Unit 12: *Kinetics and Nuclear Chemistry—Rates of Reaction*

Unit Overview

In this unit, we will learn how the rate of a chemical reaction is affected by a number of factors, including temperature and the concentration of reactants at the beginning of the reaction. While the chemical equation may show reactants turning into products as a straightforward, simple arrow, there is much more to that arrow than meets the eye. How exactly do reactants turn into products? Sometimes, the answer is simple: Two atoms bump into each other and form a bond. Most of the time, however, the process is much more complex. Controlling the rate of reactions has implications for a variety of applications, including drug design and corrosion prevention. The latter half of this unit introduces nuclear reactions.

by Thomas van Geel

Sections

Unit 12: *Kinetics and Nuclear Chemistry—Rates of Reaction*

Section 1: Introduction

The speed of chemical reactions varies tremendously (Figure 12-1). Trinitrotoluene (TNT) detonates in a fraction of a second, while the iron in a car muffler takes years to rust through. The study of the rate of chemical reactions is called "**chemical kinetics**."

A rate always involves a change over time; the speed of a car is measured in distance over time: miles per hour. In a chemical reaction, we could measure how fast the reactants are used up or how fast the products are produced.

How can the rate of a chemical reaction be controlled? Sometimes, the goal is to speed up the reaction, for example, when synthesizing a new drug to make it available faster or when increasing the rate of fuel consumption to increase the thrust of a rocket. At other times, the goal is to slow down the reaction, for example, to prevent corrosion or the spoiling of food. To better understand and control chemical reactions, chemists have discovered that many factors can influence the reaction rate. Scientists studying chemical kinetics have developed equations that accurately describe reaction rates.

Figure 12-1. The Varying Speed of Chemical Reactions

Chemical reactions happen at different rates. Low explosives, like the ones found in the fireworks at left, react relatively slowly compared with the high explosive on the right.

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To fully understand why a reaction happens at a certain rate, we also must learn much more about how the chemical reaction occurs. A chemical equation shows reactants turning into products in a very straightforward manner; a simple arrow separates the two. As we will see in this unit, there is much more to that arrow than meets the eye. How exactly do reactants turn into products? Sometimes, the answer is simple: Two atoms bump into each other and form a bond. Most of the time, however, the process is much more complex.

Although nuclear reactions occur via a process completely different from chemical reactions, they both obey the same laws of kinetics. While humans have used chemical reactions for millennia, research into nuclear reactions began only slightly more than a century ago with the discovery of radiation. The latter half of this unit traces the early development of nuclear science. Luminaries such as Marie Curie made great strides in the study of radioactivity in the late 1800s. Through the next few decades, our understanding of radiation and nuclear chemistry grew until science achieved what was once considered impossible: splitting the atom. This discovery of nuclear fission by Lise Meitner and Otto Hahn in the 1930s set the stage for a frantic race to create the first atomic weapons and the subsequent arms race that defined cold war geopolitics for decades thereafter. While often associated with doomsday scenarios in the popular imagination, radioactivity has numerous nonviolent applications. The chain reactions that power nuclear weapons also power nuclear power plants, and radiation itself has many other peaceful uses, such as the radioactive dating in archeology and geology, medical imaging, and radiation therapy.

Glossary

Chemical kinetics

The study of the rates of chemical reactions.

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Section 2: When Molecules Collide

Rate Laws

The precise way that the concentration of a reactant influences the reaction rate is called the "reaction order." If doubling the concentration doubles the rate, the reaction is said to be first order with respect to that reactant. First-order reactions have an important characteristic; they have a consistent half-life. The half-life is the amount of time required for exactly half of the reactants to turn into products, and having a consistent half-life makes it very easy to keep track of how much reactant will remain after a certain amount of time has passed. After one half-life, 50 percent of the reactant remains. After two half-lives, 25 percent remains. After three, 12.5 percent remains, and so on. As we will see in the second half of this unit, the kinetics of first-order reactions are similar to the kinetics of radioactive decay.

If the reaction rate quadruples when the concentration is doubled, the reaction is second order with respect to the reactant.

The rate law is an equation that expresses the exact relationship between the concentrations of all the reactants and the rate of the reaction. For example, if a reaction is first order with respect to reactant A and second order with respect to reactant B, the rate law is:

$\text{rate} = k[\text{A}][\text{B}]^2$

In a rate law, k is the rate constant. The higher the value of the rate constant, the faster the reaction is.

For two molecules to react, they must come in contact with each other; they must collide. But not all collisions result in a reaction; the molecules must collide with the correct orientation. In the reaction between HCl and C_2H_4, a productive collision only happens when the hydrogen of HCl approaches the double bond in C_2H_4. In other collisions, no reaction will occur. (Figure 12-2)

The reaction rate will increase if productive collisions happen more frequently. One way to increase collision frequency is to pack more molecules into a smaller space: Increase the concentration. An acid can quickly cause chemical burns if its concentration is high; even the acetic acid in harmless vinegar is hazardous when highly purified. The tanks of concentrated oxygen for medical use carry warning labels due to the risk of fire, and liquid oxygen is so concentrated that it can support the combustion of a diamond.

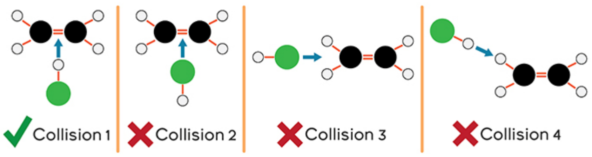

Figure 12-2. Collisions and Chemical Reactions

Not all collisions between reactants result in a chemical reaction. This figure shows four collisions in which the reactants have different orientations; only the first orientation allows for a productive collision.

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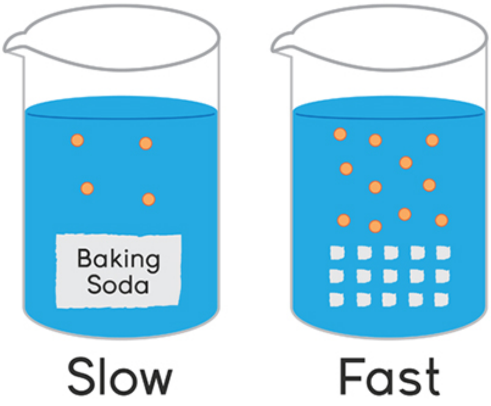

Figure 12-3. Rate of Reaction and Surface Area

The reaction on the right happens faster because the surface area of the reactants (in this case, baking soda) is greater.

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Another way to speed up a reaction is to increase the surface area of the reactants. For example, a large chunk of baking soda will react slowly with vinegar because the two substances can only react where they make contact with each other—at the surface. If the baking soda is broken into small particles, the vinegar will make contact with a lot more of the baking soda and the reaction will happen faster. (Figure 12-3)

A substance that is normally safe and inert can become dangerously reactive in powdered form. A pile of flour exposed to a flame will become singed on the surface but will not catch fire. But if the flour is dispersed as a cloud in the air, it becomes extremely flammable due to the increased contact between atmospheric oxygen and flour particles. Fires and explosions used to be major hazards in flour mills. After the Great Mill Disaster in Minneapolis in 1878 killed 18 people, flour mills began using precautions, such as ventilation and spark prevention.

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Section 3: Potential Energy Diagrams

To react, reactant molecules must collide with enough energy to break their old bonds. When OH^- and CH_3Br react to form CH_3OH and Br^-, the CH_3–Br bond must break, and a new OH–CH_3 bond must form.

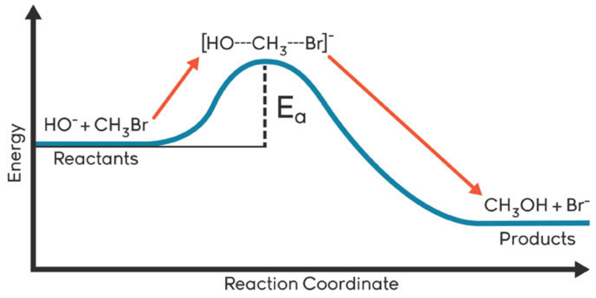

Figure 12-4. Potential Energy Diagram

A potential energy diagram showing the potential energies of the chemical species as the reaction progresses. In this case, the carbon in the center has a very high energy because it is temporarily trying to bind to five things rather than its standard four bonds.

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The reactant molecules (OH^- and CH_3Br) and the product molecules (CH_3OH and Br^-) are stable, and stability corresponds to low potential energy. But in the transition between reactants and products—in the instant that old bonds break and new bonds form—there is a high-energy, unstable state called an "**activated complex**." The potential energy of the chemical species as the reaction progresses is shown on a **potential energy diagram**.

The Arrhenius Equation

In 1889, Swedish chemist Svante Arrhenius (1859–1927) developed an equation that related the rate constant of a chemical reaction with the temperature:

$$k = Ae^{\frac{-E_a}{RT}}$$

In this equation, k is the rate constant, A is the "frequency factor," E_a is the activation energy, R is the universal gas constant, and T is the temperature in Kelvin. While explaining the details of this equation are beyond the scope of this course, we can see that the equation does coincide with what we have learned about reaction rates so far. The frequency factor A is related to the frequency of productive particle collisions. In the equation, we see that as A increases, so does *k*. Likewise, as the activation energy E_a increases, the value of *k* decreases (note the negative sign in the exponent), and we have learned that reactions with higher activation energies progress more slowly. And finally, as the temperature T increases, the value of *k* also increases, reflecting the fact that chemical reactions always go faster at higher temperatures.

Figure 12-4 shows that the reactants require a certain amount of energy to reach the activated complex—this amount of energy is called the "**activation energy**" (E_a) of the reaction. Often, this is referred to as "the hill," and in order for the reaction to happen, we have to climb the hill. If the two molecules do not collide with enough energy to overcome the activation energy and make it to the activated complex, then no products are formed; the collision is not productive. Also, the higher the hill is, the harder it is to have the energy to overcome it and the slower the reaction is.

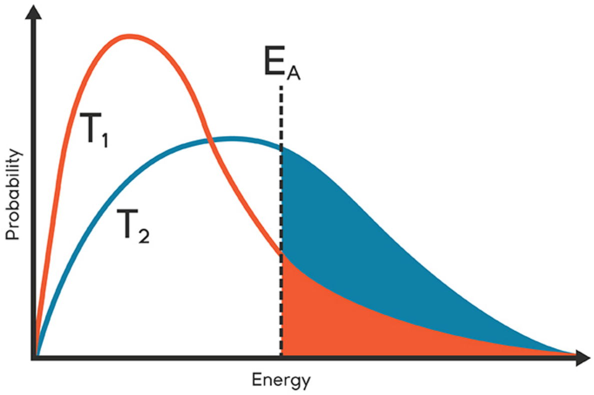

Figure 12-5. Temperature and Activation Energy

The lines on this graph represent the distribution of particles possessing a range of energy values. The orange line represents a low temperature, and the blue line represents a higher temperature. Note that at the higher temperature, a much larger fraction of the molecules will have more than enough kinetic energy to overcome the activation barrier.

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At a low temperature, only a small fraction of the molecules will have enough energy to overcome the activation energy, and the reaction will proceed slowly. At a higher temperature, more molecules will have the energy needed, and the reaction will speed up. (Figure 12-5)

The dependence of the reaction rate on temperature has many far-reaching applications. To speed up the production of ammonia in the Haber-Bosch process, the reaction is conducted at a high temperature (see Unit 9); many other industrial chemical reactions are carried out at high temperatures to boost production. Bread rises faster in a warm environment because the chemical reactions inside yeast increase at higher temperatures. The unwanted microorganisms that cause food to spoil also grow faster in warm conditions; this is why perishable food is best refrigerated.

Glossary

Activated complex

A chemical species midway between reactant molecules and product molecules.

Activation energy

The amount of energy that the reactants need to reach the activated complex.

Potential energy diagram

A graph that shows the potential energies of reactants, the activated complex, and the products as the reaction progresses. It is also called a reaction coordinate diagram.

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Section 4: Reaction Mechanisms

Most chemical reactions actually occur in a sequence of simple reactions instead of all at once. These intermediate reactions are called "**elementary steps**." Consider the following reaction:

$$CO + NO_2 \rightarrow CO_2 + NO \text{ (net equation)}$$

This reaction actually takes place in two elementary steps:

$$NO_2 + NO_2 \rightarrow NO_3 + NO$$

$$CO + NO_3 \rightarrow NO_2 + CO_2$$

The first elementary step produces NO_3 and NO, while the second combines the NO_3 with CO to make NO_2 and CO_2. Note that NO_3 is produced in one step and immediately consumed by the next. We therefore call NO_3 an "**intermediate**"—it is produced and consumed in the course of a reaction, but it does not appear in the overall equation, which is called the "**net equation**."

The elementary steps in a mechanism do not happen at the same rate. In the example above, the first step happens slowly and the second quickly. The slowest step is called the "**rate-determining step**" because it limits the rate of the overall reaction. It's similar to a production line in a factory; the slowest worker determines the overall rate of production. No matter how fast the other workers are, the slowest person will determine the rate. (Figure 12-6)

Figure 12-6. Rate-Determining Step

Chemical reactions that take place in multiple steps have their rates determined by their slowest, rate-determining step. This is the same thing that happens in an assembly line if one phase of the processes is slow. Or during rush hour, one traffic jam might have the greatest effect on the total amount of time it takes to get home.

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Knowing which step is the slowest is important if we want to speed up the reaction. In the reaction above, recall that the first step—in which two NO_2 molecules react—is the slow, rate-determining step. Because this step controls the overall rate of the reaction, we should focus on it, rather than on the second step, if we wanted to speed up this reaction. One way to speed up this step (and therefore the entire reaction) would be to increase the concentration of NO_2.

Looking only at the reactants in the overall reaction, NO_2 and CO, would be misleading; it might appear that increasing both the reactant concentrations would speed things up. But with a thorough understanding of the underlying reaction mechanism, it is clear that increasing the CO concentration will not help speed up the first slow step. Adding more CO would speed up the second step in the mechanism, which was already fast.

To put this in more technical terms, *the overall chemical equation does not determine the rate law*. If we took the chemical equation at face value and assumed that the reaction simply occurred when a molecule of NO_2 collides with a molecule of CO, we would conclude that the rate law would be:

$$\text{Rate} = k[NO_2][CO]$$

But experimentation would show this to be wrong; the concentration of CO has no impact on the rate.

Glossary

Elementary steps

A sequence of simple chemical reactions that make up the mechanism of an overall reaction.

Intermediate

A chemical species produced by an elementary step of a chemical reaction, and then consumed by another. Intermediates do not appear in the overall chemical equation.

Net equation

A chemical equation for a reaction that lists only the reactants and products participating in the reaction.

Rate-determining step

The slowest elementary step in a reaction mechanism.

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Section 5: Catalysts

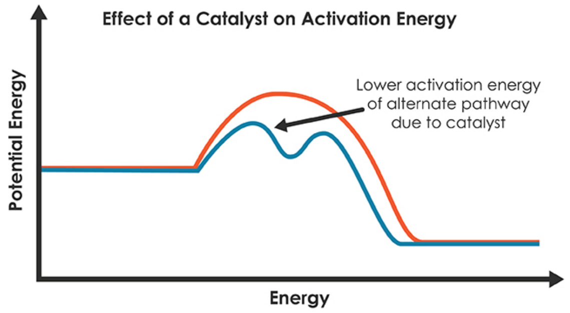

Figure 12-7. Catalysts and Activation Energy

In the presence of a catalyst, the activation energy for the reaction is lower. Note how the two new steps both have activation barriers that are much lower than the original uncatalyzed activation barrier.

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Another way to increase the reaction rate is to add a **catalyst** to the reaction. A catalyst works by providing an alternate mechanism for the reaction to occur. The alternate pathway has a lower activation energy, allowing the reaction to proceed faster. (Figure 12-7) In actuality, what happens is that the catalyst will allow for a new mechanism with new steps, each of which has a new activation barrier; but if the catalyst really speeds up the reaction, the tallest "hill" on the new path will be shorter than the original "hill" or activation barrier.

With a lower net activation energy, more reactants can make it over the hump, and the reaction goes faster.

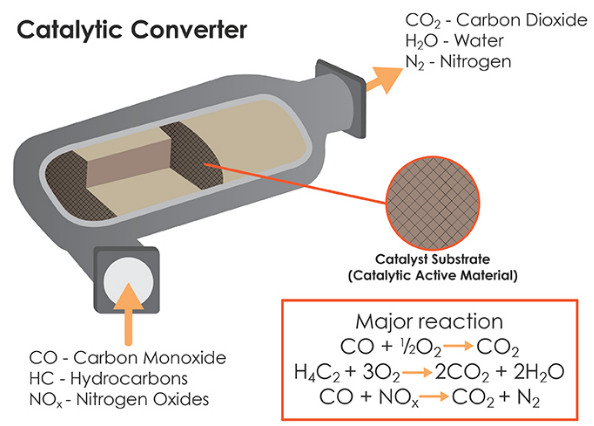

Figure 12-8. Catalytic Converter

Catalytic converters in the exhaust system of a car convert toxic substances such as carbon monoxide (CO), hydrocarbons (HC), and nitrogen oxides (NO_x) into gases that are safe to breathe.

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The catalytic converters in the exhaust system of cars use various metal catalysts to reduce pollution. Car exhaust contains toxic substances such as carbon monoxide, nitrogen oxides, and hydrocarbons. In the catalytic converter, these gases pass through the pores of a catalyst-coated mesh; the toxins react to form gases that are safe to breathe: CO_2, H_2O, and N_2. (Figure 12-8)

The thousands of chemical reactions that occur in living things could not occur without catalysts. In living things, catalysts called "**enzymes**" regulate everything from the construction of DNA to the digestion of nutrients. To digest the sugar in milk (lactose), the enzyme lactase must first break a bond to create the simpler sugars, galactose and glucose. (Figure 12-9) Human infants produce lactase to digest their mothers' milk; as most people grow older and switch to other foods, lactase production stops. The inability to digest lactose is called "lactose intolerance"; eating milk products can then cause bloating and gastrointestinal upset.

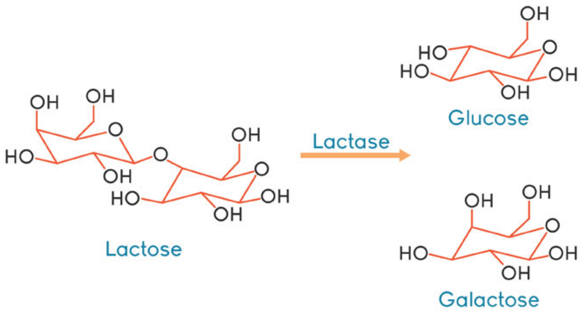

Figure 12-9. The Lactase Enzyme

The lactase enzyme breaks down lactose into simpler sugars. If the body stops producing lactase as we get older, we either have to cut back on the eating of dairy products or take supplements that contain the lactase enzyme that the body no longer makes. Without the enzyme, the reaction to digest lactose is too slow to occur in the body.

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Glossary

Catalyst
A substance that speeds up a chemical reaction, yet remains unchanged by the chemical reaction.

Enzyme
A biological catalyst.

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Section 6: The Discovery of Radioactivity

Figure 12-10. Roentgen Discovers X-rays

One of Roentgen's first X-ray images. It shows his wife's hand.

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In 1895, German physicist Wilhelm Roentgen (1845–1923) was doing research with a cathode ray tube when he made an unexpected discovery. A fluorescent screen near the tube began to glow. Roentgen soon deduced that the screen was being hit with some kind of rays or particles emitted by the cathode ray tube. The radiation from the tube was not the same as cathode rays; cathode rays were easily blocked by cardboard. The new radiation had much greater penetrating power and passed through many objects unchanged. Roentgen held his hand in front of the fluorescent screen and saw the shadow of his bones. He named the mysterious new rays "**X-rays**." (Figure 12-10)

Inspired by Roentgen's work, French physicist Henri Becquerel (1852–1908) investigated other fluorescent substances looking for other sources of X-rays.

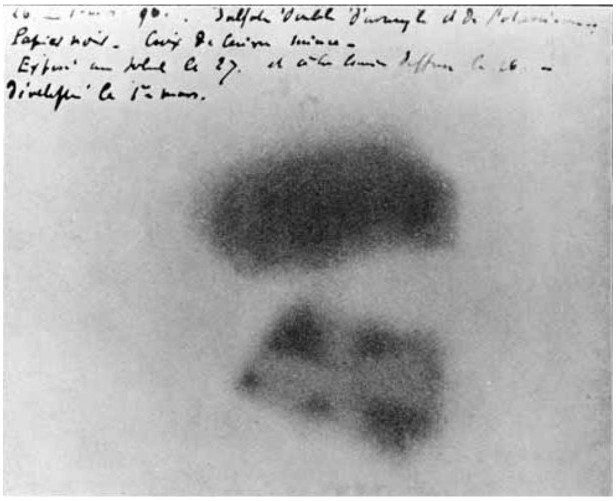

Figure 12-11. Becquerel's Photographic Plate Exposed to Uranium

A photographic plate created by Becquerel. The darkened areas were exposed to radiation from a uranium compound.

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One of the substances was a compound uranyl potassium sulfate. Becquerel sprinkled the uranium compound on a photographic plate encased in paper and put it in the sunshine. He hoped the sun's rays would cause the uranium to emit X-rays, which would produce an image on the plate. Becquerel did indeed find the expected image, and he planned to repeat the experiment the following day. The following two days were cloudy, however, so he put the plate in a drawer and waited for the weather to clear. A few days later, on a whim, Becquerel decided to develop the plate despite the fact that it had never been exposed to sunlight. To his surprise, the plate had the same kind of dark, fuzzy images where the uranium salt covered it, and the conclusion was inescapable: Some kind of radiation was coming from the uranium compound itself, which had nothing to do with sunlight or X-rays. (Figure 12-11)

Becquerel also discovered that the new radiation could ionize air. The ions made the air conductive, and by measuring the conductivity one could determine how radioactive a substance was. Using a sensitive electrometer developed by her husband, Polish scientist Marie Curie (1867–1934) investigated the radioactivity of uranium. (Figure 12-12)

Figure 12-12. Marie Curie

Marie Curie's first discovery was that radiation depended only on the quantity of uranium present and not on the amount of other substances with which it may be interacting.

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Curie discovered that the amount of radiation given off by uranium was constant over a wide range of conditions. The radiation did not depend on the uranium's temperature, whether it was in a compound or pure, or in a solution or solid. She concluded that the radiation was not produced by some kind of chemical interaction with other substances or as a result of fluorescence; the radiation came from the uranium atoms themselves. Because the production of radiation does not increase with temperature, it differs from most chemical reactions in an important way; it does not have activation energy. However, there is also an important similarity. The production of radiation follows the pattern of first-order kinetics. In other words, the amount of radiation given off depends only on the amount of radioactive material, not on the amount of any other substance that might be interacting with it.

For this pioneering work in radioactivity, Marie Curie, her husband Pierre (1859–1906), and Henri Becquerel were awarded the Nobel Prize in Physics in 1903. The Curies went on to discover two new radioactive elements, polonium and radium, and for this Marie Curie won the Nobel Prize in chemistry in 1911. She is not only the first woman to win a Nobel Prize, but also the first person to win two Nobel Prizes. The element curium (Cm) was named in her honor.

Glossary

X-rays

The second-highest energy form of electromagnetic radiation, exceeded by gamma rays.

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Section 7: Types of Radiation and Nuclear Equations

When Ernest Rutherford was working under J.J. Thomson (discoverer of the electron), he found that uranium gave off two distinct types of radiation. The first, which he called "alpha radiation," could only travel a few centimeters through air and could not penetrate a sheet of aluminum mere hundredths of an inch thick. The second type traveled through matter much more easily, and he termed it "beta radiation." Later research found that alpha radiation consisted of particles that are clusters of two protons and two neutrons. Alpha particles have the symbol ${}^{4}_{2}\alpha^{2+}$. **Beta particles**, like cathode rays, were found to be electrons. (This is a *newly formed* electron, not one of the electrons in the cloud surrounding the nucleus.) A beta particle is represented by the symbol ${}^{0}\beta^{1-}$. A third type of radiation from uranium was found in 1900 and termed "**gamma radiation**." Gamma rays are a type of high-energy electromagnetic wave like X-rays. They have no mass and no charge, and are represented by the Greek letter gamma: γ.

These three types of radiation differ in their penetrating power; alpha particles penetrate the least, and gamma rays penetrate the most. A piece of ordinary paper will stop alpha particles, a piece of aluminum or wood can stop beta particles, and lead or concrete is needed to stop gamma rays. (Figure 12-13)

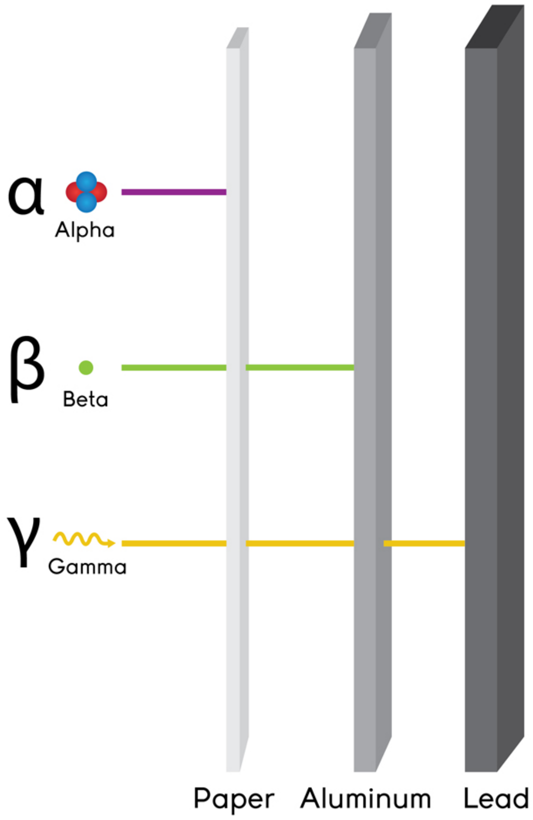

Figure 12-13. Types of Radiation

Different types of radiation penetrate substances to different degrees.

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Like chemical reactions, nuclear reactions can be described by equations. Nuclear equations must balance in terms of both mass and charge. For example, when an atom of polonium-210 undergoes alpha decay, the equation is:

$${}^{120}_{84}\mathrm{Po} \rightarrow {}^{206}_{82}\mathrm{Pb} + {}^{4}_{2}\alpha^{2+}$$

When alpha decay happens, four heavy particles are lost, so the mass number decreases by four, and the atomic number goes down by two. Other types of common nuclear decay do not affect the mass number of the element. When C-14 undergoes beta decay, the equation is:

$${}^{14}_{6}\mathrm{C} \rightarrow {}^{14}_{7}\mathrm{N} + {}^{0}\beta^{1-}$$

Note that the mass numbers (in superscripts) balance on both sides of the arrow, similar to how the number of atoms balance in a regular chemical equation. In a beta decay, one of the neutrons in the nucleus releases a beta particle, which results in the neutron becoming a proton. So, carbon-14 became nitrogen-14; this is the main reaction that is involved in the removal of ${}^{14}C$ from living material that is exploited for carbon dating. Even bananas contain a lot of naturally occurring potassium-40, which undergoes a beta decay; for this reason, bananas will set off a Geiger counter, a tool used for detecting radiation.

In **gamma emission**, the equation looks like this:

$${}^{99m}_{43}\mathrm{Tc} \rightarrow {}^{99}_{43}\mathrm{Tc} + {}^{0}\gamma^{0}$$

Because a gamma ray has no mass and no charge, the mass and charge numbers on the technetium atom don't change. The m indicates that the protons and neutrons in the technetium nucleus are in a metastable, high-energy arrangement; as the particles return to a stable state, that excess energy is released as a gamma ray. Technetium-99m is used in many radio-imaging facilities in hospitals; it is the main component of Cardiolyte™, which is used to take 3D images of the heart.

Three decades later, in the 1930s, physicists reported two additional kinds of nuclear decay: **electron capture** and **positron emission**.

In electron capture, the nucleus of an atom captures one of the innermost electrons in the electron cloud. This electron combines with a proton to create a neutron. The nuclear equation looks like this:

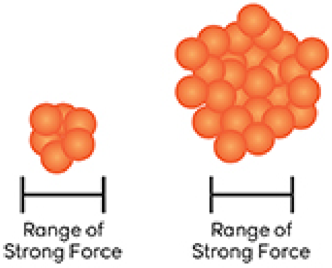
$${}^{26}_{13}\mathrm{Al} + {}^{0}\beta^{1-} \rightarrow {}^{26}_{12}\mathrm{Mg}$$

The captured electron leaves a vacancy in a low-level orbital. A higher-energy electron will fall into its place, and this transition will release an electromagnetic wave. Because this is a large drop in energy, the wave is a high-energy wave: an X-ray.

Nuclear Stability

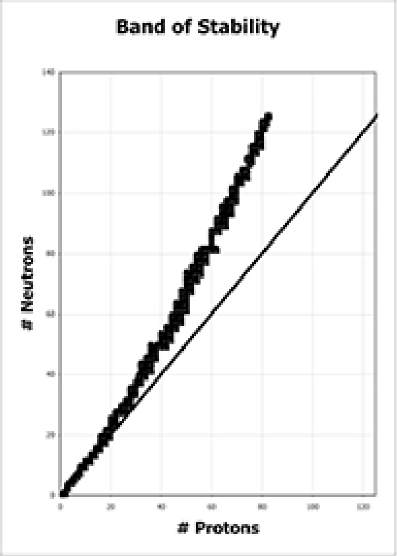
Because each proton in the nucleus carries a +1 charge, there are tremendous repelling forces constantly trying to force the protons apart—like a highly compressed spring just waiting for a chance to uncoil. So what holds the protons together?

One of the four fundamental forces of nature, the strong force, stabilizes the protons. (The other three are gravity, electromagnetism, and the weak force.) The strong force only works on objects that are within 1.5 x 10^{-15} m of each other—about the diameter of an atomic nucleus. Because the strong force has such a limited range, any nucleus that is too big will be unstable; its diameter will be larger than the range of the strong force.



The range of strong force determines whether the nucleus is more or less stable. © Science Media Group.

Neutrons are attracted to protons and other neutrons by the strong force, and so they help to hold a nucleus together. Neutrons thus act as a "glue," and with the right amount of neutrons, a nucleus can contain a lot of protons. The glue analogy is not perfect, however, because more neutrons only add stability up to a point; the ratio of protons to neutrons is what matters most. For small nuclei, the most stable ratio of neutrons to protons is about 1-to-1. For larger nuclei, the stable ratio tends toward 1.5-to-1. The line on the graph represents a 1-to-1 ratio. The dots represent stable nuclei. As the graph shows, small stable nuclei lie close to the line. Larger stable nuclei lie above the line. This means that any isotopes that are not in this band or sea of stability are unstable and will want to decay radioactively. Depending on where they are relative to the band, they can undergo alpha decay, beta decay, positron emission, or electron capture to move closer to or into that band of stability.



The band of stability starts at a ratio of about 1-to-1 (neutrons-to-protons) and increases with the atomic number to about 1.5-to-1. © Science Media Group.

In positron emission, a proton turns into a neutron and a **positron**, as follows:

$$^{11}_{6}C \rightarrow {}^{11}_{5}B + {}^{0}\beta^{1+}$$

Though it sounds like something out of science fiction, a positron is an example of **antimatter**. It has the same mass as an electron, but the opposite charge: +1 instead of -1. And when a positron collides with an electron, they annihilate each other, releasing energy in the form of gamma rays. In hospitals, positron-emitting elements are used in PET (or positron emission tomography) scanning. In this technique, the gamma rays caused by the annihilation of the positrons are captured by a camera, and an image of where these elements were in the body can be created.

Glossary

Antimatter

A substance made of antiparticles, such as positrons and antiprotons, which have the same mass but opposite charge as their matter counterparts. When a particle and its antiparticle collide, both are annihilated and energy is released.

Beta particles

A high-energy electron produced in the process of nuclear decay (β^-).

Electron capture
A type of nuclear decay in which a nucleus captures an electron from a low energy level.

Gamma emission
A type of nuclear decay in which a rearrangement of nuclear particles releases a gamma ray.

Gamma radiation
High-energy electromagnetic radiation.

Positron
An antimatter particle equal in mass to the electron but with a positive charge.

Positron emission
A type of nuclear decay that releases a positron.

Strong force
The nuclear force between protons and neutrons that holds a nucleus together.

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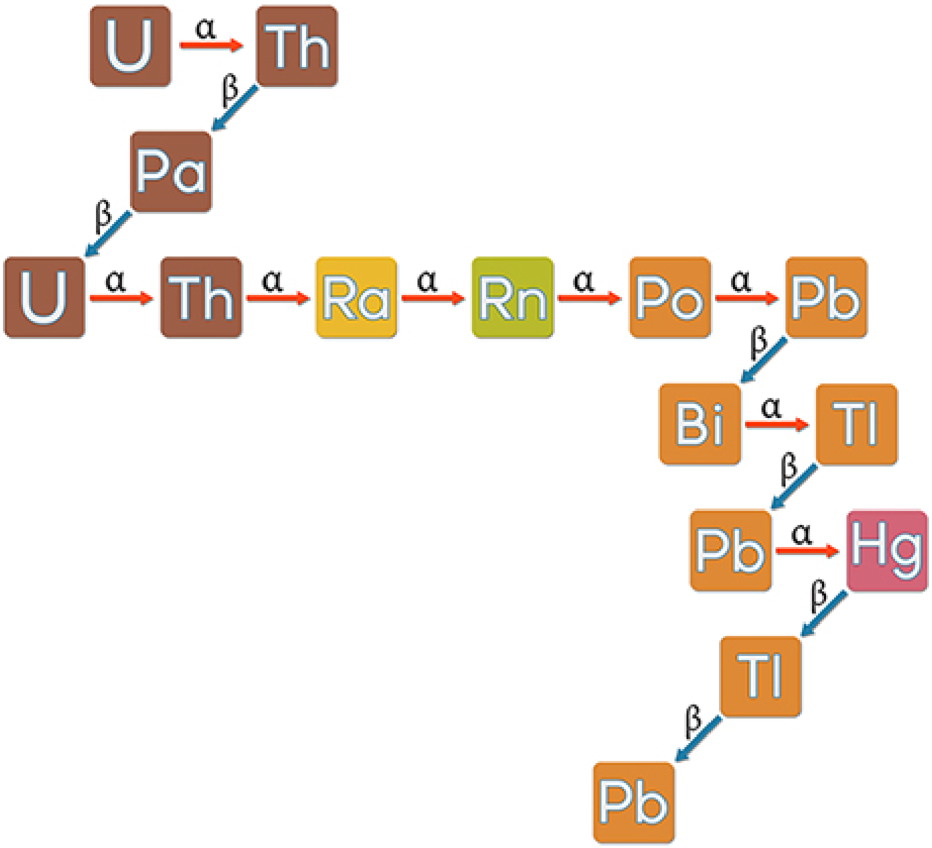
Section 8: Half-Life and Radiometric Dating

Decay Chains and Radon

For many unstable nuclei, stability will not be attained after one nuclear decay process. An unstable nucleus often will decay into another unstable nucleus, which decays into another unstable nucleus, and so on; a series of nuclear transformations follows until a stable nucleus is reached. This is called a "radioactive series" or "decay chain." The decay chain for uranium-235 is shown below; it starts with ${}^{235}_{92}U$ at the top and ends with ${}^{206}_{82}Pb$ at the bottom.



The decay chain for uranium-238. Every time an alpha particle is emitted, it becomes an element two atomic numbers lower; when a beta particle is emitted, its atomic number moves up by one, without changing its mass number. © Science Media Group.

This decay chain has an important impact on human health. Uranium-238 is naturally present in rocks and soil. After a few steps in its decay chain, uranium produces the gas, radon-222, which has a half-life of just about four days. The radon can seep through the foundation of a building from the surrounding soil, and inhaling the radioactive gas is the largest source of background radiation exposure for most people, since it decays quickly after it is formed. The radiation from radon and its subsequent decay products is a major cause of lung cancer, second only to cigarette smoking; radon causes approximately 20,000 deaths annually. If a building is found to have unsafe radon levels, it needs a ventilation system to continuously draw the radon outside.

While there is no way to predict exactly when any particular unstable nucleus will decay, a large collection of nuclei will decay in a predictable fashion—every radioactive isotope has a unique **half-life**: The time it takes for half of the sample to decay. If an isotope is unstable and decays very quickly, its half-life is short; if it is stable and decays slowly, its half-life is long. The range of half-lives is quite large:

Isotope	Half-life
Uranium-238	4.5 X 10^9 years
Carbon-14	5,715 years
Strontium-90	28.8 years
Scandium-46	83.8 days
Copper-62	9.67 minutes
Meitnerium-226	3.4 milliseconds

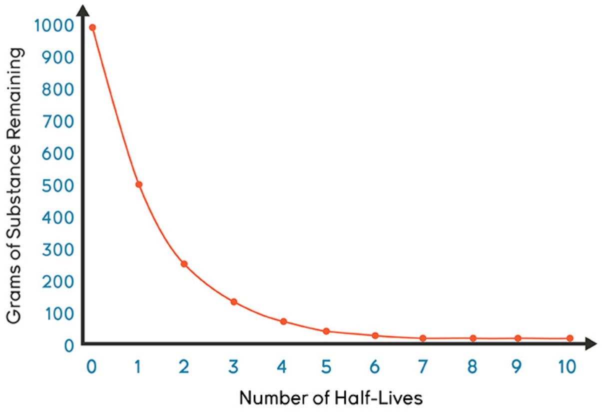


Figure 12-14. Decay of a Radioactive Substance

Most people consider that after 10 half-lives have passed, a radioactive substance is gone, as less than one-tenth of a percent of what was there originally remains.

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Figure 12-14 shows the decay of 1000 g of a radioactive isotope. Note that the amount of isotope decreases by half with every half-life.

Because radioactive substances decay in such a predictable way, they can be used to determine the age of fossils and archeological artifacts. **Radiocarbon dating** is used for organic substances up to about 60,000 years old, and it is based on the ratio of carbon-14 (radioactive) to carbon-12 (stable) in the substance. Carbon-14 is formed in the atmosphere when nitrogen is bombarded with cosmic rays; the carbon-14 enters the food chain when plants absorb CO_2 in photosynthesis. So long as a plant or animal is alive and exchanging carbon with the atmosphere, it will have the same ratio of carbon-14 to carbon-12 as its surroundings. When the organism dies, this exchange stops; as the carbon-14 undergoes radioactive decay, the ratio drops. By measuring the ratio, the age can be determined. (Figure 12-15)

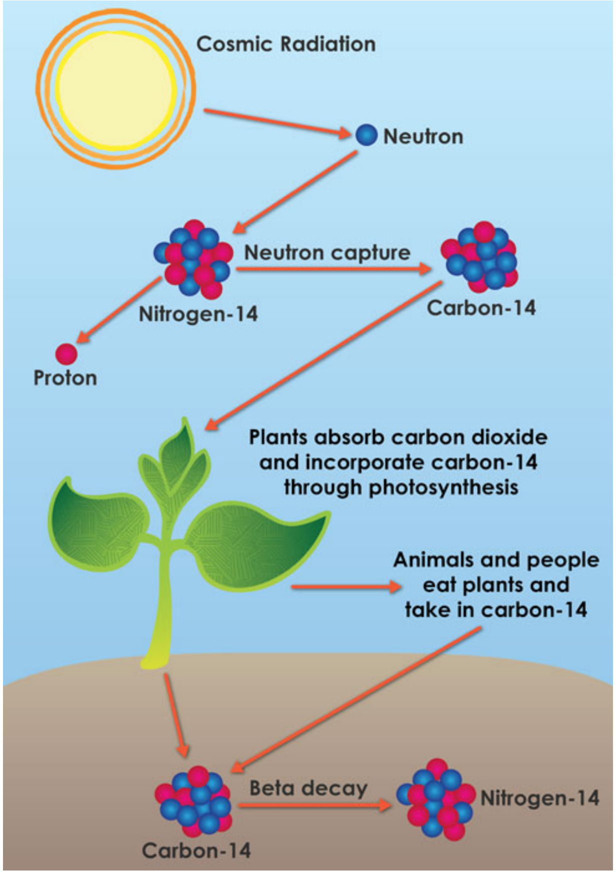

Figure 12-15. Radiocarbon Dating

Plants take up radioactive carbon-14 formed in the atmosphere. The radioactive carbon then enters the food chain. So long as a plant or animal is alive, the amount of carbon-14 remains constant. Once the life form is dead, the carbon-14 can only decay, though it takes several hundred years for the decay to be measurable.

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Radiocarbon dating works best for substances that are less than 60,000 years old. If too much time has passed, the amount of carbon-14 falls to levels that are impossible to detect. To determine the age of older substances or non-living minerals, scientists use other radioactive elements such as uranium. As shown in the sidebar, *Decay Chains and Radon*, uranium-238 undergoes a series of decays until it reaches lead-206. While each step in this process has its own half-life, the overall half-life for the entire decay chain is about 4.5 billion years. By comparing the amounts of uranium-238 and lead-206 in ancient rocks, geologists have concluded that approximately one half-life has elapsed since the Earth formed; the age of the Earth is 4.54 billion years.

Glossary

Half-life (radioactive)
The time needed for half of a radioactive substance to decay.

Radiocarbon dating
A method of determining the age of ancient artifacts by measuring the amounts of different carbon isotopes in the artifact.

Unit 12: *Kinetics and Nuclear Chemistry—Rates of Reaction*

Section 9: Lise Meitner and the Discovery of Fission

Lise Meitner (1878–1968) was born in Vienna. As a girl, she was denied admission to secondary school in Vienna. Despite rampant sexism at all levels of academia, she earned her PhD in 1905 and eventually became the first woman professor of physics in Germany in 1926. (Figure 12-16)

Figure 12-16. Lise Meitner

Lise Meitner, along with her nephew, Otto Frisch, discovered the process of nuclear fission and that energy is released when nuclei split.

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In the 1930s, Meitner and her research partner, Otto Hahn (1879–1968), began trying to produce elements heavier than uranium (the heaviest natural element) by bombarding uranium nuclei with neutrons. After Hitler's rise to power, Meitner and many other prominent Jewish scientists fled Germany. Meitner took refuge in Sweden with her nephew Otto Frisch (1904–1979), also a physicist. Hahn continued the experimental work the two had been working on, and corresponded with Meitner about the results. Hahn found a strange result: Bombarding uranium with neutrons did not produce heavier elements at all; in fact, after exposure to neutrons, Hahn found lighter elements (barium and krypton) in the uranium sample. Puzzled, he sent his findings to Meitner in Sweden. She and her nephew concluded that neutron bombardment made uranium nuclei split apart in a process called "**fission**":

$$^{238}_{92}\mathrm{U} + ^{1}_{0}\mathrm{n} \rightarrow ^{141}_{56}\mathrm{Ba} + ^{92}_{36}\mathrm{Kr} + 3^{1}_{0}\mathrm{n}$$

Meitner and Hahn noticed that the products of the fission reaction had a lower mass than the reactants. This startling result, which seemingly contradicts the Law of Conservation of Mass, occurs because some of the mass is converted into energy according to Albert Einstein's famous equation $E = mc^2$.

Protons and neutrons release energy when they cluster together to make a nucleus because this nuclear formation is a more stable arrangement than having all the particles separate. The energy released is called the "**binding energy**," and the more stable the resulting nucleus, the more energy is given off. Because nickel and iron are the most stable of all the nuclei, they also have the greatest binding energies. (Figure 12-17)

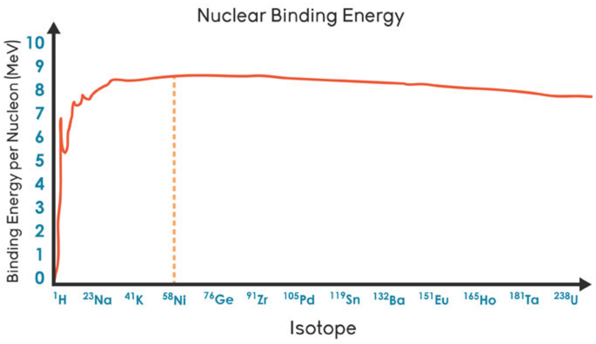

Figure 12-17. Nuclear Binding Energy

A graph of nuclear binding energy for selected nuclei. Note how the nuclear binding energy per nucleon is highest for nickel, which is why nickel and iron are the two most stable elements.

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Where does this energy come from? Energy cannot be created from nothing, and in this case the energy is created from the particles themselves. Some of the mass in the particles is converted into energy—this means that the particles themselves become lighter. The amount of mass lost is called the "**mass defect**." So, the mass of a carbon nucleus (12.00000 u) is actually less than the sum of six protons and six neutrons (12.09894 u); the mass defect of carbon is 0.09894 u, or approximately 0.82 percent. The more stable the nucleus, the greater the binding energy, and the greater the mass defect. Any nuclear reaction in which the products have a higher mass defect/binding energy than the reactants will release energy.

Uranium fission is just such a process. Much more energy is released by nuclear reactions than chemical reactions. After the discovery of fission, it wasn't long before scientists began working on how to harness this powerful new source of energy.

Glossary

Binding energy
The energy released when a nucleus is broken into individual protons and neutrons.

Fission
The splitting of an atomic nucleus into smaller particles.

Mass defect
The mass lost by nuclear particles when they come together to form a nucleus.

Unit 12: *Kinetics and Nuclear Chemistry—Rates of Reaction*

Section 10: The Development of Nuclear Weapons

When a neutron causes a uranium-235 nucleus to undergo fission, three more neutrons are released along with the energy and the smaller nuclei (Figure 12-18). The equation is shown below:

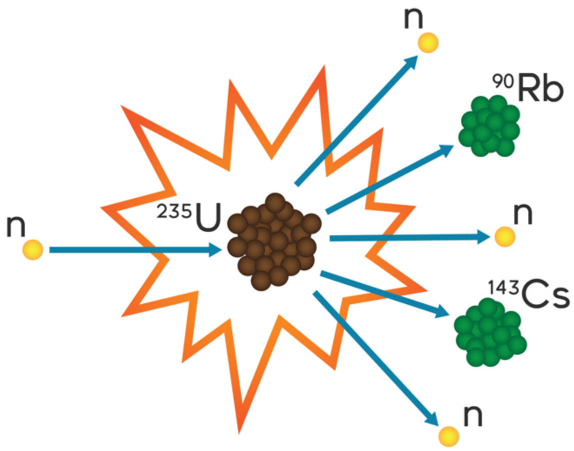

Figure 12-18. Neutron-Induced Fission of Uranium-235

When a neutron strikes a uranium-235 nucleus, it causes it to undergo nuclear fission. Along with energy, three neutrons and two smaller nuclei are produced.

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$${}^{1}_{0}n + {}^{235}_{92}U \rightarrow 3\,{}^{1}_{0}n + {}^{90}_{37}Rb + {}^{143}_{55}Cs$$

If those neutrons go on to strike other uranium nuclei, those nuclei split and produce more neutrons, which split more nuclei, which makes more neutrons, which split more nuclei, and so on—a fission **chain reaction** occurs. Shortly after Meitner and Hahn's discovery of neutron-induced fission, physicists Leó Szilárd (1898–1964) and Enrico Fermi (1901–1954) found that fission chain reactions can and do occur in uranium. Recognizing the potential for such a chain reaction to be used as a bomb, Szilárd and Albert Einstein wrote a letter to President Franklin D. Roosevelt warning that the Nazis might be working along these lines, and they urged the president to begin a competing research effort to construct an atomic bomb first. Headed by J. Robert Oppenheimer (1904–1967), the Manhattan Project called on the best physicists and engineers from top universities across the United States.

Working for the Manhattan Project, Fermi and Szilárd created the first manmade fission chain reaction in 1942 near the old football stadium at the University of Chicago. Uranium and graphite bricks were stacked together into a "nuclear pile," and the chain reaction was allowed to run for 28 minutes with very little in the way of safety precautions. Having proved that fission chain reactions were possible, research in the Manhattan Project proceeded to weaponize the technology.

After five years of strenuous effort, the team detonated the first nuclear bomb in the New Mexico desert on July 16, 1945. Less than a month later, on August 6 and 9, the United States destroyed the Japanese cities, Hiroshima and Nagasaki, with atomic bombs. Japan surrendered to the Allies on August 15, ending World War II.

Two veterans of the Manhattan Project, Edward Teller (1908–2003) and Stanislaw Ulam (1909–1984) went on to develop the next generation of nuclear weapons: weapons powered by nuclear **fusion** instead of nuclear fission. Nuclear fusion happens when two small nuclei come together to form a larger one, as in the following reaction:

$$^{1}_{1}\text{H} + ^{3}_{1}\text{H} \rightarrow ^{4}_{2}\text{He}$$

This process also releases an enormous quantity of energy. In fact, fusion releases much more energy than fission, and fusion bombs (called "hydrogen bombs" or "H-bombs") are thousands of times more powerful than fission bombs. (Figure 12-19)

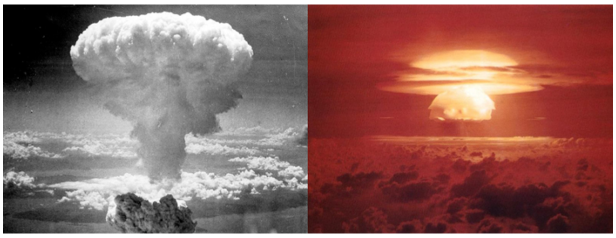

Figure 12-19. Atomic Bomb (Nuclear Fission) vs. Hydrogen Bomb (Nuclear Fusion)

Fusion releases much more energy than fission. The Fat Man A-bomb blast over Nagasaki (15 kilotons) is shown on the left. Castle Bravo H-bomb test (15 megatons) is shown on the right.

© Left: Wikimedia Commons, Public Domain. Right: Wikimedia Commons, Public Domain.

For two nuclei to get close enough to fuse, they must be moving extraordinarily fast; fusion reactions require very high temperatures to occur. A fission reaction generates the necessary heat, so a fusion bomb is actually two bombs in one. A small fission bomb explodes first, which heats up enough hydrogen to make it fuse.

Fusion reactions also power the stars; the sun is an enormous fusion reactor. Small atoms such as hydrogen and helium fuse inside the sun, making larger atoms and releasing huge quantities of heat and light.

Glossary

Chain reaction

A reaction in which the products cause further reactions to take place.

Fusion

The combining of smaller atomic nuclei to make a larger nucleus.

Unit 12: *Kinetics and Nuclear Chemistry—Rates of Reaction*

Section 11: Critical Mass and Nuclear Reactors

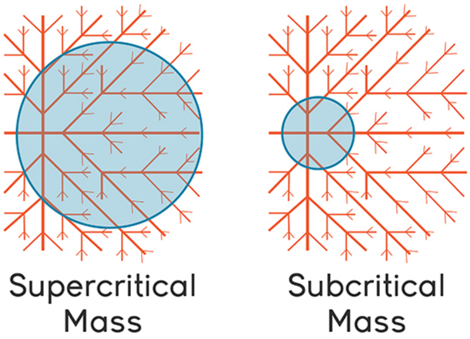

Figure 12-20. Subcritical Mass and Supercritical Mass

In a supercritical mass, neutrons produced by fission have a high probability of causing subsequent fission reactions. In a subcritical mass, the neutrons escape the material without causing more fission. Every time there is a red branch, more neutrons are formed. Note how the size of the subcritical mass in blue only allows three fission reactions creating neutrons as compared to many more within the blue area for the supercritical mass.

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A chain reaction will only be self-sustaining if the piece of fissile material is large enough. If it is too small, the neutrons end up flying out into empty space instead of colliding with nuclei inside. The amount needed to sustain the reaction is called the "**critical mass**." A smaller amount is termed a "**subcritical mass**"; a larger amount is called a "**supercritical mass**." (Figure 12-20)

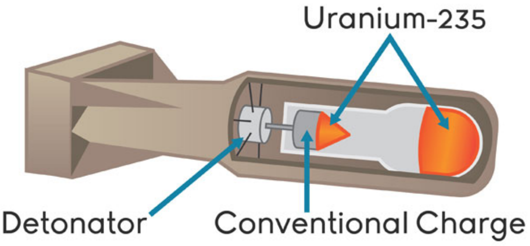

Figure 12-21. Diagram of an Atomic Bomb

The two subcritical masses of uranium-235 are kept separate until the moment of detonation.

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A nuclear bomb starts with two or more subcritical masses of uranium or plutonium. As soon as they are brought together, they form a supercritical mass, which explodes.

For the bomb to work, the subcritical masses must be propelled together extremely rapidly. This is done with a conventional (non-nuclear) explosive. (Figure 12-21)

A fission reaction can be slowed down to a consistent, stable rate; it doesn't have to happen all at once as in an explosion. This is what happens in a nuclear reactor; a controlled fission reaction generates electricity. The nuclear fuel is composed of uranium pellets inside metal tubes called "fuel rods." Each fuel rod is undergoing some fission, sending neutrons to neighboring rods, and causing their atoms to undergo fission.

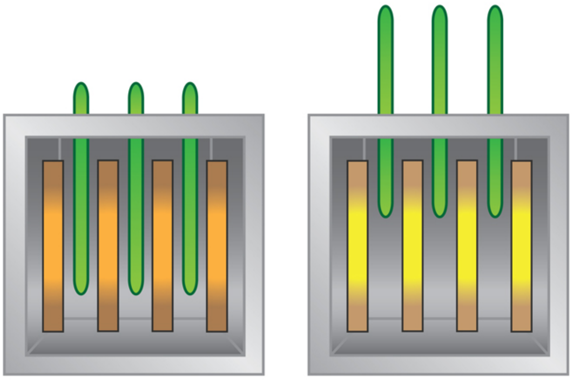

Figure 12-22. Fuel Rods and Control Rods

Lowering the control rods in a reactor core slows the reaction. Raising them allows the reaction to speed up and generate heat.

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If nothing intervened, the chain reaction could rapidly speed up and get out of control; the fuel rods would overheat and cause a meltdown. To slow down the rate of reaction, control rods are lowered between the fuel rods. The control rods are made out of a material that can absorb neutrons such as graphite. When the control rods are between the fuel rods, the neutrons of one fuel rod cannot cause as much fission in a neighboring fuel rod, and the whole reaction slows down. (Figure 12-22)

The fuel rods and the control rods make up the core of a nuclear power plant. When the reactor is active, the fission chain reaction heats a liquid coolant surrounding the rods. The hot coolant is pumped through pipes to boil water in the steam generator; the pressurized steam flows through the steam line to the turbine, which powers the generator. The steam is then cooled and condensed by water from the cooling tower, and then pumped back to the steam generator. (Figure 12-23)

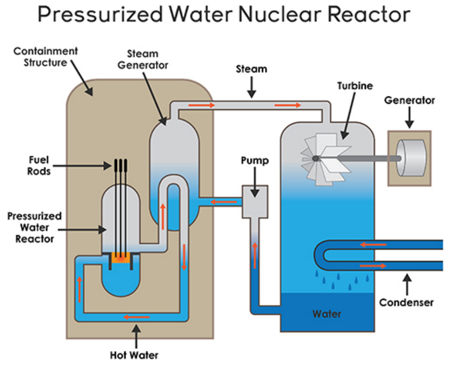

Figure 12-23. Schematic of a Nuclear Power Plant

This schematic shows how power is generated and transferred in a pressurized water reactor.

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Glossary

Critical mass

The minimum amount of a substance needed to sustain a fission chain reaction.

Subcritical mass

An amount of a fissile material below the critical mass.

Supercritical mass

An amount of a fissile material above the critical mass.

Unit 12: *Kinetics and Nuclear Chemistry—Rates of Reaction*

Section 12: Conclusion

Understanding the factors that influence the rates of chemical reactions is critical to the progress of many other scientific fields. Controlling the rates of reaction is of paramount importance in industrial and biological systems. The concept of half-life that we explored in terms of kinetics extends to other areas of science as well, including nuclear decay. Over the past century, discoveries in radioactivity and nuclear physics have revolutionized widely disparate fields, from archeology (radiometric dating) to medicine (medical imaging and cancer treatment), from power generation (nuclear reactors) to geopolitics (atomic and hydrogen bombs).

Unit 12: *Kinetics and Nuclear Chemistry—Rates of Reaction*

Section 13: Further Reading

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