, the initiator tRNA carrying methionine with its anticodon encounters the AUG start codon at the P-site of the ribosome. During elongation, the ribosome translocates in the 5' to 3' direction of the mRNA, at which point the amino acids of tRNA in P-site and amino acid of tRNA in the A-site of the large subunit bond to each other via a peptide bond. This repeated movement of the ribosome creates a long amino acid chain based on the codons in the mRNA. As the ribosome translocates, the tRNA leaves the ribosome through the E-site, while new tRNA enters the A-site in order to continue elongating the amino acid chain.

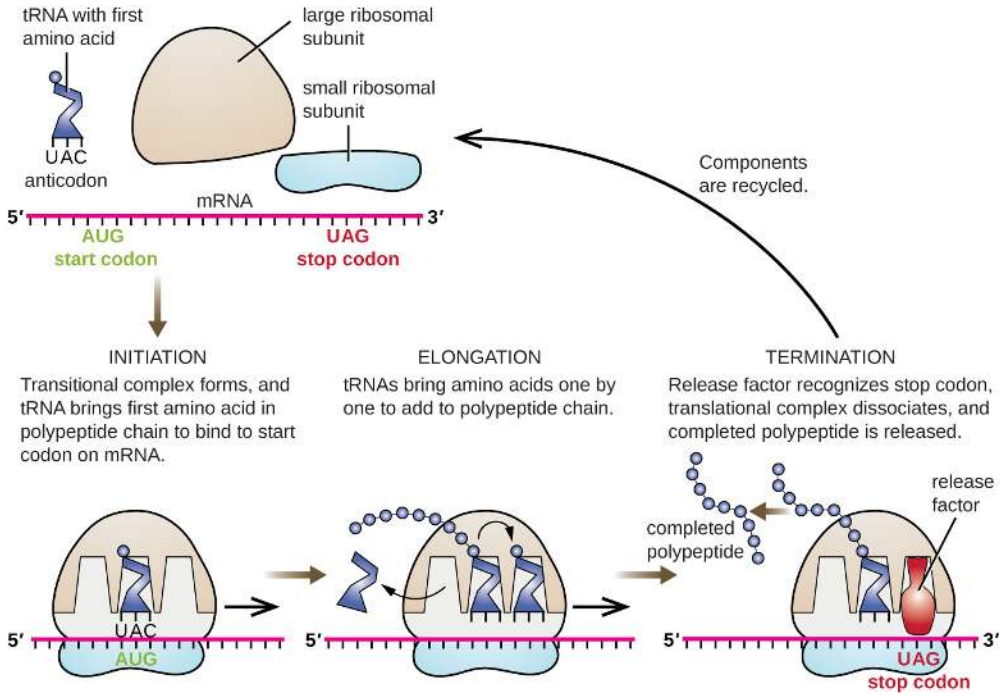


Figure **13.2.7**. Summary of protein translation. During initiation, both ribosomal subunits, mRNA, and initiator tRNA come together. The initiator anticodon of initiator tRNA hydrogen bond with the start codon. During elongation, tRNA brings amino acids one by one to add to the polypeptide chain. During termination, the release factor recognizes stop codon, all components dissociate, and the completed polypeptide is released.

WHAT HAPPENS NEXT?

After a polypeptide chain is synthesized, it may undergo additional processes. For example, it may assume a folded tertiary shape due to interactions among its amino acids. It may also bind with other polypeptides or with different types of molecules, such as lipids or carbohydrates. Many proteins travel to the Golgi apparatus within the cytoplasm to be modified for the specific job they will do.

SUMMARY OF CENTRAL DOGMA

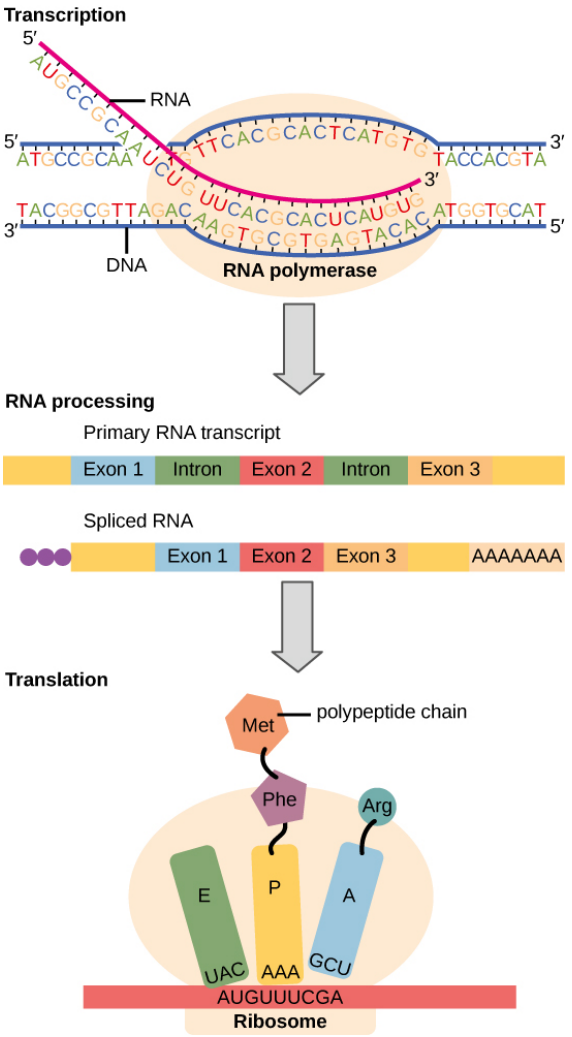


Figure **13.2.8**: The central dogma: Instructions on DNA are transcribed onto messenger RNA. Ribosomes are able to read the genetic information inscribed on a strand of messenger RNA and use this information to string amino acids together into a protein.

REVIEW

1. Relate protein synthesis and its two major phases to the central dogma of molecular biology.
2. Identify the steps of transcription, and summarize what happens during each step.
3. Explain how mRNA is processed before it leaves the nucleus.
4. Describe what happens during the translation phase of protein synthesis.
5. What additional processes may a polypeptide chain undergo after it is synthesized?
6. Where does transcription take place in eukaryotes?
7. Where does translation take place?
8. Which type of RNA (mRNA, rRNA, or tRNA) best fits each of the statements below? Choose only one type for each.
   A. Contains the codons
   B. Contains the anticodons
   C. Makes up the ribosome, along with proteins
9. If the DNA has a triplet code of CAG in one strand (the strand used as a template for transcription),
   A. What is the complementary sequence on the other DNA strand?
   B. What is the complementary sequence in the mRNA? What is this sequence called?
   C. @hat is the resulting sequence in the tRNA? What is this sequence called? What do you notice about this sequence compared to the original DNA triplet on the template strand?
10. The promoter is a region located in the:
    A. DNA
    B. mRNA
    C. tRNA
    D. Both A and B
11. *True or False.* Introns in mRNA bind to tRNA at the ribosome.
12. *True or False.* tRNAs can be thought of as the link between amino acids and codons in the mRNA.

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13.3: GENETIC CODE

CAN YOU CODE?

If someone asks you whether you can code, you probably assume they are referring to computer code. The image in Figure **13.3.1** represents an important code that you use all the time but not with a computer. It's the genetic code, and it is used by your cells to store information and make proteins.



Figure **13.3.1**: FACIL genetic code logo

WHAT IS THE GENETIC CODE?

The **genetic code** consists of the sequence of nitrogen bases in a polynucleotide chain of DNA or RNA. The bases are adenine (A), cytosine (C), guanine (G), and thymine (T) (or uracil, U, in RNA). The four bases make up the "letters" of the genetic code. The letters are combined in groups of three to form code "words," called **codons**. Each codon stands for (encodes) one amino acid unless it codes for a start or stop signal. There are 20 common amino acids in proteins. With four bases forming three-base codons, there are 64 possible codons. 61 codons are more than enough to code for the 20 amino acids, thus more than one codon codes for a single amino acid. Please find genetic codes in Table **13.3.1** or in appendix 1.

Table **13.3.1**: Codon Chart. To find the amino acid for a particular codon, find the cell in the table for the first, second, and third bases of the codon. Once you have found the codon, you can find the corresponding amino acid in the adjacent cell on the right side of the codon cell. For example CUG codes for leucine (Leu), AAG codes for lysine (Lys), and GGG codes for glycine (Gly). Text only version of the codon chart.

	Second base U	Amino acid	Second base C	Amino acid	Second base A	Amino acid	Second base G	Amino acid	
First base U	UUU	Phe	UCU	Ser	UAU	Tyr	UGU	Cys	Third base U
First base U	UUC	Phe	UCC	Ser	UAC	Tyr	UGC	Cys	Third base C
First base U	UUA	Leu	UCA	Ser	UAA	(stop) no amino acid	UGA	(stop) no amino acid	Third base A
First base U	UUA	Leu	UCG	Ser	UAG	(stop) no amino acid	UGG	Trp	Third base G
First base C	CUU	Leu	CCU	Pro	CAU	His	CGU	Arg	Third base U
First base C	CUC	Leu	CCC	Pro	CAC	His	CGC	Arg	Third base C
First base C	CUA	Leu	CCA	Pro	CAA	Gln	CGA	Arg	Third base A
First base C	CUG	Leu	CCG	Pro	CAG	Gln	CGG	Arg	Third base G
First base A	AUU	Ile	ACU	Thr	AAU	Asn	AGU	Ser	Third base U
First base A	AUC	Ile	ACC	Thr	AAC	Asn	AGC	Ser	Third base C
First base A	AUA	Ile	ACA	Thr	AAA	Lys	AGA	Arg	Third base A
First base A	AUG	Met (start)	ACG	Thr	AAG	Lys	AGG	Arg	Third base G
First base G	GUU	Val	GCU	Ala	GAU	Asp	GGU	Gly	Third base U
First base G	GUC	Val	GCC	Ala	GAC	Asp	GGC	Gly	Third base C
First base G	GUA	Val	GCA	Ala	GAA	Glu	GGA	Gly	Third base A
First base G	GUG	Val	GCG	Ala	GAG	Glu	GGG	Gly	Third base G

READING THE GENETIC CODE

If you find the codon AUG in Table **13.3.1**, you will see that it codes for the amino acid methionine. This codon is also the start codon that establishes the **reading frame** of the code. The reading frame is the way the bases are divided into codons. It is illustrated in Figure **13.3.2**. After the AUG start codon (not shown in the image), the next three bases are read as the second codon. The next three bases after that are read as the third codon, and so on. The sequence of bases is read, codon by codon, until a stop codon is reached. UAG, UGA, and UAA are all the stop codons. They do not code for any amino acids.

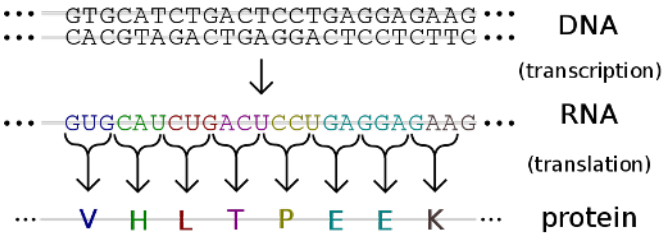


Figure **13.3.2**: Reading the Genetic Code. The genetic code is read three bases at a time. Codons are the code words of the genetic code.

CHARACTERISTICS OF THE GENETIC CODE

The genetic code has a number of important characteristics:

- The genetic code is universal. All known living things have the same genetic code. This shows that all organisms share a common evolutionary history.

- The genetic code is unambiguous. This means that each codon codes for just one amino acid (or start or stop). This is necessary so there is no question about which amino acid is the correct one.
- The genetic code is redundant. This means that each amino acid is encoded by more than one codon. For example, in the table above, four codons code for the amino acid threonine. Redundancy in the code helps prevent errors in protein synthesis. If a base in codon changes by accident, there is a good chance that it will still code for the same amino acid.

REVIEW

1. Describe the genetic code.
2. Explain how the genetic code is read.
3. Identify three important characteristics of the genetic code.
4. Summarize how the genetic code was deciphered.
5. Use the table entitled *The Genetic Code*, shown above, to answer the following questions.
   A. Is the code depicted in the table from DNA or RNA? Explain your reasoning.
   B. Which amino acid does the codon CAA code for?
   C. Does UGA code for an amino acid? Why or why not? If so, which one?
   D. Look at the codons that code for the amino acid glycine. How many of them are there? What are their similarities and differences from each other?
   E. Imagine that you are doing an experiment similar to the one performed by Nirenberg and Matthaei with 20 test tubes, each containing bacterial cell contents and all 20 amino acids, with one type of amino acid labeled in each tube. If you added synthetic RNA containing only the base cytosine, a polypeptide chain consisting of which amino acid would be produced? Explain your answer.
6. *True or False.* One codon can encode for more than one amino acid.
7. *True or False.* The codons for tyrosine in plants are the same as ones that encode for tyrosine humans.
8. *True or False.* The start codon encodes for an amino acid, in addition to its function establishing where the reading frame starts.
9. How many possible codons are there?
   A. 64
   B. 20
   C. 3
   D. It depends on the species
10. How many common amino acids are there in proteins?
    A. 64
    B. 20
    C. 3
    D. 4

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13.4: MUTATIONS

SUPERHERO

Can a mutation really turn a person into a superhero? Of course not, but mutations can sometimes result in drastic changes in living things.



Figure **13.4.1**: Superhero

WHAT ARE MUTATIONS?

Mutations are random changes in the sequence of bases in DNA. The word *mutation* may make you think of Ninja Turtles, but that's a misrepresentation of how most mutations work. First of all, everyone has mutations. In fact, most people have dozens or even hundreds of mutations in their DNA. Secondly, from an evolutionary perspective, mutations are essential. They are needed for evolution to occur because they are the ultimate source of all new genetic variation in any species.

CAUSES OF MUTATIONS

Is it possible for mutations to occur spontaneously, or does there have to be a cause of the mutation? Well, the answer is that both are possible. Mutagenesis is a process by which the genetic information of an organism is changed in a stable manner, resulting in a mutation. In nature, mutagenesis can lead to changes that are beneficial or harmful or have no effect. Harmful mutations can lead to cancer and various heritable diseases, but beneficial mutations are the driving force of evolution. In 1927, Hermann Muller first demonstrated the effects of mutations with observable changes in chromosomes. He induced mutagenesis by irradiating fruit flies with X-rays,

Mutagenesis may occur spontaneously or be induced. A spontaneous mutation can just happen. These mutations are not caused by an environmental factor but occur during normal cellular processes. A spontaneous mutation may be due to a mistake during DNA replication. Mutations may also occur during mitosis and meiosis. A mutation caused by an environmental factor, or mutagen, is known as an induced mutation. Typical mutagens include chemicals, like those inhaled while smoking, and radiation, such as X-rays, ultraviolet light, and nuclear radiation. Different mutagens have different modes of damaging DNA. For example, UV radiation may cause bonding between the adjacent nucleotides on one strand of DNA molecule (Figure **13.4.2**). This prohibits normal bonding between complementary nucleotides of the opposing strand. This causes a bulge in the DNA double helix. If this damage is not repaired, it leads to mutation. Thus, DNA does not replicate, transcribe, and translate properly.

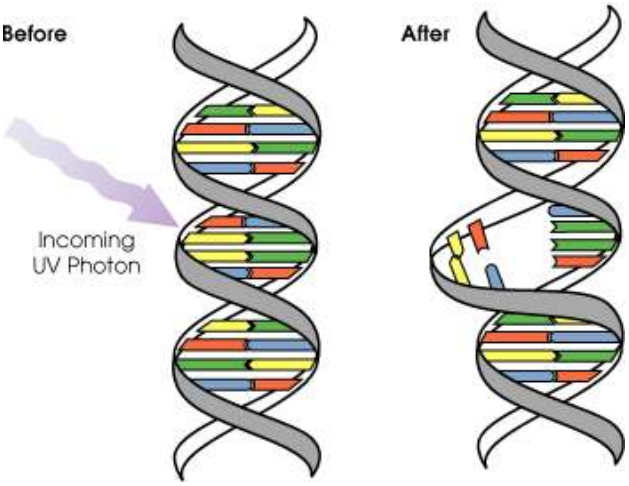


Figure **13.4.2**: Ultraviolet (UV) photons harm the DNA molecules of living organisms in different ways. In one common damage event, adjacent bases bond with each other, instead of across the “ladder.” This makes a bulge, and the distorted DNA molecule does not function properly.

TYPES OF MUTATIONS

There are a variety of types of mutations. Two major categories of mutations are germline mutations and somatic mutations.

- **Germline mutations** occur in gametes, the sex cells, such as eggs and sperm. These mutations are especially significant because they can be transmitted to offspring and every cell in the offspring will have the mutations.
- **Somatic mutations** occur in other cells of the body. These mutations may have little effect on the organism because they are confined to just one cell and its daughter cells. Somatic mutations also cannot be passed on to offspring.

Mutations also differ in the way that the genetic material is changed. Mutations may change an entire chromosome or just one or a few nucleotides.

CHROMOSOMAL ALTERATIONS

Chromosomal alterations are mutations that change chromosome structure or number. They occur when a section of a chromosome breaks off and rejoins incorrectly or does not rejoin at all. Possible ways these mutations can occur are illustrated in Figure **13.4.3**. Chromosomal alterations are very serious. They often result in the death of the organism in which they occur. If the organism survives, it may be affected in multiple ways. An example of a human chromosomal alteration is the mutation that causes Down Syndrome. It is a duplication mutation that leads to developmental delays and other abnormalities. It occurs when the individual inherits an extra copy of chromosome 21. It is also called trisomy ("three-chromosome") 21.

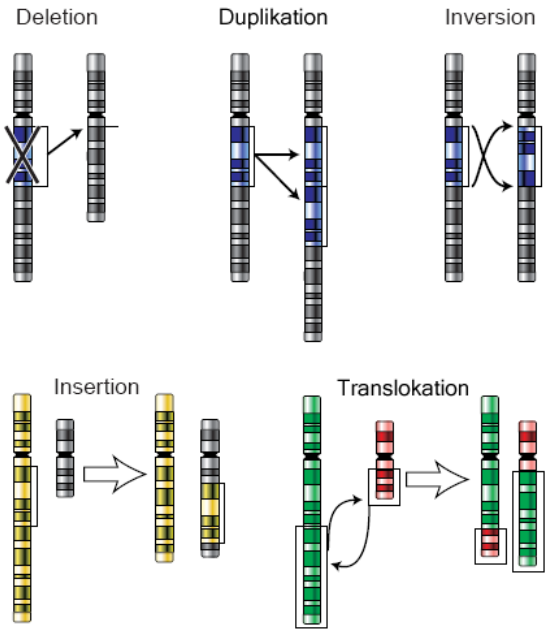


Figure **13.4.3**: Chromosomal Alterations. The chromosomal alterations may occur due to deletion or duplication of genes in a chromosome, inversion of a section of a chromosome, insertion of genes from one chromosome to another, or exchanges of genes between two chromosomes.

A **point mutation** is a change in a single nucleotide in DNA. This type of mutation is usually less serious than a chromosomal alteration. An example of a point mutation is a mutation that changes the codon UUU to the codon UCU. Point mutations can be silent, missense, or nonsense mutations, as shown in Table **13.4.1**. The effects of point mutations depend on how they change the genetic code.

Table **13.4.1**: Point Mutation Types

Type	Description	Example	Effect
Silent	mutated codon codes for the same amino acid	CAA (glutamine) → CAG (glutamine)	none
Missense	mutated codon codes for a different amino acid	CAA (glutamine) → CCA (proline)	variable
Nonsense	a mutated codon is a premature stop codon	CAA (glutamine) → UAA (stop) usually	serious

FRAMESHIFT MUTATIONS

A **frameshift mutation** is a deletion or insertion of one or more nucleotides that changes the reading frame of the base sequence. Deletions remove nucleotides, and insertions add nucleotides. Consider the following sequence of bases in RNA:

AUG-AAU-ACG-GCU = methionine-asparagine-threonine-alanine

Now assume that an insertion occurs in this sequence. Let's say an **A** nucleotide is inserted after the start codon **AUG.** Then the sequence of bases becomes:

AUG-AAA-UAC-GGC-U = methionine-lysine-tyrosine-glycine

Even though the rest of the sequence is unchanged, this insertion changes the reading frame and thus all of the codons that follow it.

As this example shows, a frameshift mutation can dramatically change how the codons in mRNA are read. This can have a drastic effect on the protein product. Another example of the frameshift mutation due to the deletion of a nucleotide is illustrated in Figure **13.4.4**. In this example, a premature stop codon is created by the mutation.

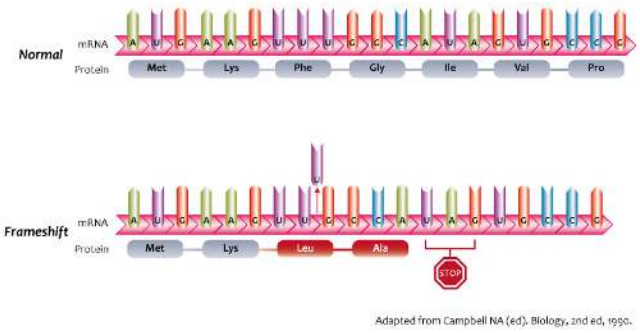


Figure **13.4.4**: The image shows how the frame of the coding sequence of a gene changes when a nucleotide gets deleted due to mutation. Normal gene codes for a polypeptide met-lys-phe-gly-ile-val-pro. When a U from the third position of the third codon gets deleted, the polypeptide reduced to met-lys-leu-ala because the third and fourth codons code for different amino acids and the fifth codon converts to a stop codon.

EFFECTS OF MUTATIONS

The majority of mutations have neither negative nor positive effects on the organism in which they occur. These mutations are called neutral mutations. Examples include silent point mutations, which are neutral because they do not change the amino acids in the proteins they encode.

Many other DNA damages or errors have no effects on the organism because they are repaired before protein synthesis occurs. Cells have multiple repair mechanisms to fix errors in DNA.

BENEFICIAL MUTATIONS

Some mutations have a positive effect on the organism in which they occur. They are referred to as beneficial mutations. They generally code for new versions of proteins that help organisms adapt to their environment. If they increase an organism's chances of surviving or reproducing, the mutations are likely to become more common over time. There are several well-known examples of beneficial mutations. Here are just two:

1. Mutations have occurred in bacteria that allow the bacteria to survive in the presence of antibiotic drugs. The mutations have led to the evolution of antibiotic-resistant strains of bacteria.
2. A unique mutation is found in people in a small town in Italy. The mutation protects them from developing atherosclerosis, which is the dangerous buildup of fatty materials in blood vessels. The individual in which the mutation first appeared has even been identified.

HARMFUL MUTATIONS

Imagine making a random change in a complicated machine such as a car engine. The chance that the random change would improve the functioning of the car is very small. The change is far more likely to result in a car that does not run well or perhaps does not run at all. By the same token, any random change in a gene's DNA is likely to result in the production of a protein that does not function normally or may not function at all. Such mutations are likely to be harmful. Harmful mutations may cause genetic disorders or cancer.

- A genetic disorder is a disease, syndrome, or other abnormal condition caused by a mutation in one or more genes or by a chromosomal alteration. An example of a genetic disorder is cystic fibrosis. A mutation in a single gene causes the body to produce thick, sticky mucus that clogs the lungs and blocks ducts in digestive organs.
- Cancer is a disease in which cells grow out of control and form abnormal masses of cells called tumors. It is generally caused by mutations in genes that regulate the cell cycle. Because of the mutations, cells with damaged DNA are allowed to divide without restrictions.

FEATURE: MY HUMAN BODY

Inherited mutations are thought to play a role in about 5 to 10 percent of all cancers. Specific mutations that cause many of the known hereditary cancers have been identified. Most of the mutations occur in genes that control the growth of cells or the repair of damaged DNA.

Genetic testing can be done to determine whether individuals have inherited specific cancer-causing mutations. Some of the most common inherited cancers for which genetic testing is available hereditary, breast, and ovarian cancer, caused by mutations in genes named BRCA1 and BRCA2. Besides breast and ovarian cancers, mutations in these genes may also cause pancreatic and prostate cancers. Genetic testing is generally done on a small sample of body fluid or tissue, such as blood, saliva, or skin cells. The sample is analyzed by a lab that specializes in genetic testing, and it usually takes at least a few weeks to get the test results.

Should you get genetic testing to find out whether you have inherited a cancer-causing mutation? Such testing is not done routinely just to screen patients for risk of cancer. Instead, the tests are generally done only when the following three criteria are met:

1. The test can determine definitively whether a specific gene is mutation is present. This is the case with the BRCA1 and BRCA2 gene mutations, for example.
2. The test results would be useful to help guide future medical care. For example, if you found out you had a mutation in the BRCA1 or BRCA2 gene, you might get more frequent breast and ovarian cancer screenings than are generally recommended.
3. You have a personal or family history that suggests you are at risk of inherited cancer.

Criterion number 3 is based, in turn, on such factors as:

- diagnosis of cancer at an unusually young age.
- several different cancers occurring independently in the same individual.
- several close genetic relatives having the same type of cancer (such as a maternal grandmother, mother, and sister all having breast cancer).
- cancer occurring in both organs in a set of paired organs (such as both kidneys or both breasts).

If you meet the criteria for genetic testing and are advised to undergo it, genetic counseling is highly recommended. A genetic counselor can help you understand what the results mean and how to make use of them to reduce your risk of developing cancer. For example, a positive test result that shows the presence of a mutation may not necessarily mean that you will develop cancer. It may depend on whether the gene is located on an autosome or sex chromosome and whether the mutation is dominant or recessive. Lifestyle factors may also play a role in cancer risk even for hereditary cancers, and early detection can often be life-saving if cancer does develop. Genetic counseling can also help you assess the chances that any children you may have will inherit the mutation.

REVIEW

1. Define mutation.
2. Identify the causes of mutation.
3. Compare and contrast germline and somatic mutations.
4. Describe chromosomal alterations, point mutations, and frameshift mutations. Identify the potential effects of each type of mutation.
5. Why are many mutations neutral in their effects?
6. Give an example of a beneficial mutation and an example of a harmful mutation.
7. Why do you think that exposure to mutagens, such as cigarette smoke, can cause cancer?
8. *True or False.* Mutations are always caused by exposure to toxic substances.
9. *True or False.* Some mutations can make chromosomes longer or shorter.
10. Explain why the insertion or deletion of a single nucleotide can cause a frameshift mutation.
11. Compare and contrast missense and nonsense mutations.
12. A mutation that substitutes one nucleotide for another is called a _____ mutation.
13. Which type of mutation is trisomy 21, or Down Syndrome?
14. Explain why mutations are important for evolution.

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13.5: REGULATION OF GENE EXPRESSION

EXPRESS YOURSELF

This sketch in Figure **13.5.1** illustrates some of the variability in human cells. The shape and other traits that make each type of cell unique depend mainly on the particular proteins that the cell type makes. For example, an ovum is a cell with a large cytoplasm because it nourishes the embryo after fertilization. Sperm is a small cell with essentially just genetic material. The job of the sperm is to transfer genetic material to the ovum. The sketch shows various other cell types. Proteins are encoded in genes. All the cells in an organism have the same genes, so they all have the genetic instructions for the same proteins. Obviously, different types of cells must use, or express, different genes to make different proteins.

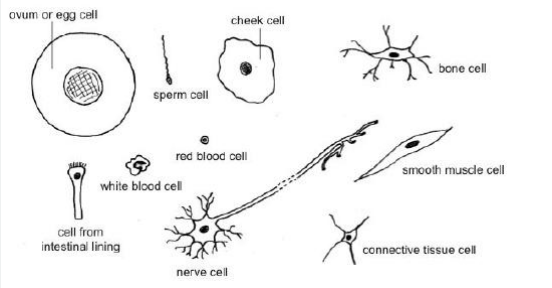


Figure **13.5.1**: Different cells have different shapes to perform their particular jobs.

WHAT IS GENE EXPRESSION?

Using a gene to make a protein is called **gene expression**. It includes the synthesis of the protein by the processes of transcription of DNA and translation of mRNA. It may also include further processing of the protein after synthesis.

Gene expression is regulated to ensure that the correct proteins are made when and where they are needed. Regulation may occur at any point in the expression of a gene, from the start of the transcription phase of protein synthesis to the processing of a protein after synthesis occurs. The regulation of transcription is one of the most complicated parts of gene regulation in eukaryotic cells and is the focus of this concept.

REGULATION OF TRANSCRIPTION

As shown in Figure **13.5.2**, transcription is controlled by **regulatory proteins** or **transcription factors**. These proteins bind to regions of DNA, called **regulatory elements** which are located near promoters. The **promoter** is the region of a gene where RNA polymerase binds to initiate transcription of the DNA to mRNA. After regulatory proteins bind to regulatory elements, the proteins can interact with RNA polymerase. Regulatory proteins are typically either activators or repressors. Activators are regulatory proteins that promote transcription by enhancing the interaction of RNA polymerase with the promoter. Repressors are regulatory proteins that prevent transcription by impeding the progress of RNA polymerase along the DNA strand so the DNA cannot be transcribed to mRNA.

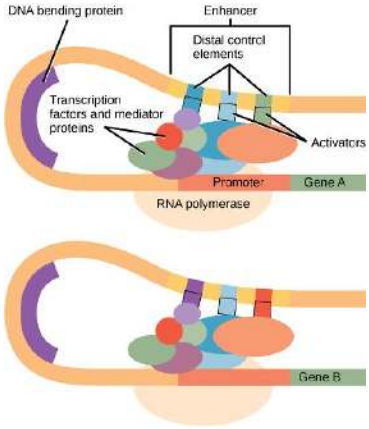


Figure **13.5.2**: An enhancer is a DNA sequence that promotes transcription. Each enhancer is made up of short DNA sequences called distal control elements. Activators bound to the distal control elements interact with mediator proteins and transcription factors. Two different genes may have the same promoter but different distal control elements, enabling differential gene expression.

ENHANCERS

Although regulatory proteins and elements are typically the key players in the regulation of transcription, other factors may also be involved. For example, regulation of transcription may also involve enhancers. Enhancers are distant regions of DNA that can loop back to interact with a gene's promoter and enhance transcription.

REGULATION DURING DEVELOPMENT

The regulation of gene expression is extremely important during the early development of an organism. Regulatory proteins must turn on certain genes in particular cells at just the right time so the individual develops normal organs and organ systems. **Homeobox genes** are a large group of genes that regulate development during the embryonic stage. In humans, there are an estimated 235 functional homeobox genes. They are present on every chromosome and generally grouped in clusters. Homeobox genes contain instructions for making chains of 60 amino acids called homeodomains. Proteins containing homeodomains are transcription factors that bind to and control the activities of other genes. The homeodomain is the part of the protein that binds to the target gene and controls its expression.

REVIEW

1. Define gene expression.
2. Why must gene expression be regulated?
3. Explain how regulatory proteins may activate or repress transcription.
4. Describe homeobox genes and their role in the development of an organism.
5. Discuss the role of regulatory gene mutations in cancer.

6. Explain the relationship between proto-oncogenes and oncogenes.
7. If a newly fertilized egg contained a mutation in a homeobox gene, what effect do you think this might have on the developing embryo? Explain your answer.
8. Which of the following are proteins?
   A. Repressors
   B. Promoters
   C. Regulatory elements
   D. All of the above
9. Which of the following is a region of DNA?
   A. Homeodomain
   B. Activator
   C. TATA box
   D. Both A and C
10. Compare and contrast enhancers and activators.
11. *True or False*. Mutations in genes that normally either promote or suppress cell division can both cause cancer.
12. *True or False*. Gene expression is only regulated at the transcriptional stage.
13. *True or False*. If RNA polymerase cannot bind to the promoter of a gene, it cannot transcribe that gene into mRNA.

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CHAPTER OVERVIEW

14: Cellular Reproduction

14.1: Cell Cycle and Cell Division

14.2: Basics of DNA Replication

14.3: Mitotic Phase - Mitosis and Cytokinesis

14.4: Mutations and Cancer

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14.1: CELL CYCLE AND CELL DIVISION

SO MANY CELLS!

The baby in Figure **14.1.1** has a lot of growing to do before they are as big as their mom. Most of their growth will be the result of cell division. By the time the baby is an adult, their body will consist of trillions of cells. Cell division is just one of the stages that all cells go through during their life. This includes cells that are harmful, such as cancer cells. Cancer cells divide more often than normal cells and grow out of control. In fact, this is how cancer cells cause illness. In this concept, you will read about how cells divide, what other stages cells go through, and what causes cancer cells to divide out of control and harm the body.



Figure **14.1.1**: Baby and mother

THE CELL CYCLE

Cell division is the process in which one cell, called the parent cell, divides to form two new cells, referred to as daughter cells. How this happens depends on whether the cell is prokaryotic or eukaryotic. Cell division is simpler in prokaryotes than eukaryotes because prokaryotic cells themselves are simpler. Prokaryotic cells have a single circular chromosome, no nucleus, and few other organelles. Eukaryotic cells, in contrast, have multiple chromosomes contained within a nucleus and many other organelles. All of these cell parts must be duplicated and then separated when the cell divides. Cell division is just one of several stages that a cell goes through during its lifetime. The **cell cycle** is a repeating series of events that include growth, DNA synthesis, and cell division. The cell cycle in prokaryotes is quite simple: the cell grows, its DNA replicates, and the cell divides. This form of division in prokaryotes is called asexual reproduction. In eukaryotes, the cell cycle is more complicated.

EUKARYOTIC CELL CYCLE

Figure **14.1.2** represents the cell cycle of a eukaryotic cell. As you can see, the eukaryotic cell cycle has several phases. The mitotic phase (M) includes both mitosis and cytokinesis. This is when the nucleus and then the cytoplasm divide. The other three phases (G_1, S, and G_2) are generally grouped together as **interphase**. During interphase, the cell grows, performs routine life processes, and prepares to divide. These phases are discussed below.

INTERPHASE

The Interphase of the eukaryotic cell cycle can be subdivided into the following phases (Figure **14.1.2**).

- **Growth Phase 1 (G_1):** The cell spends most of its life in the first gap (sometimes referred to as growth) phase, G_1. During this phase, a cell undergoes rapid growth and performs its routine functions. During this phase, the biosynthetic and metabolic activities of the cell occur at a high rate. The synthesis of amino acids and hundreds of thousands or millions of proteins that are required by the cell occurs during this phase. Proteins produced include those needed for DNA replication. If a cell is not dividing, the cell enters the G_0 phase from this phase.
- **G_0 phase:** The G_0 phase is a resting phase where the cell has left the cycle and has stopped dividing. Non-dividing cells in multicellular eukaryotic organisms enter G_0 from G_1. These cells may remain in G_0 for long periods of time, even indefinitely, such as with neurons. Cells that are completely differentiated may also enter G_0. Some cells stop dividing when issues of sustainability or viability of their daughter cells arise, such as with DNA damage or degradation, a process called **cellular senescence**. Cellular senescence occurs when normal diploid cells lose the ability to divide, normally after about 50 cell divisions.
- **Synthesis Phase (S):** Dividing cells enter the Synthesis (S) phase from G_1. For two genetically identical daughter cells to be formed, the cell's DNA must be copied through DNA replication. When the DNA is replicated, both strands of the double helix are used as templates to produce two new complementary strands. These new strands then hydrogen bond to the template strands and two double helices form. During this phase, the amount of DNA in the cell has effectively doubled, though the cell remains in a diploid state.
- **Growth Phase 2 (G_2):** The second gap (growth) (G_2) phase is a shortened growth period in which many organelles are reproduced or manufactured. Parts necessary for mitosis and cell division are made during G_2, including **microtubules** used in the mitotic spindle.

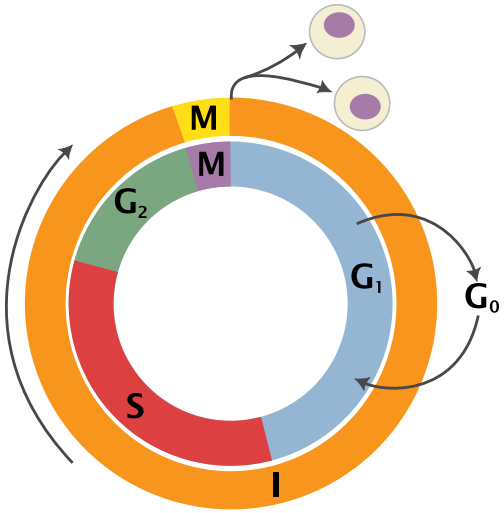


Figure **14.1.2**: Eukaryotic Cell Cycle. The First Gap (G1), Synthesis (S), and Second Gap (G2) phases make up interphase (I). The mitotic phase (yellow M) includes mitosis (purple M) and cytokinesis. During cytokinesis two cells result. Some cells do not divide and they enter into G_0 phage.

MITOTIC PHASE

Before a eukaryotic cell divides, all the DNA in the cell's multiple chromosomes is replicated. Its organelles are also duplicated. This happens in the interphase. Then, when the cell divides (mitotic phase), it occurs in two major steps, called **mitosis** and **cytokinesis**, both of which are described in greater detail in the concept *Mitotic Phase: Mitosis and Cytokinesis*.

- The first step in the mitotic phase of a eukaryotic cell is mitosis, a multi-phase process in which the nucleus of the cell divides. During mitosis, the nuclear envelope (membrane) breaks down and later reforms. The chromosomes are also sorted and separated to ensure that each daughter cell receives a complete set of chromosomes.
- The second major step is cytokinesis. This step, which occurs in prokaryotic cells as well, is when the cytoplasm divides and two daughter cells form.

Table **14.1.2**: Cell Cycle Summary

State	Name	Description
Quiescent Senescent	Resting phase (G0)	A resting phase where the cell has left the cycle and has stopped dividing.
Interphase	1st growth phase (G_1) Synthesis phase (S) 2ndgrowth phase (G_2)	Cells increase in size in G1. Cells perform their normal activities. DNA replication occurs during this phase. The cell will continue to grow and many organelles will divide during their phase.
Cell division	Mitosis (M)	Cell growth stops at this stage. Mitosis divides the nucleus into two nuclei, followed by cytokinesis which divides the cytoplasm. Two genetically identical daughter cells result.

CONTROL OF THE CELL CYCLE

If the cell cycle occurred without regulation, cells might go from one phase to the next before they were ready. What controls the cell cycle? How does the cell know when to grow, synthesize DNA, and divide? The cell cycle is controlled mainly by regulatory proteins. These proteins control the cycle by signaling the cell to either start or delay the next phase of the cycle. They ensure that the cell completes the previous phase before moving on. Regulatory proteins control the cell cycle at key checkpoints, which are shown in Figure **14.1.3**. There are a number of main checkpoints:

1. The G1 checkpoint: just before entry into the S phase, makes the key decision of whether the cell big enough to divide. If the cell is not big enough, it goes into the resting period (G_0)
2. DNA synthesis Checkpoint: The S checkpoint determines if the DNA has been replicated properly.
3. The mitosis checkpoint: This checkpoint ensures that all the chromosomes are properly aligned before the cell is allowed to divide.

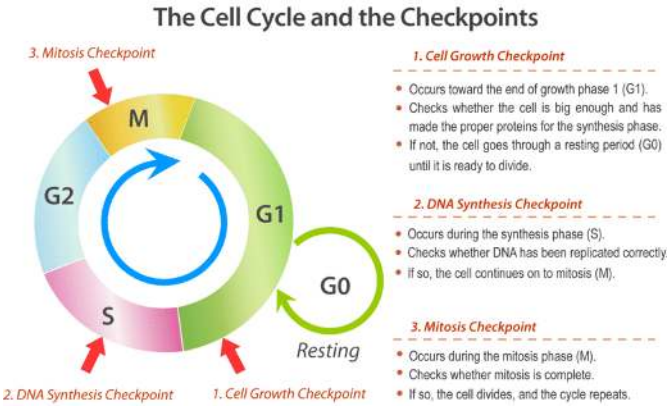


Figure **14.1.3**: Checkpoints in the eukaryotic cell cycle ensure that the cell is ready to proceed before it moves on to the next phase of the cycle.

CANCER AND THE CELL CYCLE

Cancer is a disease that occurs when the cell cycle is no longer regulated. This happens because a cell's DNA becomes damaged. This results in mutations in the genes that regulate the cell cycle. Damage can occur due to exposure to hazards such as radiation or toxic chemicals. Cancerous cells generally divide much faster than normal cells. They may form a mass of abnormal cells called a **tumor** (see Figure **14.1.4**). The rapidly dividing cells take up nutrients and space that normal cells need. This can damage tissues and organs and eventually lead to death. When uncontrolled cell division happens in the bone marrow, abnormal and nonfunctional blood cells are produced because the division is happening before the cell is ready for division. In these types of cancer, there is not any evident tumor.

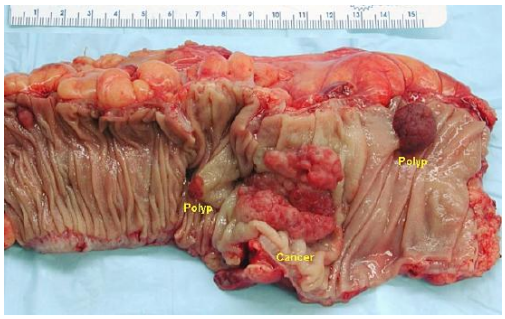


Figure **14.1.4**: Gross appearance of an opened large intestine specimen containing an invasive **colorectal carcinoma** and two **adenomatous polyps**. The cancer cells have grown out of control and forming a tumor.

FEATURE: HUMAN BIOLOGY IN THE NEWS

Henrietta Lacks sought treatment for her cancer at Johns Hopkins University Hospital at a time when researchers were trying to grow human cells in the lab for medical testing. Despite many attempts, the cells always died before they had undergone many cell divisions. Mrs. Lacks's doctor took a small sample of cells from her tumor without her knowledge and gave them to a Johns Hopkins researcher, who tried to grow them on a culture plate. For the first time in history, human cells grown on a culture plate kept dividing...and dividing and dividing and dividing. Copies of Henrietta's Lacks cells — called HeLa cells for her name — are still alive today. In fact, there are currently many billions of HeLa cells in laboratories around the world!

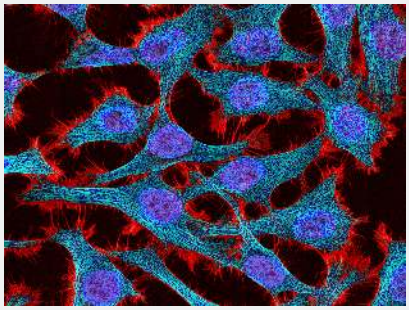


Figure **14.1.5**: Fluorescently dyed HeLa Cells. The woman named Henrietta Lacks died in 1951 of an unusual form of cervical cancer, she was just 31 years old. A poor, African-American tobacco farmer and mother of five, she (or at least her cells) would eventually be called immortal.

Why Henrietta Lacks' cells lived on when other human cells did not is still something of a mystery, but they are clearly extremely hardy and resilient cells. By 1953, when researchers learned of their ability to keep dividing indefinitely, factories were set up to start producing the cells commercially on a large scale for medical research. Since then, HeLa cells have been used in thousands of studies and have made possible hundreds of medical advances. For example, Jonas Salk used the cells in the early 1950s to test his polio vaccine. Over the decades since then, HeLa cells have been used to make important discoveries in the study of cancer, AIDS, and many other diseases. The cells were even sent to space on early space missions to learn how human cells respond to zero gravity. HeLa cells were also the first human cells ever cloned, and their genes were some of the first ever mapped. It is almost impossible to overestimate the profound importance of HeLa cells to human biology and medicine.

You would think that Henrietta Lacks' name would be well known in medical history for her unparalleled contributions to biomedical research. However, until 2010, her story was virtually unknown. That year, a science writer named Rebecca Skloot published a nonfiction book about Henrietta Lacks, named *The Immortal Life of Henrietta Lacks*. Based on a decade of research, the book is riveting, and it became an almost instantaneous best seller. As of 2016, Oprah Winfrey and collaborators planned to make a movie based on the book, and in recent years, numerous articles about Henrietta Lacks have appeared in the press.

Ironically, Henrietta herself never knew her cells had been taken, and neither did her family. While her cells were making a lot of money and building scientific careers, her children were living in poverty, too poor to afford medical insurance. The story of Henrietta Lacks and her immortal cells raises ethical issues about human tissues and who controls them in biomedical research. However, there is no question that Henrietta Lacks deserves far more recognition for her contribution to the advancement of science and medicine.

REVIEW

1. What are the two main phases of the cell cycle in a eukaryotic cell?
2. Describe the three phases of interphase in a eukaryotic cell.
3. Explain how the cell cycle is controlled.
4. How is cancer-related to the cell cycle?
5. What are the two major steps of cell division in a eukaryotic cell?
6. In which phase of the eukaryotic cell cycle do cells typically spend most of their lives?
7. Which phases of the cell cycle will have cells with twice the amount of DNA? Explain your answer.
8. If there is damage to a gene that encodes for a cell cycle regulatory protein, what do you think might happen? Explain your answer.
9. *True or False*. Cells go into G_0 if they do not pass the G_1 checkpoint.
10. In which phase within interphase does the cell make final preparations to divide?
    A. Mitosis
    B. Cytokinesis
    C. G_2
    D. S
11. What were scientists trying to do when they took tumor cells from Henrietta Lacks? Why did they specifically use tumor cells to try to achieve their goal?

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14.2: Basics of DNA Replication

Skills to Develop

- Explain how the structure of DNA reveals the replication process
- Describe the Meselson and Stahl experiments

The elucidation of the structure of the double helix provided a hint as to how DNA divides and makes copies of itself. This model suggests that the two strands of the double helix separate during replication, and each strand serves as a template from which the new complementary strand is copied. What was not clear was how the replication took place. There were three models suggested (Figure 14.2.1): *conservative*, *semi-conservative*, *and dispersive*.

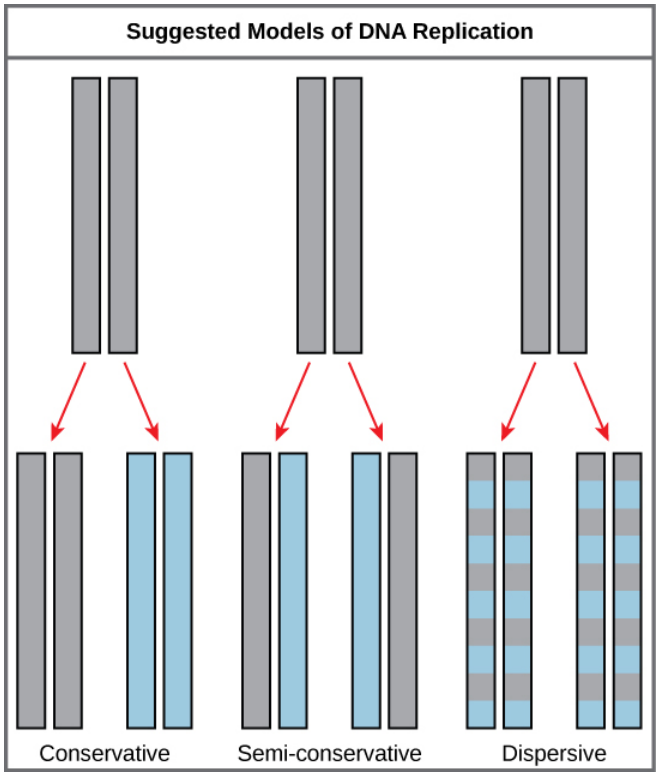


Figure 14.2.1: The three suggested models of DNA replication. Grey indicates the original DNA strands, and blue indicates newly synthesized DNA

In conservative replication, the parental DNA remains together, and the newly formed daughter strands are together. The semi-conservative method suggests that each of the two parental DNA strands act as a template for new DNA to be synthesized; after replication, each double-stranded DNA includes one parental or “old” strand and one “new” strand. In the dispersive model, both copies of DNA have double-stranded segments of parental DNA and newly synthesized DNA interspersed.

Meselson and Stahl were interested in understanding how DNA replicates. They grew *E. coli* for several generations in a medium containing a “heavy” isotope of nitrogen (^{15}N) that gets incorporated into nitrogenous bases, and eventually into the DNA (Figure 14.2.2).

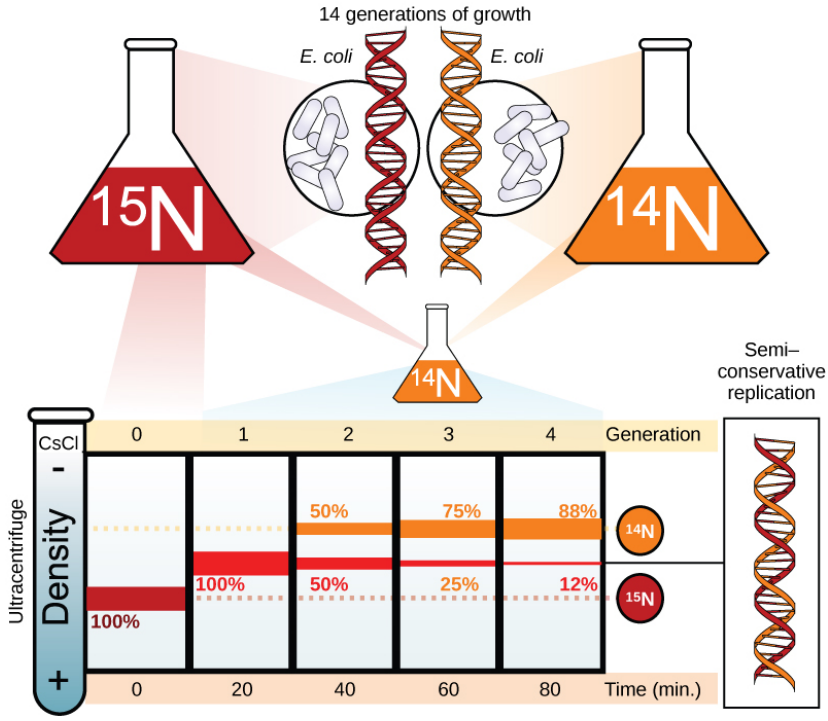
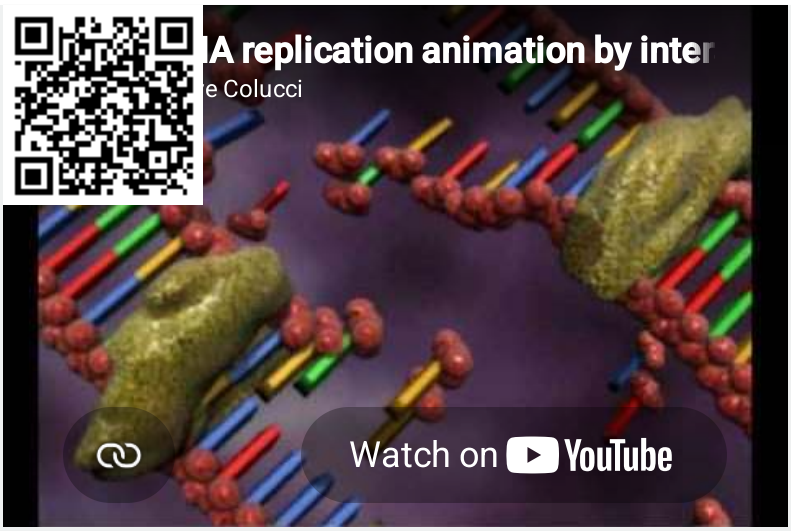


Figure 14.2.2: Meselson and Stahl experimented with E. coli grown first in heavy nitrogen (^{15}N) then in ^{14}N. DNA grown in ^{15}N (red band) is heavier than DNA grown in ^{14}N (orange band), and sediments to a lower level in cesium chloride solution in an ultracentrifuge. When DNA grown in ^{15}N is switched to media containing ^{14}N, after one round of cell division the DNA sediments halfway between the ^{15}N and ^{14}N levels, indicating that it now contains fifty percent ^{14}N. In subsequent cell divisions, an increasing amount of DNA contains ^{14}N only. This data supports the semi-conservative replication model. (credit: modification of work by Mariana Ruiz Villareal)

The *E. coli* culture was then shifted into medium containing ^{14}N and allowed to grow for one generation. The cells were harvested and the DNA was isolated. The DNA was centrifuged at high speeds in an ultracentrifuge. Some cells were allowed to grow for one more life cycle in ^{14}N and spun again. During the density gradient centrifugation, the DNA is loaded into a gradient (typically a salt such as cesium chloride or sucrose) and spun at high speeds of 50,000 to 60,000 rpm. Under these circumstances, the DNA will form a band according to its density in the gradient. DNA grown in ^{15}N will band at a higher density position than that grown in ^{14}N. Meselson and Stahl noted that after one generation of growth in ^{14}N after they had been shifted from ^{15}N, the single band observed was intermediate in position in between DNA of cells grown exclusively in ^{15}N and ^{14}N. This suggested either a semi-conservative or dispersive mode of replication. The DNA harvested from cells grown for two generations in ^{14}N formed two bands: one DNA band was at the intermediate position between ^{15}N and ^{14}N, and the other corresponded to the band of ^{14}N DNA. These results could only be explained if DNA replicates in a semi-conservative manner. Therefore, the other two modes were ruled out.

During DNA replication, each of the two strands that make up the double helix serves as a template from which new strands are copied. The new strand will be complementary to the parental or “old” strand. When two daughter DNA copies are formed, they have the same sequence and are divided equally into the two daughter cells.

Link to Learning



Click through this tutorial on DNA replication.

Summary

The model for DNA replication suggests that the two strands of the double helix separate during replication, and each strand serves as a template from which the new complementary strand is copied. In conservative replication, the parental DNA is conserved, and the daughter DNA is newly synthesized. The semi-conservative method suggests that each of the two parental DNA strands acts as template for new DNA to be synthesized; after replication, each double-stranded DNA includes one parental or “old” strand and one “new” strand. The dispersive mode suggested that the two copies of the DNA would have segments of parental DNA and newly synthesized DNA.

Contributors and Attributions

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14.3: MITOTIC PHASE - MITOSIS AND CYTOKINESIS

DIVIDE AND SPLIT

Can you guess what this colorful image represents? It shows a eukaryotic cell during the process of cell division. In particular, the image shows the nucleus of the cell dividing. In eukaryotic cells, the nucleus divides before the cell itself splits in two; and before the nucleus divides, the cell's DNA is replicated, or copied. There must be two copies of the DNA so that each daughter cell will have a complete copy of the genetic material from the parent cell. How is the replicated DNA sorted and separated so that each daughter cell gets a complete set of genetic material? To answer that question, you first need to know more about DNA and the forms it takes.

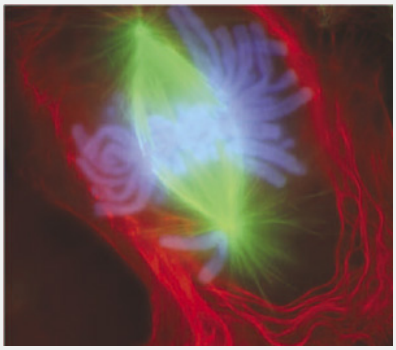


Figure **14.3.1**: Dividing cell stained with fluorescent dyes. You can see chromosomes in blue and spindles in green.

THE FORMS OF DNA

Except when a eukaryotic cell divides, its nuclear DNA exists as a grainy material called **chromatin.** Only when a cell is about to divide and its DNA has replicated does DNA condense and coil into the familiar X-shaped form of a **chromosome,** like the one shown in Figure **14.3.2**. Because DNA has already replicated, each chromosome actually consists of two identical copies. The two copies of a chromosome are called sister **chromatids.** Sister chromatids are joined together at a region called a centromere.

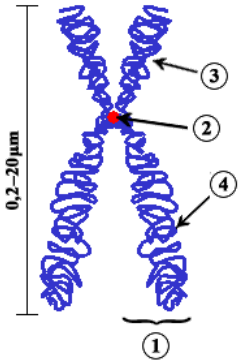


Figure **14.3.2**: Chromosome. After DNA replicates, it forms X-shaped chromosomes like the one shown here. 1. Chromatid, 2. Centromere, 3. short arm, 4. long arm. Centromere contains proteins called kinetochores (not shown) where spindles attach during mitosis.

The process in which the nucleus of a eukaryotic cell divides is called **mitosis.** During mitosis, the two sister chromatids that make up each chromosome separate from each other and move to opposite poles of the cell. Mitosis occurs in four phases. The phases are called prophase, metaphase, anaphase, and telophase. They are shown in Figure **14.3.3** and described in detail below.

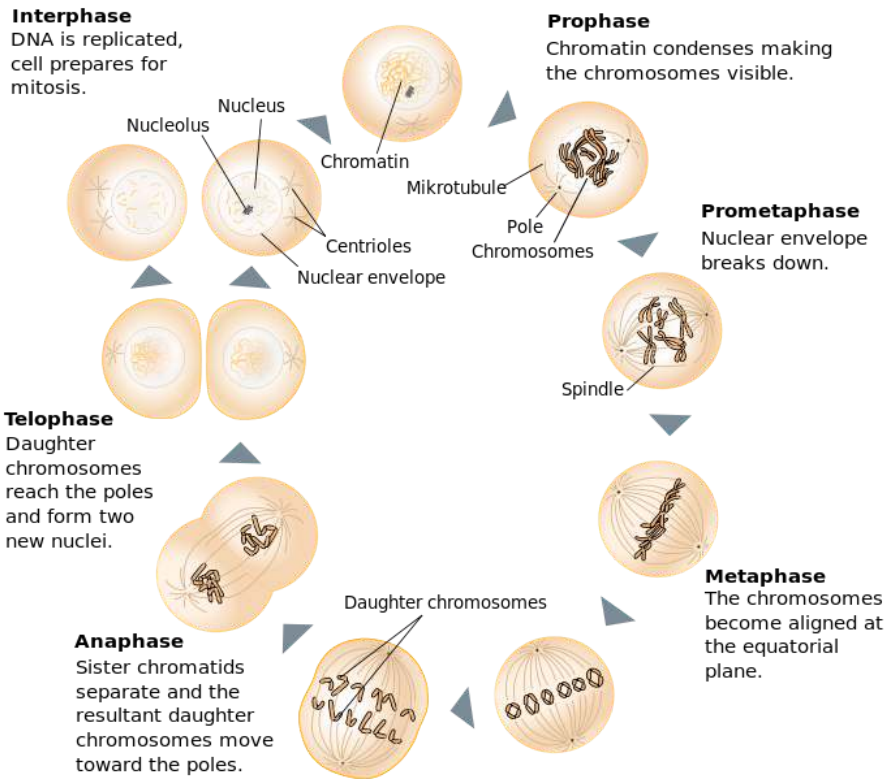


Figure **14.3.3**: Mitosis is the phase of the eukaryotic cell cycle that occurs between DNA replication and the formation of two daughter cells. Mitosis has four substages, prophase, metaphase, anaphase, and telophase.

PROPHASE

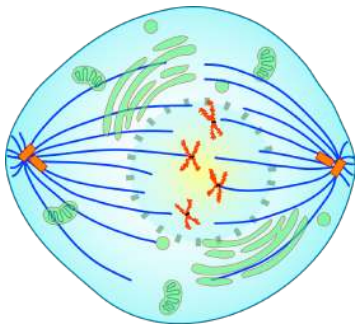


Figure **14.3.4**: Prophase in later stage is called prometaphase. The spindle starts to form during the prophase of mitosis. The spindles start to attach to the Kinetochores of centromeres of sister chromatids during Prometaphase.

The first and longest phase of mitosis is prophase. During prophase, chromatin condenses into chromosomes, and the nuclear envelope (the membrane surrounding the nucleus) breaks down. In animal cells, the centrioles near the nucleus begin to separate and move to opposite poles of the cell. Centrioles are small organelles found only in eukaryotic cells that help ensure the new cells that form after cell division each contain a complete set of chromosomes. As the centrioles move apart, a spindle starts to form between them. The blue spindle, shown in Figure **14.3.4**, consists of fibers made of microtubules.

METAPHASE

During **metaphase**, spindle fibers fully attach to the centromere of each pair of sister chromatids. As you can see in Figure **14.3.5**, the sister chromatids line up at the equator, or center, of the cell. The spindle fibers ensure that sister chromatids will separate and go to different daughter cells when the cell divides. Some spindles do not attach to the kinetochore protein of the centromeres. These spindles are called non-kinetochore spindles that help in the elongation of the cell. This is visible in Figure **14.3.5**.

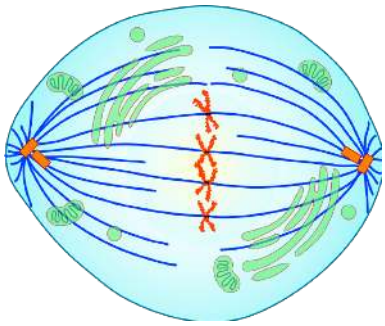


Figure **14.3.5**: Chromosomes, consisting of sister chromatids, line up at the equator or middle of the cell during metaphase. The blue lines are spindles, and the orange rectangles at the cell poles are centrioles. Some spindles from the opposing centrioles attach with each other, and some spindles attach to the kinetochores of the sister chromosomes from their respective sides. Each chromosome is attached to two spindles.

ANAPHASE

During **anaphase**, sister chromatids separate and the centromeres divide. The sister chromatids are pulled apart by the shortening of the spindle fibers. This is a little like reeling in a fish by shortening the fishing line. One sister chromatid moves to one pole of the cell, and the other sister chromatid moves to the opposite pole (see Figure

14.3.6). At the end of anaphase, each pole of the cell has a complete set of chromosomes

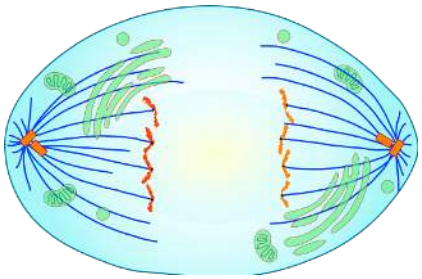


Figure 14.3.6: Anaphase: Sister chromatids break apart and move to the opposite pole with the help of spindles. The newly separated sister chromatids are called chromosomes now.

TELOPHASE

The chromosomes reach the opposite poles and begin to *decondense* (unravel), relaxing once again into a stretched-out chromatin configuration. The mitotic spindles are depolymerized into tubulin monomers that will be used to assemble cytoskeletal components for each daughter cell. Nuclear envelopes form around the chromosomes, and nucleosomes appear within the nuclear area (see Figure 14.3.7.

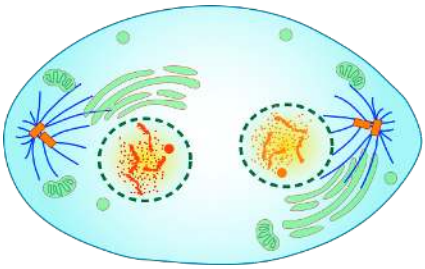


Figure 14.3.7: Telophase: The chromosomes decondense, spindles start to disappear, two nuclei form in a cell.

CYTOKINESIS

Cytokinesis is the final stage of cell division in eukaryotes as well as prokaryotes. During cytokinesis, the cytoplasm splits in two and the cell divides. The process is different in plant and animal cells, as you can see in Figure 14.3.8. In animal cells, the plasma membrane of the parent cell pinches inward along the cell's equator until two daughter cells form. In the plant cells, a cell plate forms along the equator of the parent cell. Then, a new plasma membrane and cell wall form along each side of the cell plate.

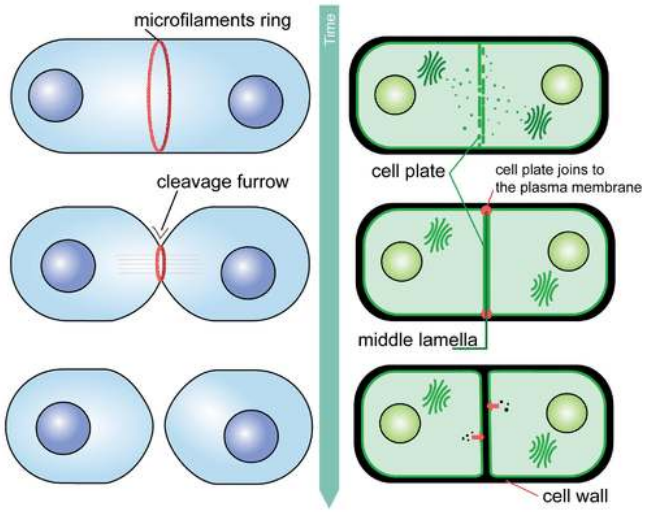


Figure 14.3.8: Cytokinesis is the final stage of eukaryotic cell division. It occurs differently in animal (left) and plant (right) cells. You can see a microfilament ring forming at the center of the elongated animal cell. This creates a depression called cleavage furrow. This invagination ultimately separates the cell cytoplasm into two cells. A cell plate forms at the center of the elongated plant cell. Then a new plasma membrane and cell wall form along each side of the cell plate.

REVIEW

1. Describe the different forms that DNA takes before and during cell division in a eukaryotic cell.
2. Identify the four phases of mitosis in an animal cell, and summarize what happens during each phase.
3. Explain what happens during cytokinesis in an animal cell.
4. What are the main differences between mitosis and cytokinesis?
5. The familiar X-shaped chromosome represents:
   A. How DNA always looks in eukaryotic cells
   B. How DNA in eukaryotic cells looks once it is replicated and the cell is about to divide
   C. Female sex chromosomes only
   D. How DNA appears immediately after cytokinesis
6. Which of the following is not part of a chromosome in eukaryotic cells?
   A. Centriole
   B. Centromere
   C. Chromatid
   D. DNA
7. What do you think would happen if the sister chromatids of one of the chromosomes did not separate during mitosis?
8. Put the following processes in order of when they occur during cell division, from first to last:
   A. separation of sister chromatids
   B. DNA replication
   C. cytokinesis
   D. lining up of chromosomes in the center of the cell
   E. condensation and coiling of DNA into a chromosome

9. Why do you think the nuclear envelope breaks down at the start of mitosis?
10. What are the fibers made of microtubules that attach to the centromeres during mitosis are called?
11. *True or False.* Chromosomes begin to uncoil during anaphase.
12. *True or False.* During cytokinesis in animal cells, sister chromatids line up along the equator of the cell.
13. *True or False.* After mitosis, the result is typically two daughter cells with identical DNA to each other.

EXPLORE MORE

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14.4: MUTATIONS AND CANCER

WHAT WOULD HAPPEN IF THIS CYCLE PROCEEDS AT WILL?

Your cells may grow and divide without performing their necessary functions, or without fully replicating their DNA, or without copying their organelles. Probably not much good could come of that. So the cell cycle needs to be highly regulated and tightly controlled. And it is.

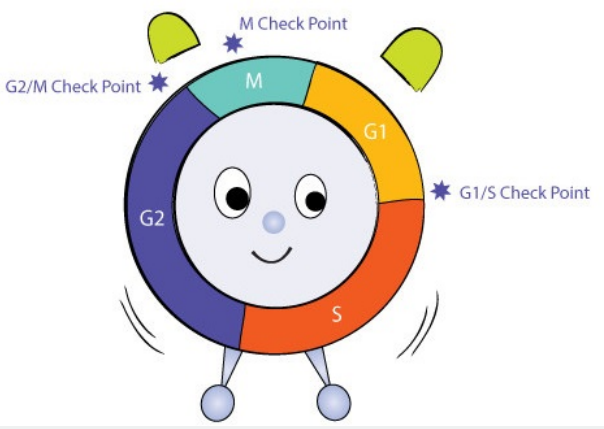


Figure **14.4.1**: Cell Cycle

CONTROL OF THE CELL CYCLE

How does the cell know when to divide? How does the cell know when to replicate its DNA? How does the cell know when to proceed into mitosis or cytokinesis? The answers to these questions have to do with the control of the cell cycle. But how is the cell cycle controlled or regulated? Regulation of the cell cycle involves processes crucial to the survival of a cell. These include the detection and repair of damage to DNA, as well as the prevention of uncontrolled cell division. Uncontrolled cell division can be deadly to an organism; its prevention is critical for survival.

CYCLINS AND KINASES

The cell cycle is controlled by a number of protein-controlled feedback processes. Two types of proteins involved in the control of the cell cycle are **kinases** and **cyclins**. Cyclins activate kinases by binding to them, specifically they activate **cyclin-dependent kinases (CDK)**. **Kinases** are enzymes that catalyze the transfer of a phosphate group from ATP to another molecule in a cell. They function as a control switch in many cellular functions, turning a function on or off, and regulating other cellular processes. Many times they are involved in activating a cascade of reactions. Cyclins comprise a group of proteins that are rapidly produced at key stages in the cell cycle. Once activated by a cyclin, CDK enzymes activate or inactivate other target molecules through phosphorylation. It is this precise regulation of proteins that triggers advancement through the cell cycle. Leland H. Hartwell, R. Timothy Hunt, and Paul M. Nurse won the 2001 Nobel Prize in Physiology or Medicine for their discovery of these critical proteins.

WHAT MAKES A CELL CANCEROUS?

Cancer is a disease characterized by a population of cells that grow and divide without respect to normal limits. These cancerous cells invade and destroy adjacent tissues, and they may spread throughout the body. The process by which normal cells are transformed into cancer cells is known as **carcinogenesis**. This process is also known as oncogenesis or tumorigenesis.

Nearly all cancers are caused by mutations in the DNA of abnormal cells. These mutations may be due to the effects of **carcinogens**, cancer-causing agents such as tobacco smoke, radiation, chemicals, or infectious agents. These carcinogens may act as an environmental "trigger," stimulating the onset of cancer in certain individuals and not others. Do all people who smoke get cancer? No. Can secondhand smoke increase a nonsmoking person's chance of developing lung cancer? Yes. It also increases a nonsmoking person's chance of developing heart disease.

Complex interactions between carcinogens and an individual's genome may explain why only some people develop cancer after exposure to an environmental trigger and others do not. Do all cancers need an environmental trigger to develop? No. Cancer-causing mutations may also result from errors incorporated into the DNA during replication, or they may be inherited. Inherited mutations are present in all cells of the organism.

ONCOGENES AND TUMOR SUPPRESSOR GENES

Some types of cancer occur because of mutations in genes that control the cell cycle. Cancer-causing mutations most often occur in two types of regulatory genes, called proto-oncogenes and tumor-suppressor genes.

- Proto-oncogenes are genes that normally help cells divide. When a proto-oncogene mutates to become an oncogene, it is continuously active, even when it is not supposed to be. This is like a car's accelerator pedal being stuck at full throttle. The car keeps racing at top speed. In the case of a cell, the cell keeps dividing out of control, which can lead to cancer.
- Tumor suppressor genes are genes that normally slow down or stop cell division. When a mutation occurs in a tumor suppressor gene, it can no longer control cell division. This is like a car without brakes. The car can't be slowed or stopped. In the case of a cell, the cell keeps dividing out of control, which can lead to cancer.

Several Mutations to Cause Cancer

Oncogenes may be growth factors, protein kinases, GTPases or transcription factors. **Growth factors** are naturally occurring substances, usually a protein or steroid hormone, capable of stimulating cellular growth, proliferation, and differentiation. They are important for regulating a variety of cellular processes. Usually, they must bind to an extracellular or intracellular receptor to initiate a cellular reaction.

Typically, a series of several mutations that constitutively activate oncogenes and inactivate tumor suppressor genes is required to transform a normal cell into a cancer cell (Figure **14.4.2**). Cells have developed a number of control mechanisms to overcome mutations in proto-oncogenes. Therefore, a cell needs multiple mutations to transform into a cancerous cell. A mutation in one proto-oncogene would not cause cancer, as the effects of the mutation would be masked by the normal control of the cell cycle and the actions of tumor suppressor genes. Similarly, a mutation in one tumor suppressor gene would not cause cancer either, due to the presence of many "backup" genes that duplicate its functions. It is only when enough proto-oncogenes have mutated into oncogenes and enough tumor suppressor genes have been deactivated that the cancerous transformation can begin. Signals for cell growth overwhelm the signals for growth regulation, and the cell quickly spirals out of control. Often, because many of these genes regulate the processes that prevent most damage to the genes themselves, DNA damage accumulates as one ages.

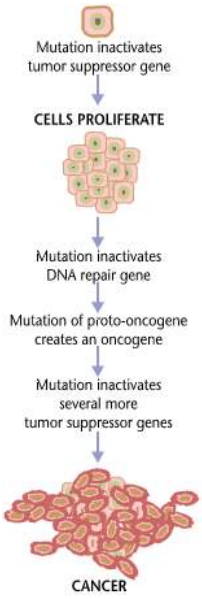


Figure **14.4.2**: How Cancer Develops. Mutations in a tumor suppressor gene allow the proliferation of cells. As many times the cells divide, they acquire more mutation. Some mutations may lead to the inactivation of the DNA repair genes. Also, proto-oncogenes may convert into oncogenes due to mutations. Several other mutations inactivate many tumor suppressor genes. Eventually, a series of mutations in tumor-suppressor genes and proto-oncogenes leads to cancer

Usually, oncogenes are dominant alleles, as they contain gain-of-function mutations. The actions of the mutant allele gene product, many times resulting in a constitutively activated protein, are dominant to the gene product produced by the "normal" allele. Meanwhile, mutated tumor suppressors are generally recessive alleles, as they contain loss-of-function mutations. A proto-oncogene needs only a mutation in one copy of the gene to generate an oncogene; a tumor suppressor gene needs a mutation in both copies of the gene to render both products defective. There are instances when, however, one mutated allele of a tumor suppressor gene can render the other copy non-functional. These instances result in what is known as a dominant negative effect.

REVIEW

1. Define cancer.
2. What are cyclin-dependent kinases? What is their role?
3. Discuss the role of oncogenes and tumor suppressor genes in carcinogenesis.
4. Why are multiple mutations required for transformation into a cancerous cell?
5. Identify all the categories of oncogenes and describe two categories.

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