Chemistry and Hazards of Hazardous Materials and Weapons of Mass Destruction

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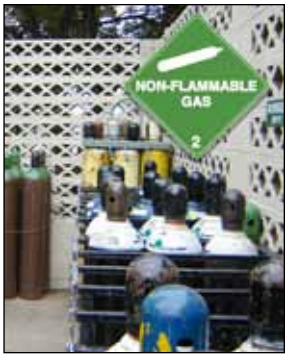
Chemistry and Hazards of Hazardous Materials and Weapons of Mass Destruction

Learning Objectives

1. Define atoms.
2. Describe the basic arrangement of the periodic table of elements.
3. Explain the four significant families of elements.
4. Describe matter. [NFPA® 472, 7.2.2.2(10, 36, 44)]
5. Explain the concept of bonding. [NFPA® 472, 7.2.2.2(24, 25)]
6. Explain the various types of reactions. [NFPA® 472, 7.2.2.2(7-8, 23, 37)]
7. Describe common families of hazardous materials. [NFPA® 472, 7.2.2.2(2, 4, 9, 13, 27, 31, 41, 42)]
8. Identify special hazards of chemicals and weapons of mass destruction. [NFPA® 472, 7.2.2.2 (4, 5, 26, 30, 33, 40, 52)]
9. Discuss radiation. [NFPA® 472, 7.2.1.4, 7.2.2.2(20)]

Chapter 4

Chemistry and Hazards of Hazardous Materials and Weapons of Mass Destruction



Case History

A cargo tank carrying styrene was involved in a serious accident on a busy highway in a highly populated area. A haz mat team was called to the scene. Visual assessments and detection and monitoring determined that the tank had not breached and no leaks had occurred.

The chemical company responsible for shipping the styrene was contacted, and it was determined that the styrene was shipped with a time-sensitive inhibitor. This meant that the natural polymerization of the styrene would eventually overcome the inhibitor, potentially resulting in a rapid, runaway polymerization reaction. This set a timetable for mitigation of the incident that was under 24 hours.

Plans for a worst-case scenario were developed and preliminary evacuations conducted. Until the chemical shipper's own emergency response personnel arrived at the scene to take over, the haz mat team monitored the tank with a temperature gun to detect any rapid changes in temperature that might indicate an accelerating reaction.

While it is not critical for hazardous materials technicians to be chemistry experts, some knowledge of chemistry can help hazardous materials technicians comprehend how and why chemicals behave the way they do. This is an important skill-set, especially when reference sources are not immediately available.

This chapter provides a brief and basic introduction to chemistry — enough to address terminology and concepts that will make it easier to understand the behavior of hazardous materials. As much as possible, these concepts are presented in terms of what it means to the hazardous materials technician in the field. For example, the Periodic Table of Elements (also known as the Periodic Table) is examined to provide clues that may help responders predict how various elements will behave.

Examples provided in the chapter are used to illustrate concepts and are not meant to be all-inclusive. For instance, in presenting the Periodic Table of Elements, the chapter highlights four "families" of elements that have similar characteristics and then explores one or two elements within each family.

Out in the field, hazardous materials technicians must be diligent about checking reference sources rather than relying solely on generalizations in this book or any other.

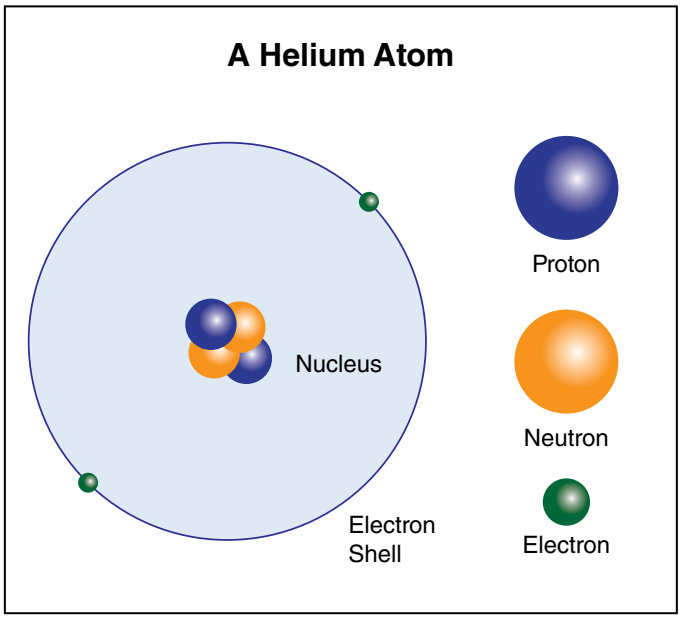


Figure 4.1 A helium atom has two protons, two neutrons, and two electrons in the electron shell. Because it has the same number of protons and electrons, it is electrically neutral.

This chapter explores the following topics:

- Atoms and molecules
- The Periodic Table of Elements
- Four significant families
- Matter
- Bonding
- Reactions
- Common families of hazardous materials
- Radiation

Atoms

The basic building block of any substance is the **atom**. Every element and compound is made up of one or more atoms. Each atom consists of several different parts. At the center of the atom is a **nucleus** or core consisting of **protons**, which are positively charged, and **neutrons** that have no charge. **Electrons** orbit the nucleus. These electrons reside in **shells**, sometimes called *orbits*, *orbitals*, or *rings* **(Figure 4.1)**. How elements interact with one another is primarily a function of their electrons. A pure atom of an element has the same number of protons and electrons and the atom is electrically neutral.

Atom — Basic unit of matter consisting of a nucleus surrounded by a cloud of electrons.

Nucleus — Center of an atom, consisting of protons and neutrons.

Proton — Subatomic particle that possesses a positive electric charge.

Neutron — Part of the nucleus of an atom that has a neutral electrical charge and a mass slightly larger than a proton.

Electron — Minute component of an atom that possesses a negative charge.

Shells — The distance or orbit of electrons around the nucleus; shape of the electron cloud. *Also known as* Orbits, Orbitals, or Rings.

Elements differ from one another by the number of protons in the nucleus. For example, hydrogen always has one proton in its nucleus, oxygen always has eight protons, and sulfur always has sixteen protons. Some elements have an equal number of protons and neutrons, but it is not unusual for elements to have more neutrons than protons. For example, sodium (atomic number 11) has eleven protons and twelve neutrons. Hydrogen, the smallest of all elements, is an oddity; its dominant form has one proton but no neutrons **(Figure 4.2)**.

The atomic number of an element is the number of its protons. The number of protons always equals the number of electrons in an atom. The atomic mass is the weight of an atom. It is determined by the number of neutrons and protons that are present in the nucleus.

Periodic Table of Elements

The *Periodic Table of Elements* is a tool for organizing and displaying the **elements** in a way that provides some basic information about their characteristics. The first 92 elements are found in nature and the remainders are manmade. As such, the periodic table continues to evolve as new elements are created and named. **Figure 4.3, p. 148,** is one version of the table that is commonly used. There are other tables that show different numbers of elements, but the differences that exist between periodic tables are not significant to the hazardous materials technician because they involve elements not likely to be encountered.

Once the organization of the periodic table is understood, it can be used quickly to obtain a wealth of information about any of the more than 112 elements. However, to realize its full potential as a valuable chemical resource, it is necessary to understand its organization. The elements of the periodic table are arranged horizontally by order of increasing atomic number. Notice that the

table consists of several horizontal rows. These horizontal rows are called *periods*. The vertical rows found in the periodic table are called *groups*, or *families* **(Figure 4.4, p. 149)**. Elements within a specific group have similar chemical properties. As discussed in the next section, the similar chemical properties of elements within a group occur because these elements have the same number of electrons in their outer shells. These groups can be divided into three categories: metals, nonmetals, and metalloids. The diagonal line (that resembles a staircase) in the right side of the periodic table separates the metals from the nonmetals **(Figure 4.5, p. 150)**.

Each element in the periodic table is identified by name, symbol, atomic number, and atomic weight **(Figure 4.6, p. 151)**. A key feature of the periodic table is the dividing line between metals and nonmetals **(Figure 4.7, p. 151)**. Metals are located on the left side of the periodic table; nonmetals are located on the right. (Hydrogen, which is located in the upper-left corner above the thick dividing line, is also a nonmetal.) Metalloids and semiconductors are the materials that straddle that line. Elements 113 through 118 are artificial or synthetic elements created in laboratories.

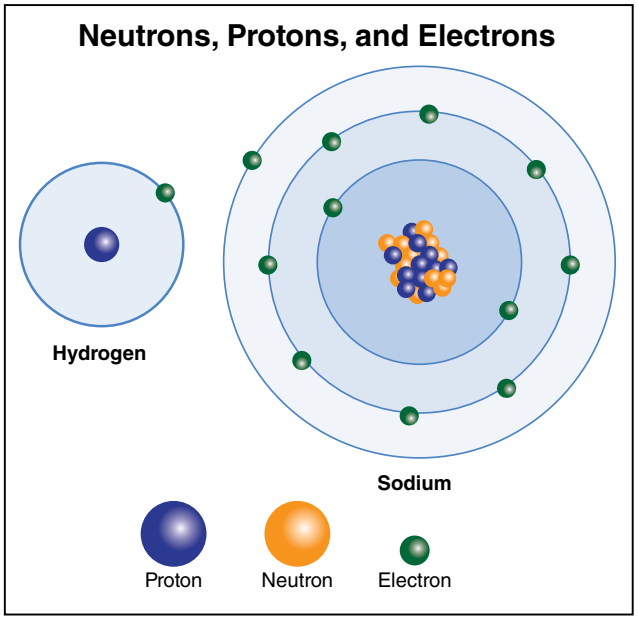


Figure 4.2 The atomic number of an element is the same as its number of protons, so hydrogen is 1, and sodium is 11. This is also the number of electrons. The number of protons and neutrons do not always match.

Element — Most simple substance that cannot be separated into more simple parts by ordinary means.

Elements are arranged in the periodic table in order by atomic number. However, for the most part, as the atomic number increases, so does the atomic weight. Therefore, when considering the hazardous properties of individual elements, the hazardous materials technician can predict that elements lower on the periodic table will be solids and those higher on the table will be gases **(Figure 4.8, p. 152)**. The weight of an element or compound becomes important when evaluating vapor density, specific gravity, and other related properties.

There are three major regions or areas on the periodic table. The representative elements on either side of the table are the most important to the study of hazardous materials. As a category, they are more chemically active and encountered more often than the transition metals and the rare earth elements.

Four Significant Families

Elements are arranged vertically in groups called *families* based on their chemical structure. All members of the same family have similar chemical characteristics, though each has unique properties. Four families are significant because they are the most predictable **(Figure 4.9, p. 152)**:

- Group I — Alkali metals
- Group II — Alkaline earths
- Group VII — Halogens
- Group VIII — Noble gases

Hazardous materials technicians can make generalizations about elements that comprise each family prior to — *not in lieu of* — checking reference sources and trust that the differences between the elements are not so significant that anyone will be led astray. **Table 4.1, p. 153,** provides a summary of the four families. The following briefly describes each family with one or two specific examples.

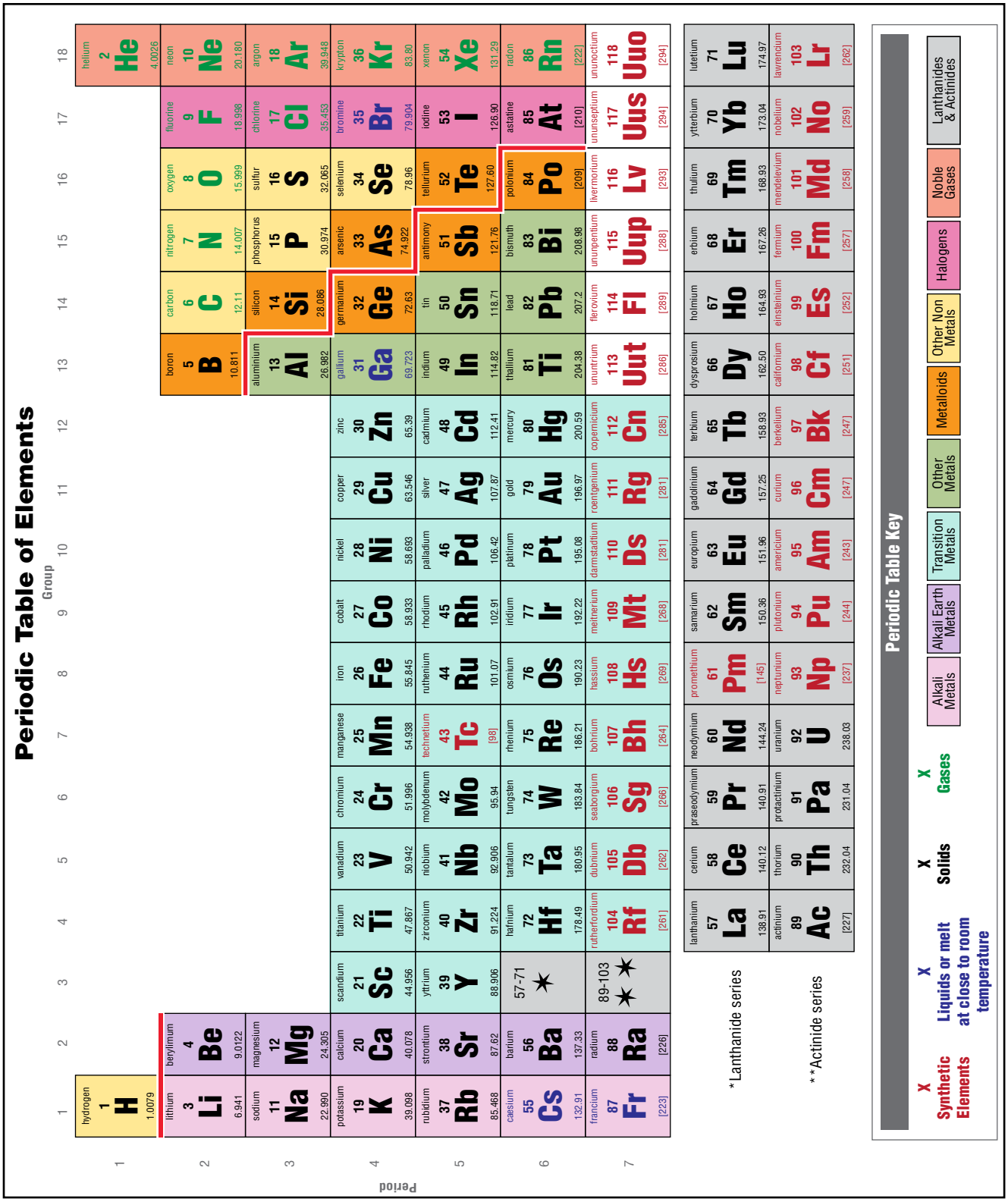


Figure 4.3 The Periodic Table provides a wealth of information about the elements including their atomic number, atomic weight, name, atomic symbol, group, period, and state of matter.

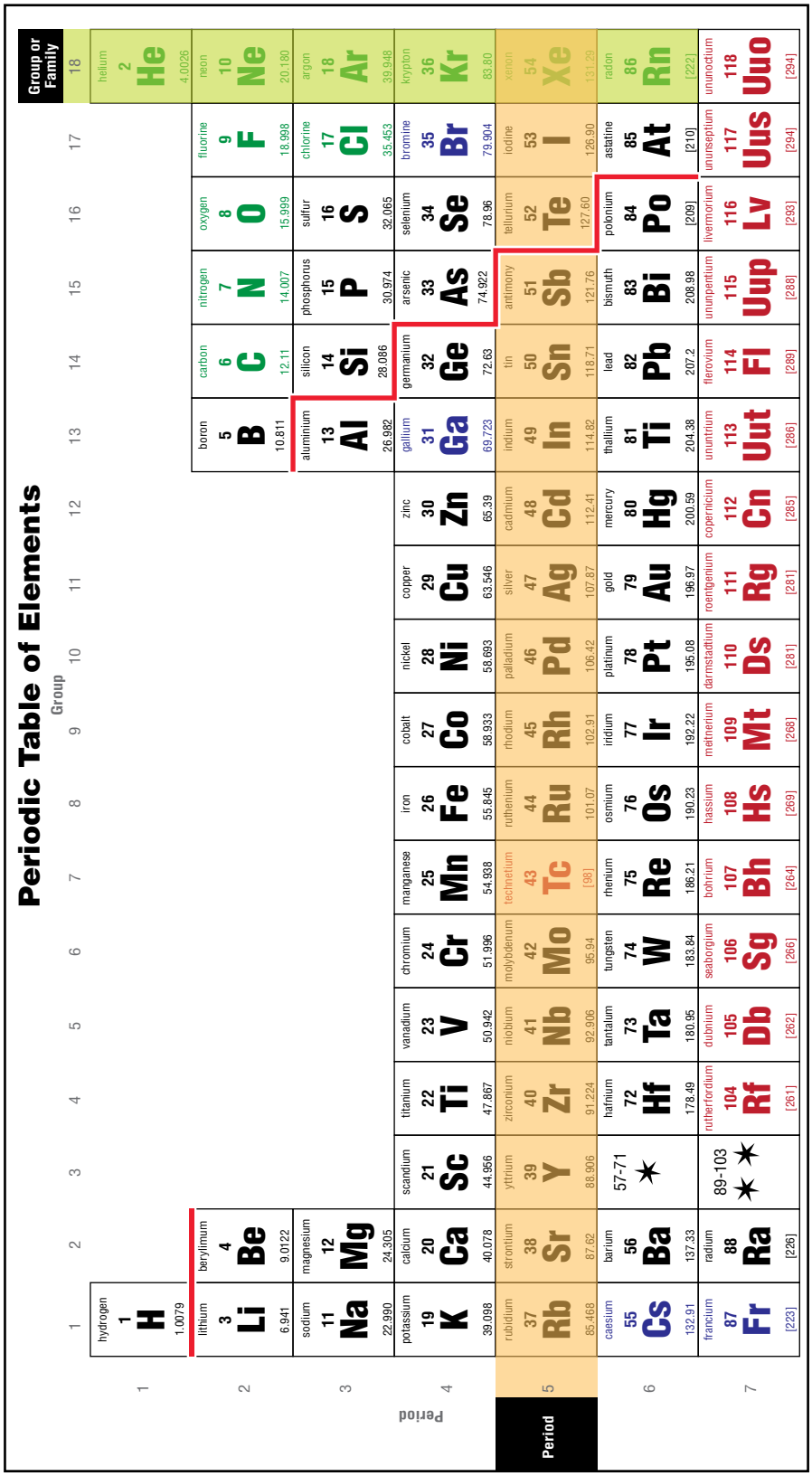


Figure 4.4 Horizontal rows are called periods, while vertical rows are called groups or families. Families and groups have similar chemical properties.

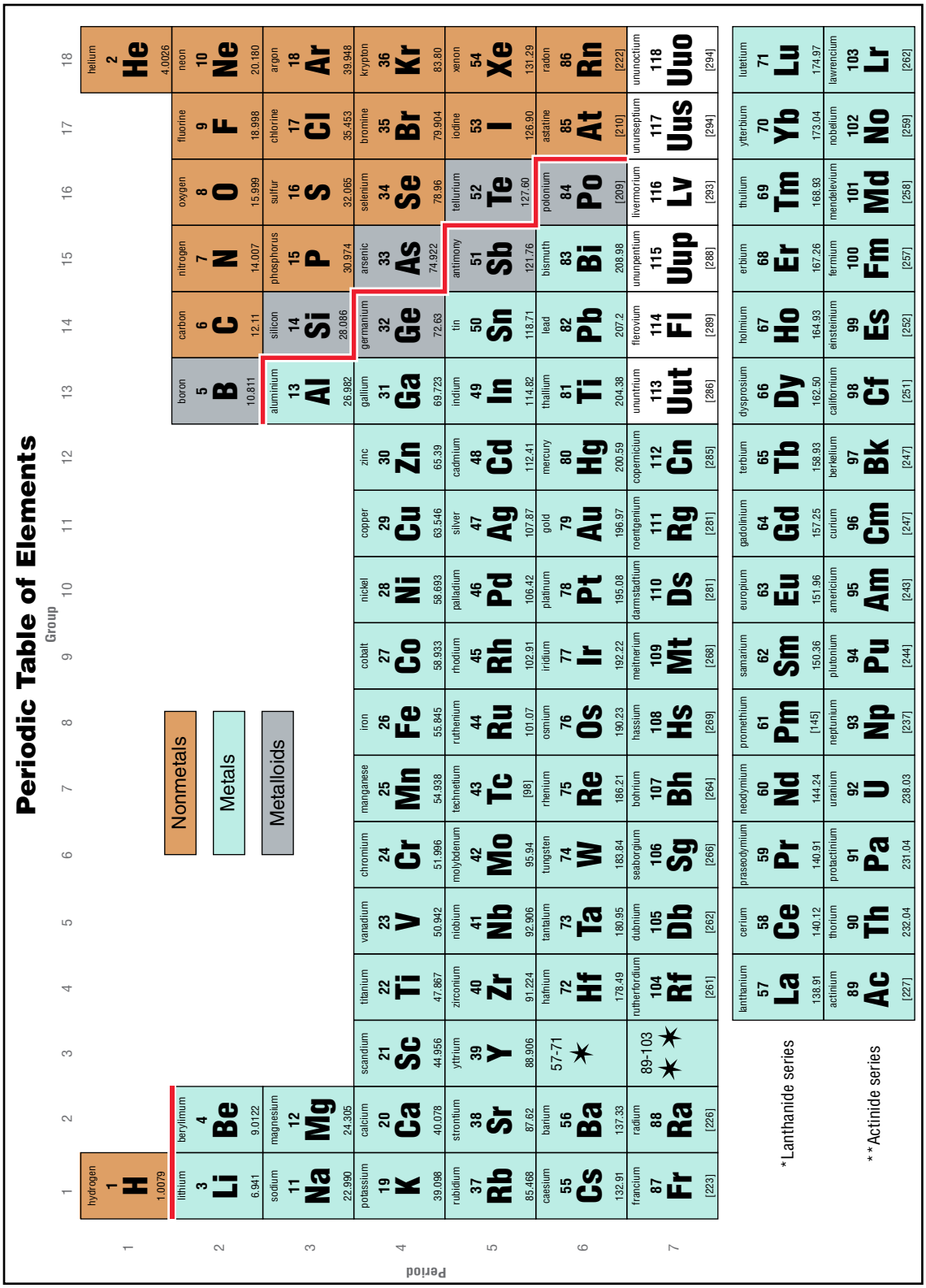


Figure 4.5 The majority of elements are metals, represented in green, and the nonmetals are represented in orange. The metalloids, represented in gray, may exhibit chemical properties of both.

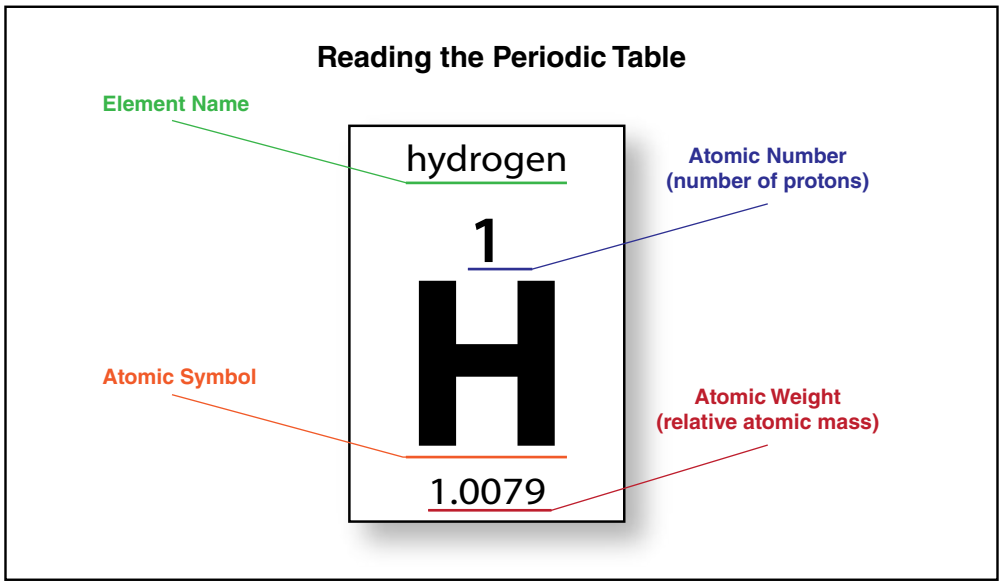


Figure 4.6 Each box in the table shows the element's name, atomic symbol, atomic number, and atomic weight.

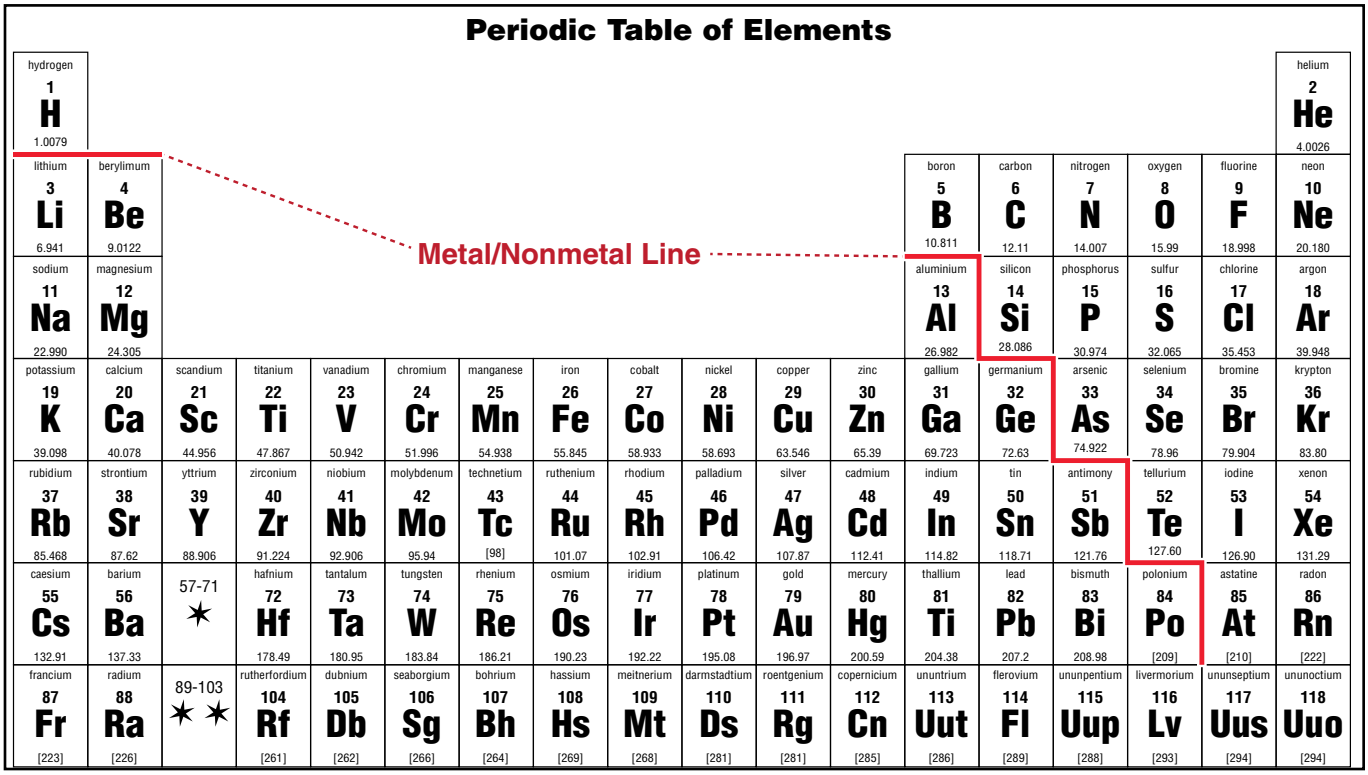


Figure 4.7 The red line separates metals and nonmetals. Hazardous materials involving elements from above the line often present challenges to emergency responders, for example, chlorine.

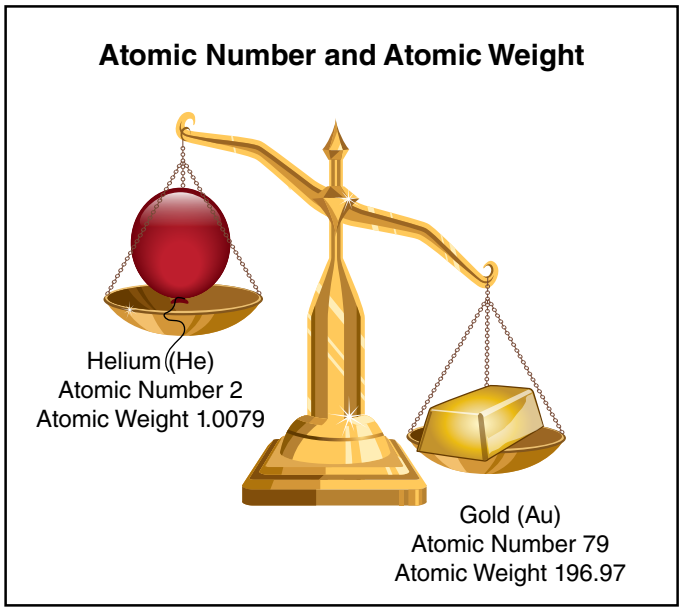


Figure 4.8 Typically, the atomic number is a reflection of the atomic weight; the lower the number, the lighter it is. The element's weight will affect its behaviors and properties including such factors such as state of matter, vapor density, and specific gravity.

Periodic Table of Elements
Four Families

I	II															VII	VIII
hydrogen 1 H 1.0079																	helium 2 He 4.0026
lithium 3 Li 6.941	berylimum 4 Be 9.0122											boron 5 B 10.811	carbon 6 C 12.11	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305											aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.63	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
caesium 55 Cs 132.91	barium 56 Ba 137.33	57-71 ✶	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Ti 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
francium 87 Fr [223]	radium 88 Ra [226]	89-103 ✶ ✶	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	darmstadtium 110 Ds [281]	roentgenium 111 Rg [281]	copernicium 112 Cn [285]	ununtrium 113 Uut [286]	flerovium 114 Fl [289]	ununpentium 115 Uup [288]	livermorium 116 Lv [293]	ununseptium 117 Uus [294]	ununoctium 118 Uuo [294]

Figure 4.9 The Roman numerals at the top of the colored columns designate the four significant families: Group I, the alkali metals; Group II, the alkaline earths; Group VII, the halogens; and Group VIII, the noble gases.

Table 4.1
Four Families Summary

Group	Name	Elements	Characteristics
I	Alkali Metals	Lithium Sodium Potassium Rubidium Cesium Franium	• Highly reactive • In contact with water, produce: – Hydrogen gas – Strong caustic runoff – Excessive heat
II	Alkaline Earths	Beryllium Magnesium Calcium Strontium Barium Radium	• Often water reactive • Burn intensely
VII	Halogens	Fluorine Chlorine Bromine Iodine Astatine	• Highly reactive • Highly toxic • Nonflammable, but powerful oxidizers
VIII	Noble Gases	Helium Neon Argon Krypton Xenon Radon	• Inert gases • Nonreactive but simple asphyxiants • Often stored/transported as cryogenic liquids

Group I – The Alkali Metals

Group I - The alkali metals include lithium, sodium, potassium, rubidium, cesium, and francium **(Figure 4.10, p. 154)**. These elements are highly reactive. Reactivity increases with the elements lower down in the column. When these elements come in contact with water, they produce flammable hydrogen gas, a strong caustic runoff, and excessive heat. This heat may be enough to ignite the hydrogen.

Sodium and potassium are the most common of the alkali metals. Both are very water-reactive, enough to ignite the hydrogen spontaneously if exposed to moist air **(Figure 4.11, p. 154)**. Small pieces (pea size) of sodium will move

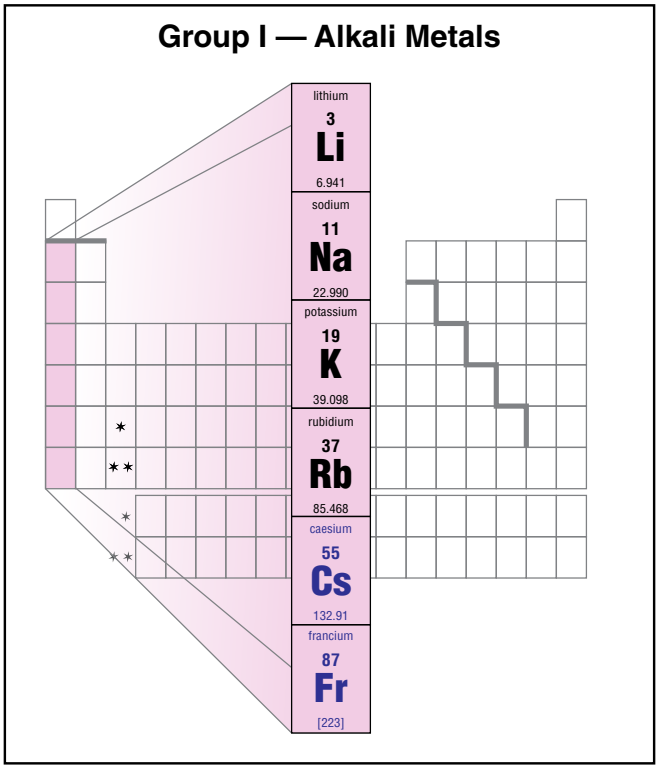


Figure 4.10 The alkali metals include lithium, sodium, potassium, rubidium, cesium, and francium, all highly reactive.

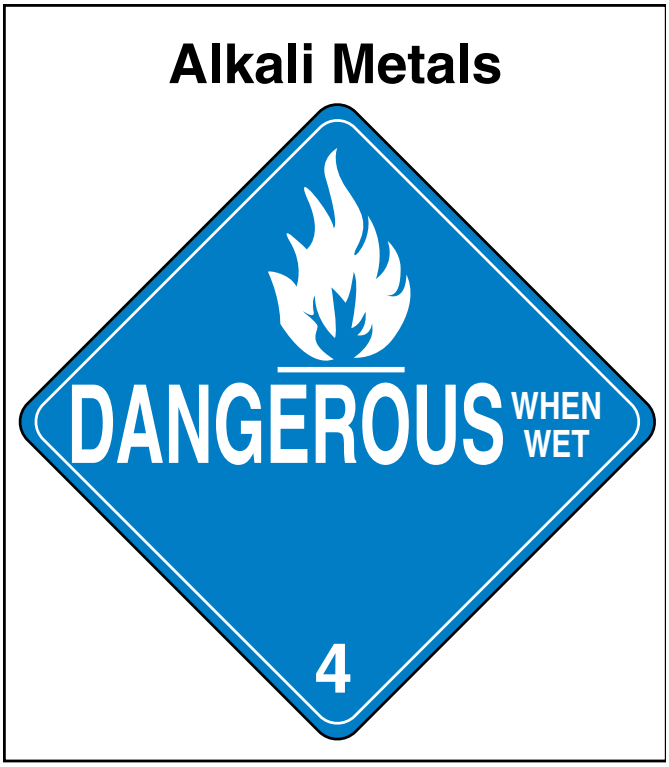


Figure 4.11 Alkali metals are dangerous when wet.

around quickly on top of the water, while larger pieces will generally explode. These metals are usually stored under kerosene or in vacuum-packed containers to prevent exposure to air or water.

Contact between these metals and water separates or disassociates the water molecules, allowing other compounds to be formed from the individual elements. Sodium and potassium combine with free oxygen and hydrogen atoms to form sodium hydroxide (NaOH) and potassium hydroxide (KOH) solutions, respectively. Both are very corrosive. Another by-product of the reaction in both cases is hydrogen gas (H_2), which is highly flammable. The reaction with water is so violent that it generates enough heat to melt the metal, ignite the hydrogen gas, and ignite nearby combustibles. Special extinguishing agents must be used on fires involving alkali metals to avoid intensifying the fire.

Group II – The Alkaline Earths

Group II - The alkaline earths (metals) include beryllium, magnesium, calcium, strontium, barium, and radium **(Figure 4.12)**. These are often water-reactive, though less so than the alkali metals (Group I).

Magnesium, a metal often found in machine shops, burns very intensely with such a bright white flame that staring at it can cause retinal damage. With an ignition temperature of 1202°F (650°C), magnesium does not ignite easily. However, the risk of ignition increases in proportion with the amount of surface area exposed to air. In other words, magnesium powder, dust, chips, and shavings are far more dangerous than a solid block of magnesium. Magnesium powder can explode on contact with water depending on how oxidized the metal is.

Magnesium is very water-reactive when burning. Water used as an extinguishing agent intensifies the fire because it has been broken down to an oxidizer (oxygen) and a fuel (hydrogen). Water molecules that are not separated can be instantly converted to steam by the heat of the fire, resulting in a steam explosion **(Figure 4.13)**. Both of these possibilities are dangerous for emergency responders. Flooding with large amounts of water can cool fires involving solid blocks of magnesium, but most magnesium fires require the application of special extinguishing agents.

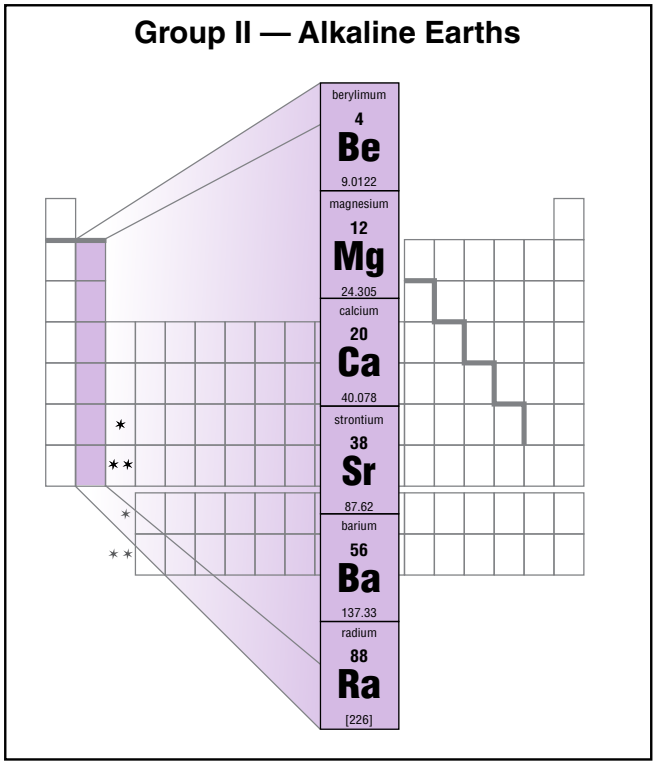


Figure 4.12 The alkaline earths are beryllium, magnesium, calcium, strontium, barium, and radium. These are often dangerous when wet, but less so than the alkali metals.

Group VII – The Halogens

Group VII - The halogens include fluorine, chlorine, bromine, iodine, and astatine (a very rare element) **(Figure 4.14, p. 156)**. These elements are highly reactive and toxic **(Figure 4.15, p. 156)**. They are nonflammable but are powerful oxidizers that support combustion.

Chlorine is the most common of the halogens. Its characteristic suffocating odor is easy to recognize. What makes chlorine so toxic is that the gas reacts with moisture in the respiratory system to form corrosive hydrochloric acid (HCl) and hypochlorous acid (HOCl). It reacts the same way with moisture on the skin, which is why chemical protective clothing is more appropriate than structural fire fighting clothing for handling chlorine emergencies in the hot zone. Fluorine, another halogen, reacts with water to form hydrofluoric acid (HF) and hydroflourous acid, which are even more destructive to human tissue.

While chlorine and fluorine do not burn, they are such powerful oxidizers that fires can burn intensely in the presence of chlorine or fluorine even when no oxygen is present.

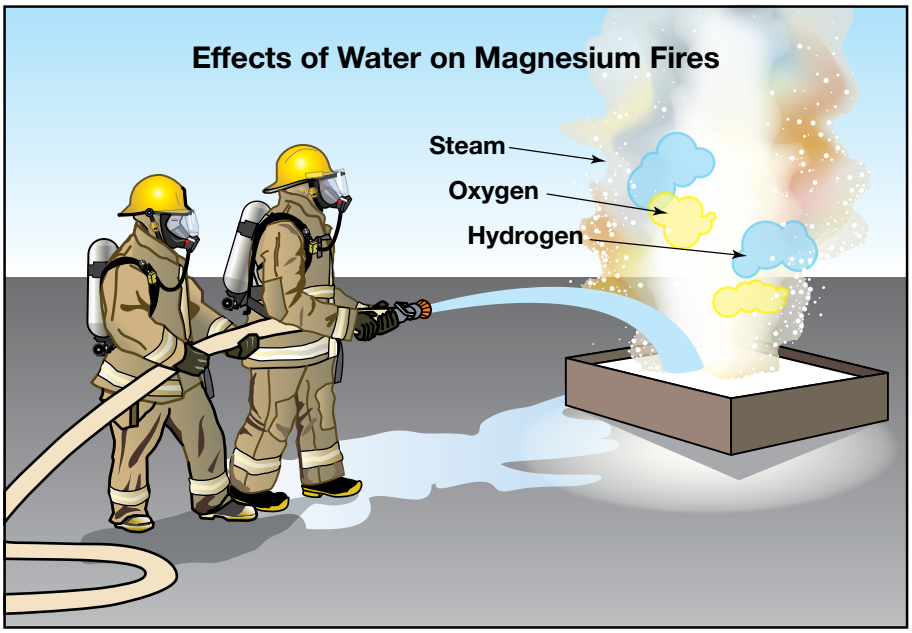


Figure 4.13 Magnesium is extremely water-reactive when burning.

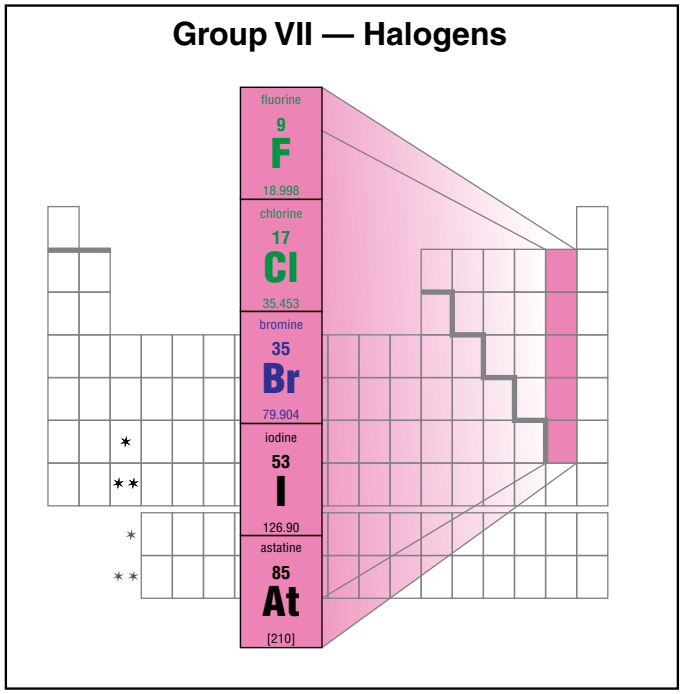


Figure 4.14 The halogens include fluorine, chlorine, bromine, iodine, and astatine.

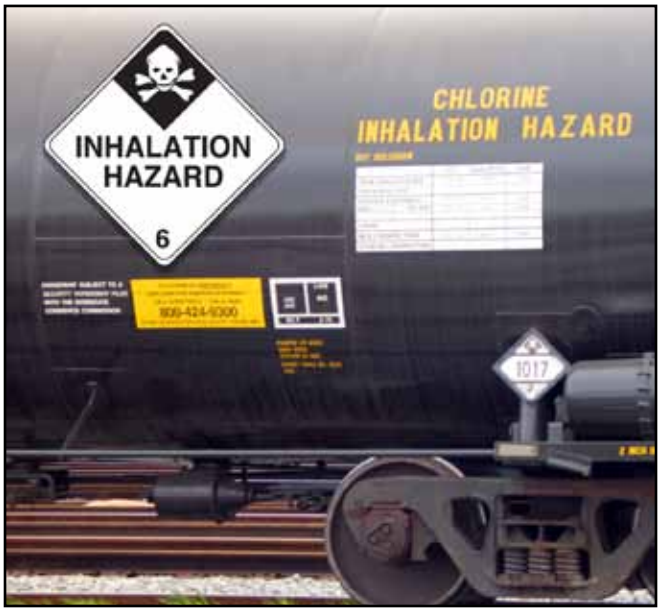


Figure 4.15 Halogens are highly toxic and reactive. Although they don't burn, they are oxidizers that support combustion. *Courtesy of Rich Mahaney.*

Inert Gas — Gas that does not normally react chemically with another substance or material; any one of six gases: helium, neon, argon, krypton, xenon, and radon.

Group VIII – The Noble Gases

Group VIII - The noble gases include helium, neon, argon, krypton, xenon, and radon **(Figure 4.16)**. These are **inert gases**, nonreactive but simple asphyxiants that are often stored and transported as cryogenic liquids **(Figure 4.17)**.

Among these, helium is familiar to responders and the public alike. It is not toxic or flammable and will not react with other materials. However, an uncontrolled release of helium, like any other noble gas, can still cause significant problems. When gas expands to fill an enclosed space, such as a small room, it will displace oxygen in the environment. Like all noble gases, helium can asphyxiate anyone who is unable to get an adequate supply of fresh air.

Helium, like the other noble gases, is often transported as a cryogenic liquid. The U.S. DOT establishes cryogenic liquids as those colder than -130°F (-90°C). These extremely cold products can cause immediate and severe damage to human tissue and other materials such as steel, rubber, and plastic.

Like all cryogenic liquids, the noble gases in cryogenic form have very high expansion ratios. This information is important because, in the event of a leak, there is a significant risk of displacing oxygen in the atmosphere, far greater than the risks associated with a leak from a compressed gas cylinder. There is also a risk of catastrophic container failure in the event of a fire or other scenario where the product temperature is elevated beyond the capacity of pressure-relief devices.

Matter

As discussed in Chapter 3, there are three primary states (or *phases*) of matter: solid, liquid, gas **(Figure 4.18)**. A fourth state of matter, plasma, begins as a gas. However, the gas is modified at the atomic level by the application of energy, often in the form of electricity. Extra energy applied to the gas causes some

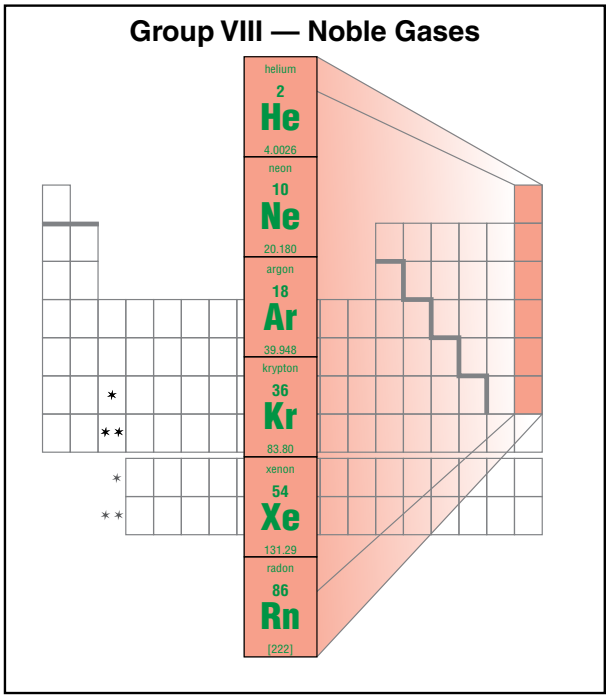


Figure 4.16 Noble gases include helium, neon, argon, krypton, xenon, and radon.

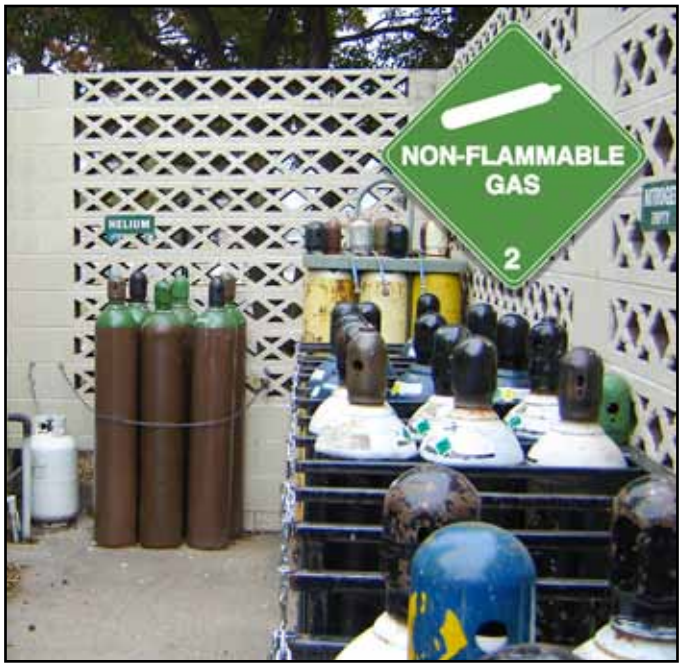


Figure 4.17 Inert gases are nonreactive, but they can cause asphyxiation by displacing the oxygen in confined spaces.

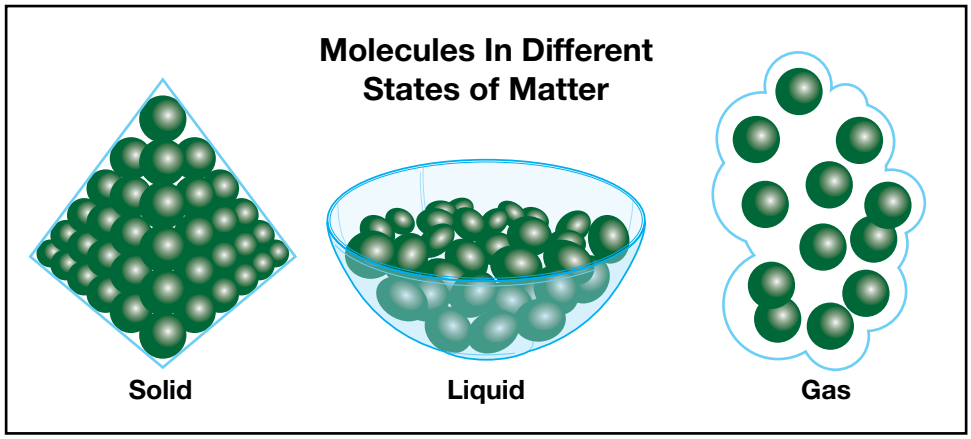


Figure 4.18 The spacing of atoms and molecules in matter is most compact in solid form. They are least compact when a gas. Also, they are least energetic in solid form, and most energetic as a gas.

of the electrons to break away from the atoms, leaving an atmosphere of free electrons and positively and negatively charged particles (or *ions*). The result is a glowing gaseous mass called *plasma*.

Some matter can exist in different states. A perfect example is water. Water is liquid in its natural state and can become a solid (ice) below 32°F (0°C) or a gas (steam) above 212°F (100°C). Temperature is the determining factor, as is the case with many materials that change state. Pressure is sometimes used to cause a change in state, as is the case with liquefied compressed gases. Both temperature and pressure are used to transform gases into cryogenic liquids.

Matter can exist in multiple states at the same hazardous materials incident, such as when a liquefied gas vaporizes as it escapes a breached container. In these instances, the product exists as a liquid inside the container and as a gas outside. Even *within* a container, there may be liquid space at the bottom and a vapor space

at the top — a distinction that impacts the incident. For example, fire impinging on the vapor space stresses a container far more so than fire impinging on the liquid space because the liquid helps absorb the heat whereas vapors do not.

Matter can be classified by physical classification (state of matter) or chemical classification (mixtures and pure substances). Pure substances can be divided into elements and compounds **(Figure 4.19)**. The sections that follow will explore:

- Elements
- Compounds
- Mixtures

Elements

A pure substance may be either a single element (such as sodium, chlorine, hydrogen, or oxygen) or a **compound** (such as sodium chloride or water) that is comprised of two or more elements chemically bonded to form a **molecule**. In other words, compounds can be broken down to release simpler substances (the individual elements), whereas elements cannot be broken down into anything simpler without getting into atomic structure (protons, neutrons, and electrons).

Compound — Substance consisting of two or more elements that have been united chemically.

Molecule — The smallest particle of a substance that retains all the properties of the substance and is composed of one or more atoms.

Diatomic Molecule — Molecules composed of two atoms.

Elements are represented by a single capital letter (e.g., H or O) or by a capital letter followed by a lowercase letter (e.g., Na or Cl). Compounds are represented by formulas showing multiple elements (e.g., NaCl) **(Figure 4.20)**. When the formula contains numbers, it indicates that more than one atom of the same element is present, for example, H_2O **(Figure 4.21)**. However, some elements such as oxygen (O_2), Chlorine (Cl_2) and Nitrogen (N_2) can exist as **diatomic molecules**. The hazardous materials technician may encounter these elements and must be able to recognize them as elements rather than compounds **(Table 4.2)**. As shown in the following sections, elements can be divided into metals, nonmetals, and metalloids.

Metals and Nonmetals

Metals generally have a characteristic lustrous appearance and are good conductors of heat and electricity. They can also be hammered to form sheets or can be drawn into wires. Most metals are solids in their natural states **(Figure 4.22, p. 160)**. Mercury is the only exception.

Nonmetals typically do not have a lustrous appearance and are not good conductors of heat and electricity. They cannot be formed into sheets or wire. All the nonmetals are either solids or gases, with the exception of bromine (Br), which is a liquid **(Figure 4.23, p. 160)**.

While periodic tables show a distinction between metals and nonmetals, some elements do not fit the classic profile of either. The technicalities are beyond the scope of this book. However, it is necessary for hazardous materials technicians to recognize that any discussion of metals and nonmetals must be considered a generalization because exceptions sometimes apply. This is why it is essential to check reference sources at a hazardous materials incident rather than to rely solely on one's knowledge of chemistry.

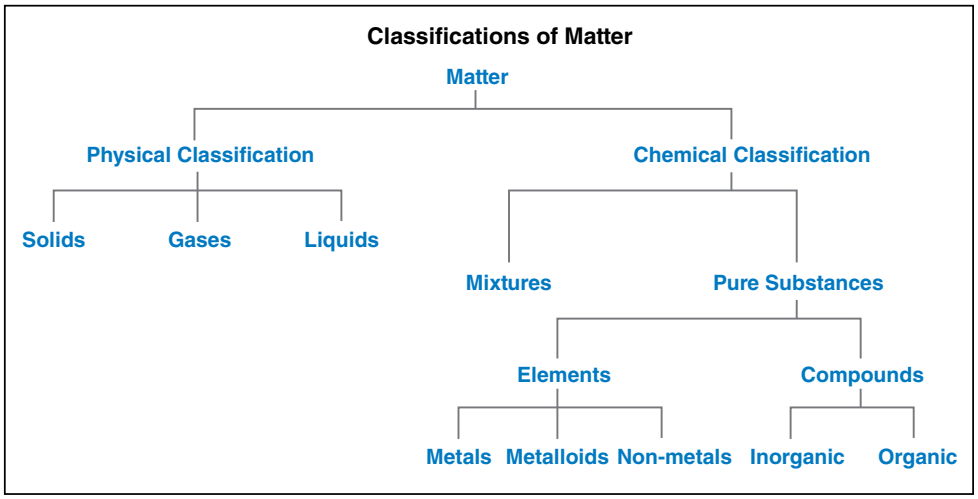


Figure 4.19 There are different ways to classify matter: physical state or chemical composition.

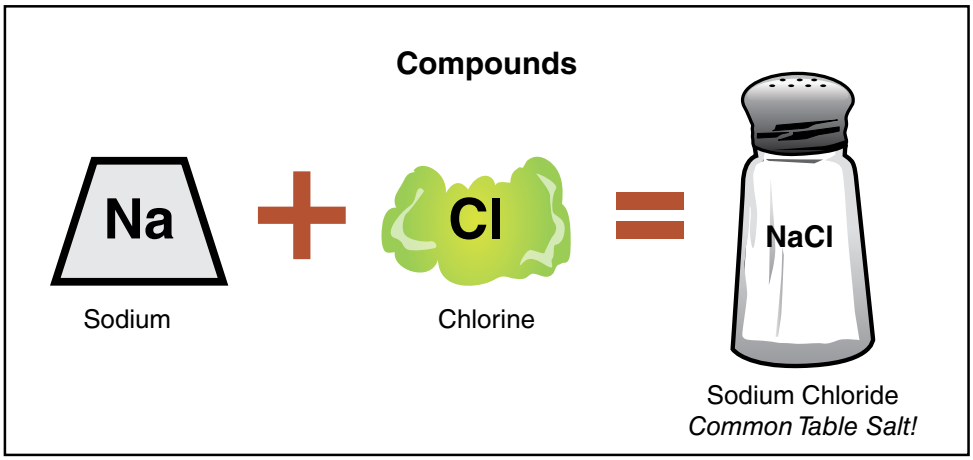


Figure 4.20 Compound molecules are formed from two or more elements. For example, one atom of sodium and one atom of chlorine combine to make the compound, sodium chloride.

Table 4.2
Diatomic Molecules

Element	Elemental State (77° F [25° C])	Color	Molecule
Hydrogen	Gas	Colorless	H_2
Nitrogen	Gas	Colorless	N_2
Oxygen	Gas	Pale Blue	O_2
Fluorine	Gas	Pale Yellow	F_2
Chlorine	Gas	Pale Green	Cl_2
Bromine	Liquid	Reddish Brown	Br_2
Iodine	Solid	Dark Purple, Lustrous	I_2

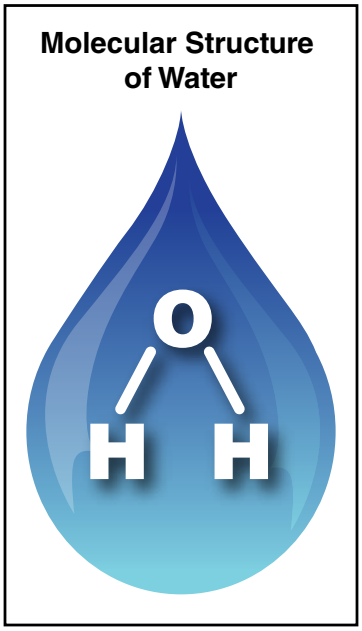


Figure 4.21 H_2O is the chemical formula for water, a molecule with two atoms of hydrogen and one atom of oxygen.

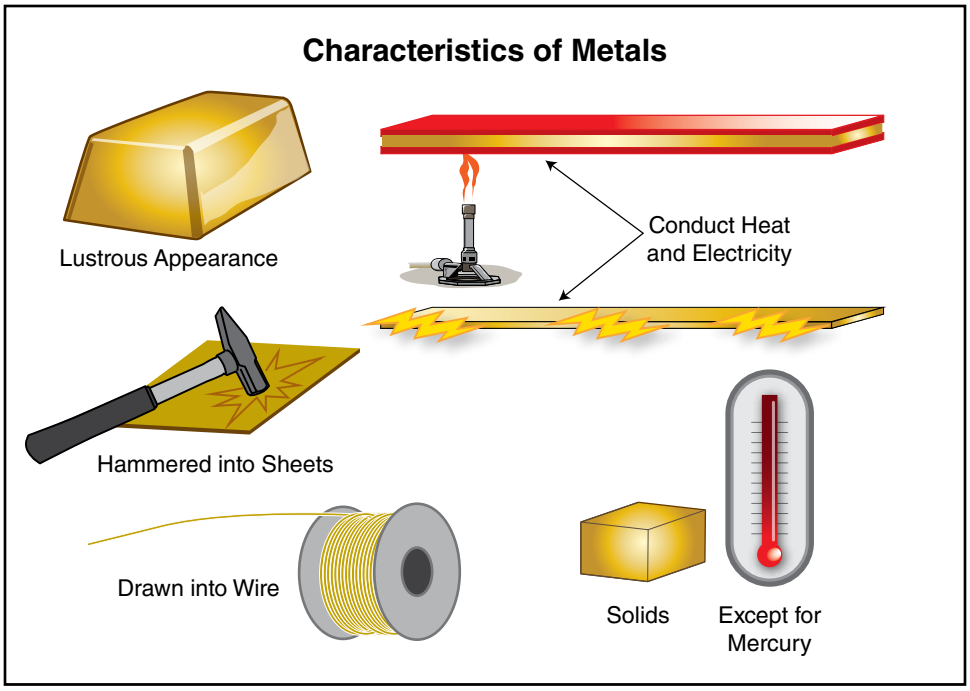


Figure 4.22 Metals typically have many characteristics in common, including being solid at room temperature, with the exception of mercury.

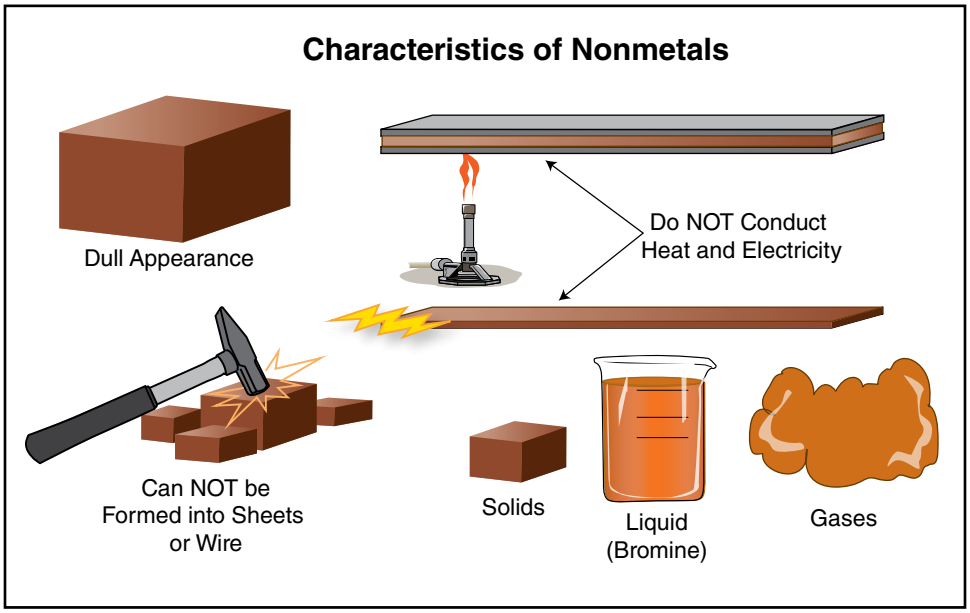


Figure 4.23 Nonmetals differ significantly from metals. Nonmetals are either solids or gases at room temperature, with the exception of bromine.

Metalloids

Metalloids are elements that have properties between the obvious metals and obvious nonmetals. Metalloids can donate or receive electrons and have properties common to both metals and nonmetals **(Figure 4.24)**. Metals are an electron donor, and nonmetals are electron receptors. Metalloids can form alloys with metals.

Compounds

Compounds are substances that are made up of two or more elements. A good example of a compound is water which is made up of two parts hydrogen (H_2) and one part oxygen (O). Both are elements in their own right, but the combination of

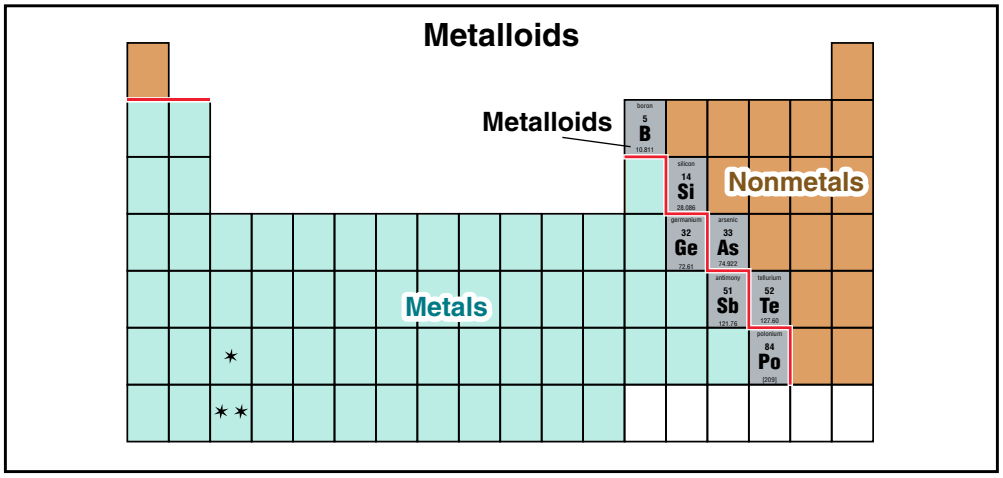


Figure 4.24 Metalloids straddle the line between metals and nonmetals and have properties similar to both. For example, they can donate or receive electrons. Metals only donate electrons, and nonmetals are electron receptors.

the two makes it a compound. Another example of a compound is sodium chloride or common table salt (NaCl). The combination of the two elements (sodium and chloride) turns into a widely used household product.

NOTE: Mixtures consist of separate elements or compounds that are mixed together. It is essential to understand that compounds are not mixtures and not the result of a chemical bonding. Mixtures will be addressed later in this chapter.

Figure 4.25 Like most salts, cinnabar (mercury sulfide, HgS) is a solid.

Binary Salt — An ionic compound composed of two elements, one metal and one nonmetal.

Salts

Compounds are divided into salts and nonsalts; both of which are described in more detail in the section on chemical bonding. In general, *salt compounds* are comprised of a metal element bonded to one or more nonmetal elements. Common traits of salts include the following:

- Most are solids **(Figure 4.25)**
- Generally do not burn with a flame, though some may undergo smoldering combustion
- Most dissolve in water or react with water
- Many are very toxic
- Most will conduct electricity when dissolved in water
- Many can stimulate combustion
- Salts are formed through ionic bonding (covered later in this chapter)
- Metals give up electrons
- Nonmetals accept electrons

Binary salts are comprised of a metal and a nonmetal as long as the nonmetal is not oxygen **(Figure 4.26)**. When naming a binary salt, the metal will always be named first with the nonmetal following. The nonmetal name will be altered to end in a different suffix (-*ide*). For example, chlor*ine* becomes chlor*ide*.

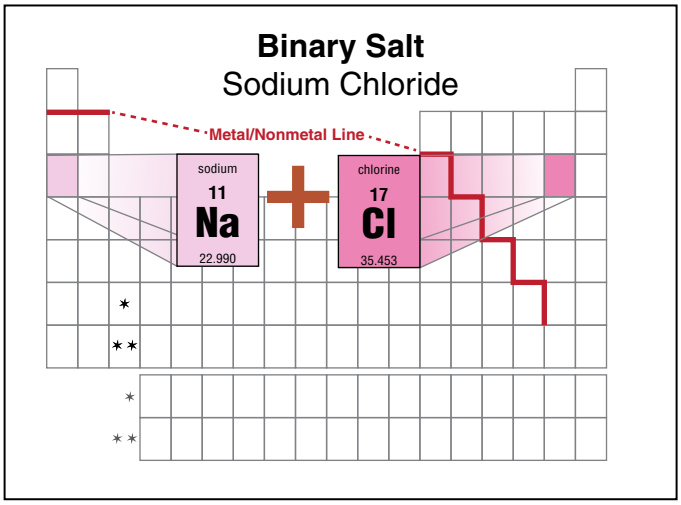


Figure 4.26 Binary salts, such as sodium chloride, are composed of a metal and a nonmetal, other than oxygen.

Table 4.3
Special Hazards of Binary Salts

Binary Salt	Special Hazards
Nitrides	• Release irritating ammonia gas when in contact with moisture
Carbides	• Release unstable and flammable gas when in contact with moisture • Calcium carbide - generates acetylene • Aluminum carbide - generates methane
Hydrides	• Release heat and hydrogen gas when in contact with moisture
Phosphides	• Release poisonous phosphine gas when in contact with moisture

Binary salts can have wide-ranging properties **(Table 4.3)**. Some binary salts such as table salt (sodium chloride) can be less hazardous, while others such as sodium fluoride may be toxic. Binary salts may also be reactive with water (nitrides, carbides, hydrides and phosphides). Other salts are described in **Table 4.4**.

Nonsalts

Nonsalt compounds can be divided into two categories: organic and inorganic. Organic nonsalts are comprised of hydrocarbon and hydrocarbon derivatives. These will be discussed later in the chapter. Most inorganic nonsalts are liquids and gases with very few being solid. They primarily tend to be toxic and poisonous and many have corrosive and/or flammability properties. For naming purposes, the name of one nonmetal will fall first with the suffix "ide." Some examples of inorganic nonsalts are phosphorous and chlorine creating phosphorous chloride or fluorine and chlorine creating fluorine trichloride.

Similar to the binary salts, the hazards of the nonsalts can be far ranging. Some hazards of the nonsalts may include the following:

- Highly water reactive
- Highly toxic
- Flammable
- Oxidizing capabilities
- Corrosive properties

Other nonsalt compounds are described in **Table 4.5**. Nonsalt compounds include nonmetal oxides, hydrogen compounds, binary acids, and oxy acids.

Mixtures

Mixture — Substance containing two or more materials not chemically bonded.

A **mixture** consists of two or more substances that are physically mixed, but not chemically bonded to one another. For instance, sodium chloride and water mix to form salt water, but neither substance is chemically altered within the mixture. Gasoline, kerosene, and fuel oil are common examples of other mixtures. Unlike pure substances, mixtures can vary from one sample to another. For example, gasoline purchased from two different service stations may contain ingredients and additives in different percentages. The following sections identify different types of mixtures.

Solutions

Solution — Mixture in which all the ingredients are completely dissolved.

A **solution** is a mixture in which all the ingredients are completely dissolved. Solutions are often assumed to be liquids because many of them are. However, solids and gases can also be solutions, or they can be components of a solution in liquid form. Salt water is composed of a solid dissolved into a liquid. Carbonated beverages are comprised of a gas (carbon dioxide) dissolved into a liquid. Air is a solution made up primarily of two gases (nitrogen and oxygen). Alloys, such as steel, brass, and bronze, are solutions composed of two or more solids. With any solution, the result is uniform blend of all ingredients.

Table 4.4
Salts: Make-Up, Examples, Formulas, and Hazards

Salt	Make-Up	Example (Name)	Formula	Hazard
Cyanide Salts	Metal/cyanide	Sodium cyanide	NaCN	• Toxic by every route • Characteristic of cyanide poisoning
Metal Oxides	Metal/oxygen	Sodium oxide	Na_2O	• May produce an intense reaction • Produce caustic liquid and intense heat when mixed with water
Hydride Salts	Metal/hydride radical	Lithium aluminum hydride	$LiAlH_4$	• Produce a caustic solution, hydrogen gas, and intense heat when mixed with water • May be pyrophoric
Peroxide Salts	Metal/peroxide anion	Sodium peroxide	Na_2O_2	• Will form corrosive liquids when dissolved in water along with a liberal amount of oxygen and heat
Oxy-Salts	Metal/oxy-anion	Sodium perchlorate	$NaClO_4$	• Potent oxidizer
Ammonium Salts	Ammonium ion	Ammonium chlorate	NH_4ClO_3	• Act like a metal in chemical reactions • May be strong oxidizer

Table 4.5
Nonsalts: Make-Up, Examples, Formulas, and Hazards

Nonsalt	Make-Up	Example (Name)	Formula	Primary Hazards
Nonmetal Oxides	Nonmetal/oxygen	Sulfur dioxide	SO_2	• Toxic • Corrosive
Hydrogen Compounds	Hydrogen/nonmetal	Hydrogen chloride	HCl	• Toxic • Corrosive
Binary Acids	Hydrogen halide gas dissolved in water	Hydrofluoric acid	HF	• Corrosive • May migrate through tissue
Oxy Acids	Nonmetal oxide that is ionized and dissolved in water	Nitric acid	HNO_3	• Corrosive • Oxidizer

Some solutions are easily separated into their component parts. When the water in salt water evaporates, it leaves the salt behind. Carbon dioxide will escape a carbonated beverage if heated. However, most solutions do not separate so easily.

Heat normally *increases* the solubility of substances. Once again using familiar beverages to illustrate the point, it is easier to dissolve sugar in hot tea than in iced tea. However, the opposite applies with *gases* dissolved into liquids and some solids. Raising the temperature *decreases* the solubility. Because carbon dioxide is a gas dissolved into a liquid, warm carbonated beverages lose their carbonation faster than cold beverages do. To put this in the context of a hazardous materials incident, one can take the example of a release of ammonia gas at a refrigerant plant. Because ammonia is very soluble in cold water, it is possible to use a fine fog stream of cold water to pull the ammonia out of the air. Doing so creates a weak caustic solution of ammonium hydroxide (NH_4OH) but significantly decreases the risk of ignition.

Slurry — (1) Watery mixture of insoluble matter such as mud, lime, or Plaster of Paris. (2) Suspension formed by a quantity of powder mixed into a liquid in which the solid is only slightly soluble.

Slurries

When a material cannot totally dissolve in water, the end result may be **slurry**. Slurries are a suspension of insoluble particles, usually in water. Slurry is a pourable mixture of a solid and a liquid (although not necessarily one that remains pourable). Cement and plaster are both examples of slurries created by adding solids to water.

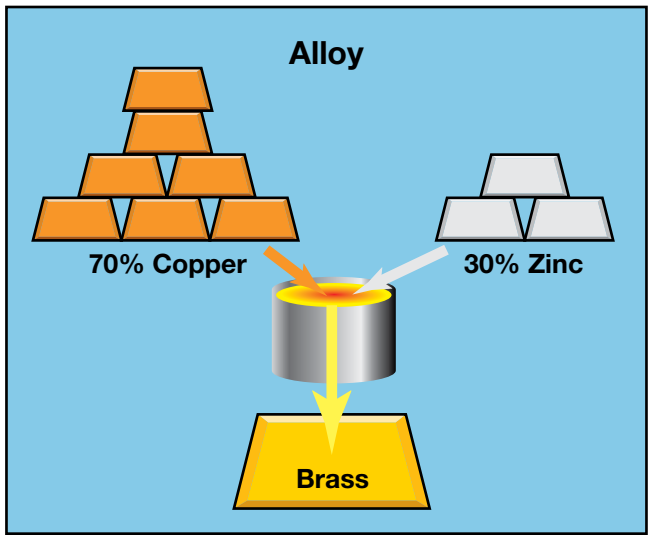


Figure 4.27 Alloys are mixtures of two or more metals.

Alloys

Alloys (or *metal alloys*) are generally described as a mixture of two or more metals, the purpose of which is to create a material that is somehow stronger or better for a particular application than any one metal would be alone **(Figure 4.27)**. The alloys in the following list contain approximate concentrations of each metal:

- Brass: 70% copper (Cu) and 30% zinc (Zn)
- Bronze: 90% copper (Cu) and 10% tin (Sn)
- Solder: 70% lead (Pb) and 30% tin (Sn)
- Titanium alloy: 90% titanium (Ti), 5% aluminum (Al), and 5% vanadium (V)
- Duraluminum: 94% aluminum (Al), 4% copper (Cu), and 1% magnesium (Mg)

Alloys sometimes contain a small percentage of nonmetal elements. For example, steel is comprised primarily of iron (Fe), but also contains 0.1% to 1.5% carbon (C) **(Figure 4.28)**. Stainless steel is roughly 80% iron (Fe), 15% chromium (Cr), 4% nickel (Ni), and 0.5% to 1% carbon (C).

Bonding

The study of hazardous materials is really about how substances react — how they react with their environment and how they react with other materials. At the core of most of those reactions is chemical bonding, with bonds being formed and/or broken between elements, compounds, or some combination thereof. The following sections will explore what is happening at the molecular level when materials react with one another.

The Octet/Duet Rule

As indicated earlier, all atoms must have an equal number of protons and electrons to be *electrically neutral*. To be *stable*, an atom must have a completely filled outer shell (two electrons on hydrogen and helium, eight on all others)**(Figure 4.29)**. However, this poses a conflict and thus the basis for chemical reactivity.

Elements in Group VIII, the noble gases, are the exception to the chemical bonding process that will be described over the next few pages. Noble gases already have filled outer shells, so they are inert and have no reason to react with other elements. However, inert does not necessarily mean harmless. As previously indicated, the noble gases are simple asphyxiants. They are often stored or transported as cryogenic liquids, making them a thermal hazard with high expansion ratios. But when it comes to chemical bonding, these elements are not normally available to bond.

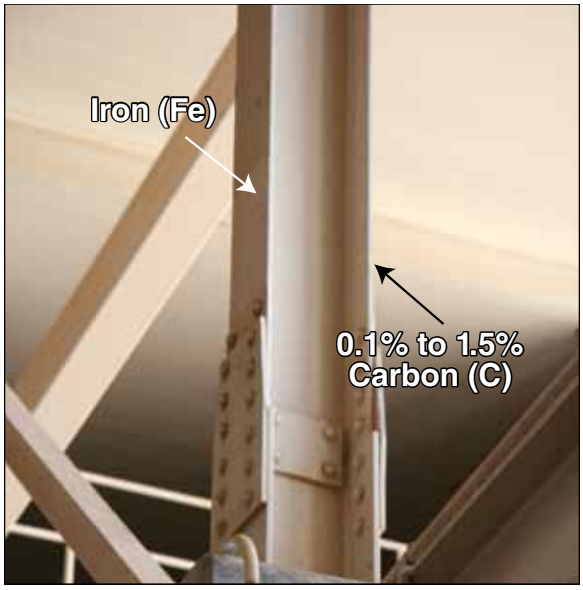


Figure 4.28 Alloys often contain small amounts of nonmetals. For example, steel contains a small percentage of carbon.

Other elements are available to bond or share their electrons because their outer shells are *not* filled to the maximum. These elements must bond or share with others to create a filled outer shell. Hydrogen, with only one shell, needs one more electron to obtain a total of *two*. This is called the *Duet Rule*. The rest will attempt to achieve *eight* electrons on their outer shells to fulfill what is called the *Octet Rule* **(Figure 4.30, p. 166)**.

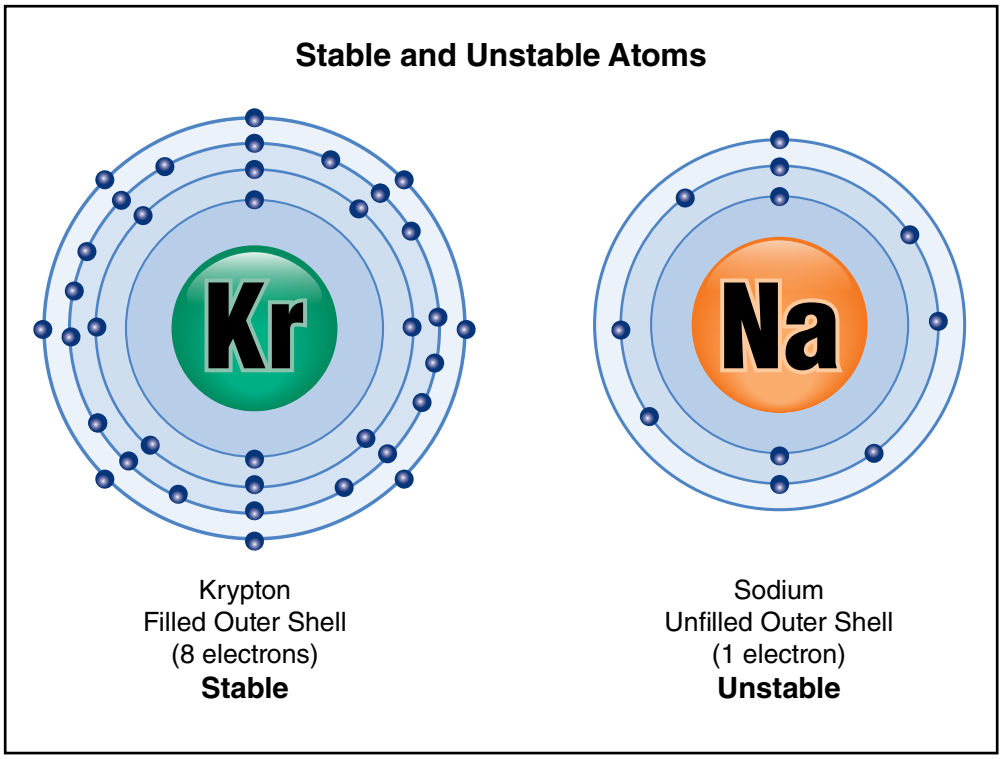


Figure 4.29 Stable atoms have filled outer shells whereas unstable atoms do not.

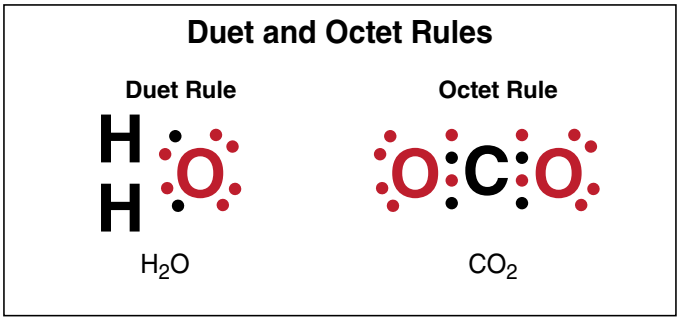


Figure 4.30 Hydrogen, with only one electron, will bond with and share an electron with another atom in order to fill its shell with two electrons (the Duet Rule). Oxygen and other elements will bond with and share electrons in order to achieve eight (the Octet Rule).

Stability of Elements and Compounds

Stability refers to elements possessing filled outer shells. Again, it is this need to fill the outer shell that causes elements to react (bond) with one another chemically. Most of the time, the discussion of *stability* and *instability* refers to the tendency of some chemical compounds to break down into their component parts with little provocation. (The term *instability* is often used interchangeably with the term *reactivity*.) Unstable compounds are very sensitive to heat, shock, friction, or contamination and often decompose violently. For example, contaminated nitroglycerine decomposes explosively if heated or shocked. Unstable compounds do not need to mix with other chemicals or be contaminated by other chemicals to react. Organic peroxides will decompose rapidly if simply overheated. Once the reaction starts, it cannot be stopped.

Diatomic Molecules (Compounds)

Compounds were described earlier as two or more elements chemically bonded to form a molecule. Once again, these elements bond to create filled outer shells. A simple example can be illustrated with the element chlorine (Cl). A single atom of chlorine has seven electrons in its outer shell; it needs one more to be stable. (Remember the Octet Rule.) When two atoms of chlorine bond, they share electrons to complete the need to have eight electrons in their outer shell. The result is a stable compound.

Gases that exist as a compound of two identical atoms are called *diatomic gases* (or *diatomic molecules*). Oxygen (O_2) is the most common diatomic gas. Others are hydrogen (H_2), nitrogen (N_2), fluorine (F_2), and chlorine (Cl_2). Diatomic molecules are not limited to gases. For example, Bromine (Br_2) is a liquid, and Iodine (I_2) is a solid.

When electrons are shared between atoms, as previously illustrated, it is called a *covalent bond* **(Figure 4.31)**. However, sometimes electrons are transferred from one atom to another in what is called an *ionic bond*. The mechanics of those bonds will be explained next.

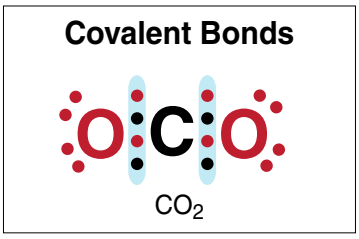


Figure 4.31 In a covalent bond, electrons are shared between atoms.

Ionic Bonds

Ionic Bonds — Chemical bond formed by the transfer of electrons from a metal element to a nonmetal element.

Ionic bonds are formed by the transfer of electrons from a metal element to a nonmetal element **(Figure 4.32)**. Understanding the dividing line between metals and nonmetals on a periodic table is helpful. In the case of sodium chloride, sodium "donates" the one electron on its outer shell, essentially shedding its outer shell and exposing a filled shell beneath it. Chlorine, which has seven electrons on its outer shell, "accepts" the donated electron from the sodium atom, also ending up with a filled outer shell.

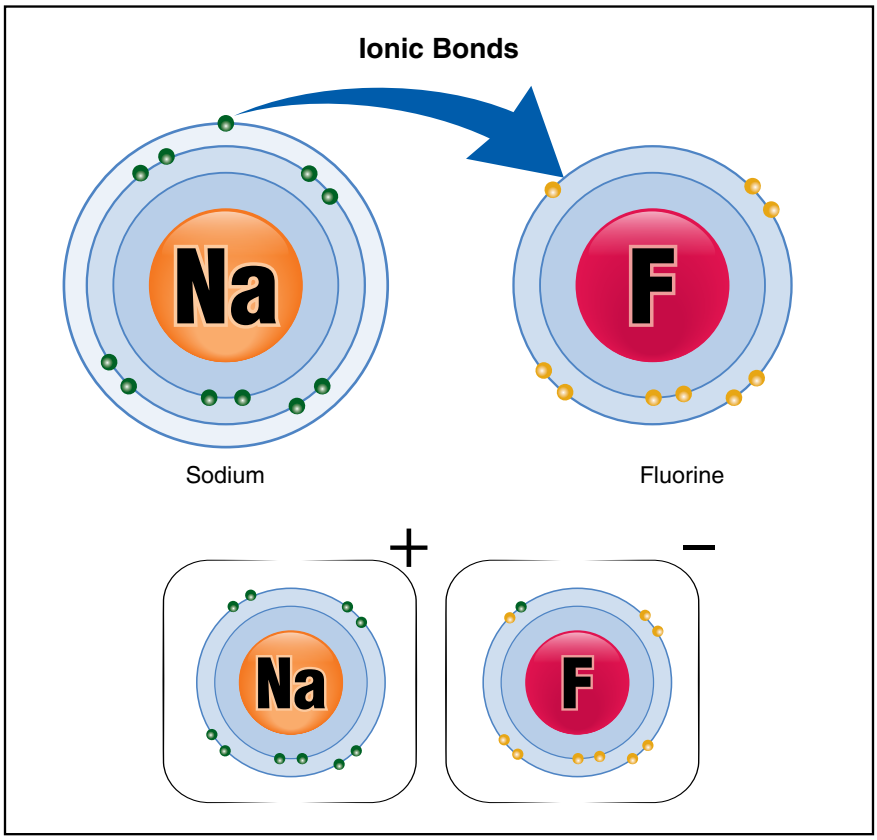


Figure 4.32 In an ionic bond, a metal donates an electron to a nonmetal, thereby "shedding" its outer shell. This results in both atoms having filled outer shells.

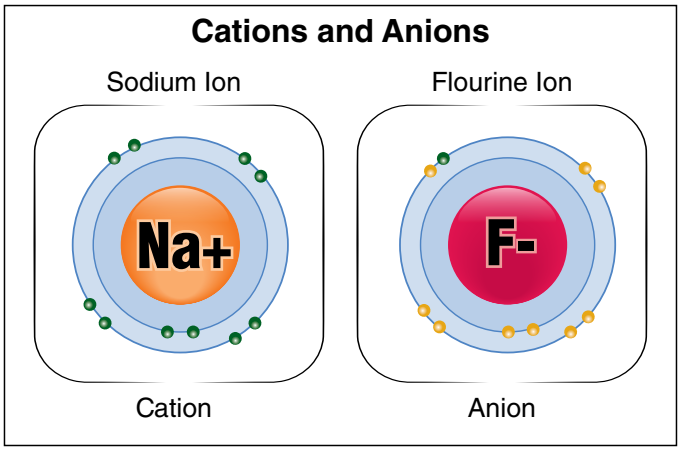


Figure 4.33 Although stable, in an ionic bond, the elements are not electrically balanced. Cations have a positive charge, while anions have a negative charge.

Ion — An atom which has lost or gained an electron and thus has a positive or negative charge.

While the two elements are now stable, they are no longer electrically balanced. Sodium has one more proton than electrons; chlorine has one electron more than protons. Atoms that have gained or lost electrons are no longer referred to as atoms; rather, they are called **ions**. An ion with more protons than electrons (the sodium ion in this example) has a net positive charge, whereas one with more electrons than protons (the chloride ion) has a net negative charge. Positively and negatively charged ions are referred to as **cations** and **anions**, respectively **(Figure 4.33)**.

Cations — Atom or group of atoms carrying a positive charge.

Anions — Atom or group of atoms carrying a negative charge.

Oppositely charged ions attract each other, forming the bond that holds them together. In essence, although there has been a transfer of electrons, the elements involved cannot stray far apart because ions cannot exist by themselves.

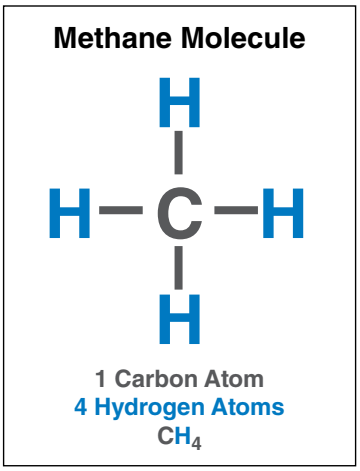


Figure 4.34 Methane has covalent bonds, making it a nonsalt.

Table 4.6
Examples of Common Salts and Their Uses

Salt	Formula	Use
Sodium Chloride	NaCl	Seasoning of food
Sodium Bisulfate	$NaHSO_4$	Photographic purposes
Potassium Dichromate	$K_2Cr_2O_7$	Photographic purposes
Calcium Chloride	$CaCl_2$	Removes humidity from packaging

Sodium chloride (NaCl) is commonly used as an example because it is a compound with which most people are familiar. However, its close cousin, sodium fluoride (NaF), is very hazardous as most salts are. **Table 4.6** shows examples of common salts. The characteristics and hazards of salts are explored later. For now, it is sufficient to recognize that compounds comprised of a metal element bonded with one or more nonmetal elements all belong in the category called *salts*.

Covalent Bonds

Covalent Bond — A chemical link between two atoms in which electrons are shared between them.

Covalent bonds are formed between two or more nonmetal elements. Elements involved in covalent bonds share electrons rather than transfer them. Their outer shells overlap to the point that electrons seem to belong to each atom at the same time. This union results in a nonsalt, like diatomic oxygen. Another familiar compound, methane, is formed by the union of one carbon atom and four hydrogen atoms and is shown in **Figure 4.34**.

Many covalent compounds are comprised of nonmetal elements only. However, some organic metallic compounds exist that are covalently bonded. The majority of covalent compounds that hazardous materials technicians encounter consist solely of carbon, hydrogen, and oxygen in various combinations. Of the compounds that contain other elements, most are limited to nitrogen, phosphorus, sulfur, silicon, and the halogens (chlorine, fluorine, bromine, and iodine). **Table 4.7** lists examples of covalent compounds containing some of these elements. Once again, the focus of this chapter is simply recognizing the different types of bonds.

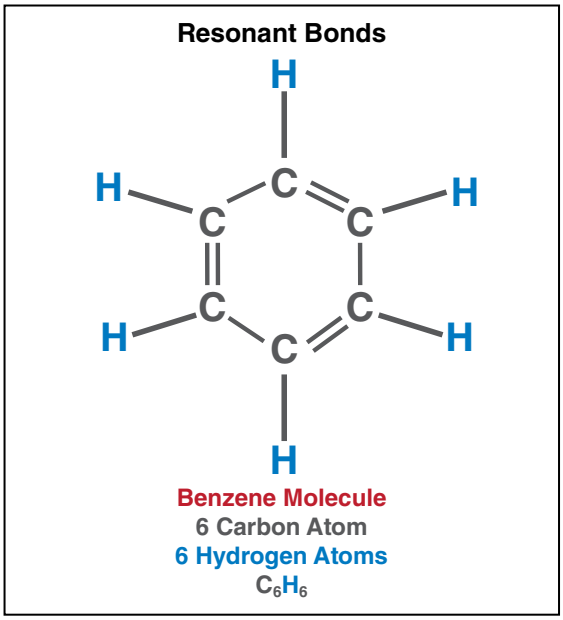


Figure 4.35 The hexagonal configuration of the carbon atoms in this benzene molecule indicates a resonant bond. In a resonant bond, electrons rapidly rotate or alternate between the atoms.

Resonant Bonds

Resonant Bond — Chemical bond in which shared electrons alternate very rapidly between carbon atoms.

Resonant bonds resemble covalent bonds in that electrons are shared between elements. However, when compounds contain resonant bonds, as do the aromatic hydrocarbons (benzene, toluene, xylene, styrene, and cumene), the electrons actually rotate or alternate very rapidly between the carbon atoms. The compound shown in **Figure 4.35** is benzene (C_6H_6). Benzene's ring structure can be represented either by elements connected with dashes or by a ring within a hexagon.

Table 4.7
Covalent Compounds

Compound Name	Formula	Hazards
Carbon Monoxide	CO	• Toxic to humans and animals in high concentrations • Highly flammable
Nitrogen Trioxide (also known as Dinitrogen Trioxide)	N_2O_3	• Toxic • Water and air reactive • Produces toxic gas when heated
Hydrogen Iodide, anhydrous	HI	• Toxic • Water and air reactive • Dissolves exothermically in water
Phosphine (also known as Phosphorus Trihydride)	PH_3	• Highly flammable • Strong reducing agent • Air reactive • Can explode with powerful oxidizers • Highly toxic gas

Bond Energy

Every bond stores some amount of energy that is the measure of the strength of the connection(s) between atoms in a chemical bond. This energy is called **bond energy**, and it is released when the bond is broken. The amount of energy released will depend on the number and type of elements that comprise the bond and on what causes the bond to be broken. Some compounds can release a tremendous amount of energy (in the form of light and heat) when their bonds are broken.

Bond Energy — The amount of energy that has to be supplied to break a chemical bond between two atoms in a molecule.

Chemical reactions that generate heat are exothermic. Most reactions are exothermic and some are enough to ignite a fire. Other reactions are endothermic and instead absorb heat from the atmosphere.

Bonding in Haz Mat Response

Knowing the difference between *ionic* and *covalent bonds* can help the responder in predicting the behavior of the chemical and the detection capability of some instrumentation. Characteristics of ionically bonded compounds:

- Are solid
- Have limited to no vapor
- Do not have flash point (FP)
- Do not have lower explosive limit (LEL)
- Do not polymerize
- May form caustic or basic solutions
- May be air or water reactive
- Are generally not seen by infrared (IR) spectroscopy and/or PID

Covalently bonded compounds:

- Are solids, liquids, and gases
- Produce vapors
- Have flash points
- Have lower explosive limits (LEL)
- Can polymerize
- May be seen by infrared (IR) monitoring spectroscopy and/or PID

CAUTION

All chemical and physical properties must be verified through reference materials and validated by instrumentation.

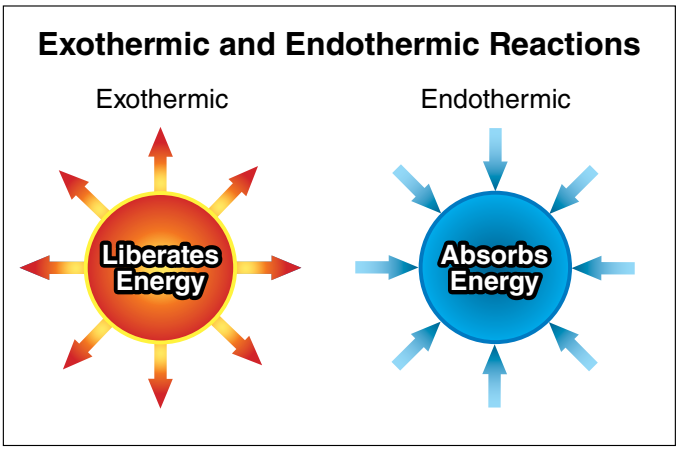


Figure 4.36 Most chemical reactions release energy and are called exothermic. Reactions that absorb energy are called endothermic.

Reactions

Hazardous materials emergency responders are always concerned when two or more chemicals are mixed during any incident or when chemicals are exposed to heat from a fire or other source. This is especially true when the incident is complex such as a major industrial incident or fire, a motor vehicle accident involving a transport container, or a train derailment. All chemical reactions require energy changes in order to occur. The majority of reactions liberate energy as heat and sometimes heat, light, and sound. These reactions are termed exothermic. In a minority of reactions, energy is absorbed into the products; when this occurs the reaction is described as endothermic **(Figure 4.36)**.

The questions that normally arise in such situations include:

- Will the mixing or heating of these chemicals cause the release of large amounts of energy as heat or with explosive force?
- Will the mixing or heating of these chemicals cause a fire or will it generate a greater flammability hazard than that found with the same chemicals without a chemical reaction?
- Will the mixing or heating of these chemicals increase the toxicity hazards at the scene compared to the toxicity of the unreacted chemicals?
- Will the mixing or heating of these chemicals form products with more vapors and/or fumes than the original chemicals?
- Will the products formed by the mixing or heating of these chemicals create additional environmental hazards or problems beyond those from the unreacted chemicals?

The answers to these questions will determine every aspect of the emergency response including the following:

- Size of the control zones needed — especially the size of the Hot Zone
- Whether a shelter-in-place or civilian evacuation is appropriate
- Choice of PPE needed for a safe response
- Scope and type of decontamination used
- Type of air and environmental monitoring needed
- Choice of response option chosen to yield a positive impact on the situation
- Type of remediation that will be needed to limit both long- and short-term environmental damage

A **reactive material** is one that can undergo a chemical reaction under certain specified conditions. This term is generally used to refer to a substance that can undergo a violent or abnormal reaction in the presence of water, air, or under normal ambient conditions. Reactive materials could be shock or friction sensitive, pyrophoric, or hypergolic in nature. Pyrophoric materials react with dry air, but never assume that they will not react with moist air.

Reactive Material — Substance capable of or tending to react chemically with other substances; examples: materials that react violently when combined with air or water.

Water-reactive materials react on contact with water. The reaction can be mild to severe as can be seen with the alkali metals (the reaction may occur slowly as with lithium or violently with potassium). A water-reactive material is defined by the gases it gives off — toxic, corrosive, or flammable. The results of these reactions can be explosive and may result in a very corrosive solution. More information on reactive materials will be covered in this chapter.

Exothermic and Endothermic Reactions

A chemical reaction is a process that results in the interconversion of chemical species. Exothermic reactions can be the most dangerous because of the potential for a fire or explosion. A separate source of heat is needed to maintain endothermic reactions. A common example of an endothermic reaction is a chemical ice pack. When the pack is broken, the reaction of the two chemicals inside generates cold. Removing the heat from an exothermic reaction slows and eventually stops the reaction. Adding heat to an endothermic reaction slows the reaction.

Oxidation and Combustion

When ionic bonds were described earlier in this chapter, it was explained how sodium loses one electron and chlorine gains one to form table salt. This is an example of an *oxidation-reduction reaction*, or *redox reaction* for short. In an oxidation-reduction reaction, electrons are transferred from one atom, compound, or molecule to another.

When sodium gives up an electron (which carries a negative charge of 1), it ends up with a net positive charge (+1). Conversely, when chlorine gains the electron, it ends up with a net negative charge (-1). However, the combined sodium chloride molecule is electrically neutral. Every oxidation-reduction reaction involves the simultaneous loss and gain of an equal number of electrons. Neither reaction (oxidation or reduction) can happen without the other.

The substance that loses electrons is called a *reducing agent* (or *reducer*). The one that gains electrons is called an *oxidizing agent* (or *oxidizer*) **(Figure 4.37, p. 172)**. Substances that either give up or gain electrons easily are said to be *strong reducing*

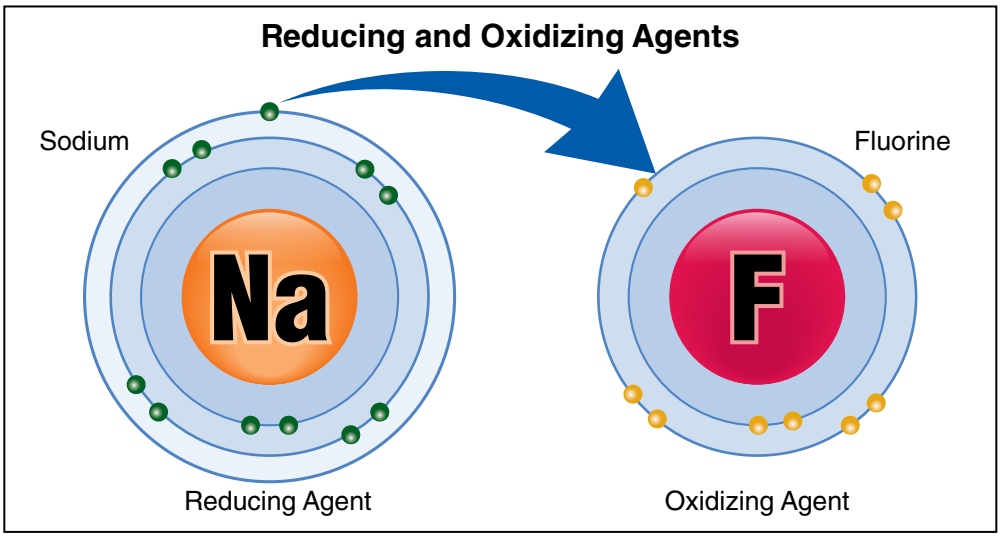


Figure 4.37 The reducing agent loses electrons while the oxidizing agent gains them.

agents or *oxidizing agents*, respectively. Earlier in the chapter, the elements called halogens (particularly fluorine and chlorine) were described as strong oxidizers. The reason for this is that with seven electrons on their outer shells, fluorine and chlorine are anxious to gain an electron to fill the outer shell. Oxygen has six electrons on its outer shell. It needs two more to satisfy the Octet Rule. An element that has to gain or lose two electrons will not be as reactive as an element that is only one electron away from having a filled outer shell.

What can be confusing are the terms used to describe what happens to oxidizing and reducing agents after the transfer of electrons takes place. The oxidizing agent is said to have been *reduced*, whereas the reducing agent is said to have been *oxidized*. A more practical approach is to consider how the oxidation-reduction reaction leads to a hazardous materials incident.

Oxidation is the chemical combination of oxygen (or another oxidizer) with another substance. The chemical reaction can vary in speed from very slow (such as when oxygen combines with iron to create rust) or very fast (a reaction manifested as a fire or explosion). In fact, fire (combustion) is nothing more than a complex oxidation-reduction reaction involving fuel (the reducing agent) and an oxidizing agent (usually oxygen).

Figure 4.38 illustrates the chemical combustion of methane (CH_4). Methane burns in an atmosphere of oxygen to release carbon dioxide and water vapor. (Electrical charges and electrons are not shown in this illustration. It is important to recognize that there has been a transfer of elements, not just electrons, creating new substances and generating heat in the process.)

Firefighters are familiar with the concept of *complete* combustion versus *incomplete* combustion. Here again are oxidation-reduction reactions, one with adequate oxygen to produce a substance that will not burn (carbon dioxide) and one in which an inadequate oxygen supply results in a substance that *is* flammable (carbon monoxide) and will propagate the combustion process.

A material's propensity to give up oxygen atoms, making them available to react with other substances, is a measure of the material's *oxidation potential*. The more readily a material yields oxygen, the greater the hazard it presents. The more readily a material yields oxygen *or* any other element that acts as an oxidizer, the more powerful the entire compound.

Polymerization

Polymerization is a special chemical reaction in which small compounds called **monomers** react with themselves to form larger molecules called **polymers**. These polymers are "repeating units" that resemble the original molecule. **Figure 4.39, p. 174,** represents how ethylene (C_2H_4), the most common of all the monomers, is transformed into polyethylene, a chain of C_2H_4 repeating units. Polyethylene is a very common man-made plastic.

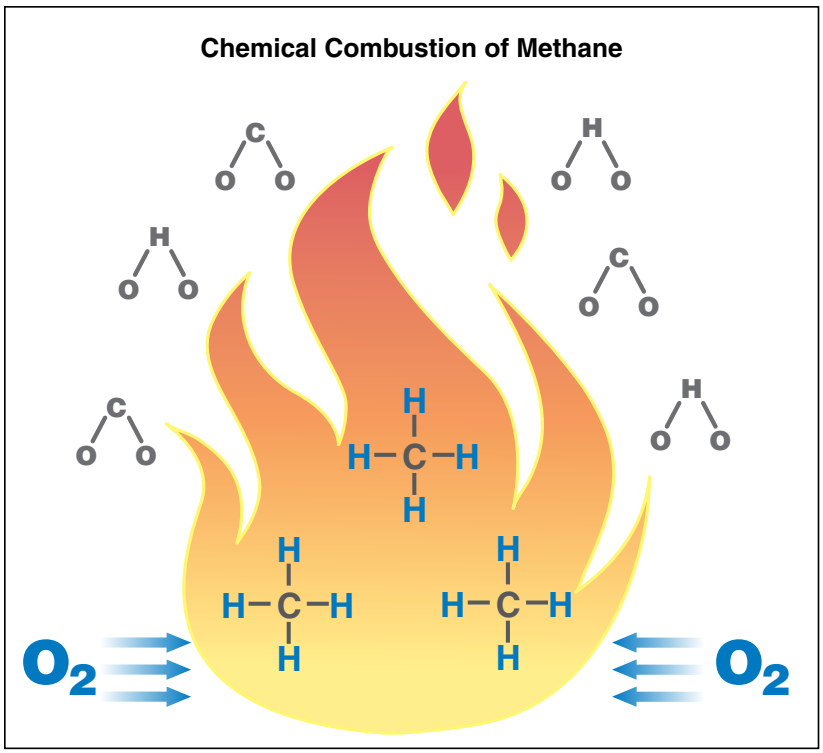


Figure 4.38 When methane burns, it reacts with oxygen in the atmosphere and releases heat, light, carbon dioxide, and water vapor.

Ethylene in its natural state has a double bond between its two carbon atoms. Double bonds between carbon atoms are not as stable as single bonds; therefore, ethylene is prone to polymerization. To create polyethylene, manufacturers initiate a chemical reaction through the careful application of heat, pressure, and a catalyst. This reaction breaks one of the bonds between carbon atoms, leaving a single bond in place of the double bond and an open bond on either side. Open bonding sites (unpaired electrons) create a very unstable situation that nature does not allow to exist for very long. These incomplete molecules combine to create more stable compounds (polymers). Different polymers can be created by varying the monomer used and the rate of the reaction.

Because polymers are not as dense as monomers, they take up more space. The reaction also generates heat. Heat and overpressurization can cause catastrophic container failure in uncontrolled or runaway polymerization.

Polymerization — Reactions in which two or more molecules chemically combine to form larger molecules; reaction can often be violent.

Monomer — A molecule that may bind chemically to other molecules to form a polymer.

Polymer — Large molecule composed of repeating structural units.

WARNING!

Uncontrolled polymerization cannot be safely stopped. A response in these instances is a high-risk event.

Catalysts

The polymerization process previously described is initiated by the use of a **catalyst**. Catalysts are substances added to other products either to initiate or to speed up chemical reactions. Catalysts themselves are not used up in the reaction. They may sometimes be recovered and reused. If catalysts are used improperly, they can increase the speed of a reaction beyond the point where the container can withstand the buildup of pressure and heat.

Catalyst — A substance that influences the rate of chemical reaction between or among other substances.

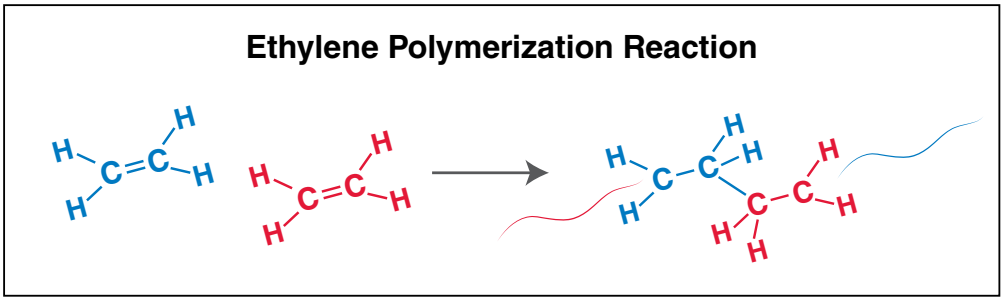


Figure 4.39 In this example of polymerization, the monomer, ethylene, reacts with itself to form a polymer, polyethylene.

Inhibitor — Material that is added to product that easily polymerizes in order to control or prevent an undesired reaction. *Also called* Stabilizer.

Inhibitors

Inhibitors, sometimes referred to as *stabilizers* or *negative catalysts*, are added to other products to stop or slow a reaction such as to prevent uncontrolled polymerization. Inhibitors have a limited shelf life, meaning that they will not stop or slow a reaction indefinitely. If an inhibitor is allowed to degrade, to escape, or to drop below the necessary concentration, the resulting polymerization may cause catastrophic container failure. Likewise, if an inhibitor is not added where needed, it can cause disaster. You may find different amounts of inhibitors in storage tanks and shipments of the same product.

Decomposition

A decomposition reaction, sometimes referred to as an *analysis* or *breakdown reaction* is one of the most common types of chemical reactions. Simply put, when a decomposition reaction occurs, a compound is broken down into smaller components. Chemical decomposition is often an undesired chemical reaction that can be extremely violent or not even noticeable depending on the chemical.

The electrolysis of water is a good example of a decomposition reaction. Water (H_2O) is the whole product and can be broken apart into a hydrogen component and an oxygen component.

Synergistic Reactions

A synergistic reaction can be described as an interaction between two or more individual compounds that produce an effect that is different from the original starting materials. A synergistic reaction will make the end product greater as a whole than the individual compounds. A synergistic effect is usually thought of as two or more items working together in tandem, but with a synergistic reaction, the effects may not always be desired.

An example of a synergistic reaction is the mixing of household bleach and household ammonia to generate a compound called chloramine. Chloramine (NH_2Cl) can be used in low concentrations as a disinfectant in municipal water supplies and is starting to replace chlorine (free chlorine) in water treatment use. Chloramine tends to be more stable than chlorine and will not dissipate in the water before reaching consumers.

The Fundamentals of a Reaction

Many hazardous situations at a haz mat incident involve the inadvertent mixing of chemicals. Knowing the compatibility of the materials being mixed is important. If the materials are incompatible, the results of the mixing could range from the formation of an innocuous gas or liquid to a violent explosion to one involving very toxic reaction products. Unknown materials must be identified before compatibilities can be determined. Determining the compatibility of more than two reactants is very difficult and requires extensive knowledge of chemistry. **Table 4.8** provides examples of what could happen when incompatible materials are combined.

WARNING!

Whenever an incident involves the mixing of two or more materials, consult a chemist to determine the possibility of increased hazards.

Table 4.8
Reactions Caused by Mixing Incompatible Chemicals

Incompatible Chemicals	Reactions
Acids with cyanide salts	Produces highly toxic hydrogen cyanide gas
Acids with sulfide salts	Produces highly toxic hydrogen sulfide gas
Acids with bleach	Produces highly toxic chlorine gas
Oxidizing acids with alcohols	May result in fire
Silver salts with ammonia and a strong base	May produce an explosively unstable solid
Unsaturated compounds (containing carbonyls or double bonds) and an acid or a base	May polymerize violently
Hydrogen peroxide and acetic acid mixtures	May explode upon heating
Hydrogen peroxide and sulfuric acid mixtures	May detonate spontaneously

For a chemical reaction to occur, a certain amount of energy must be overcome. **Activation energy** is the minimum amount of energy needed to start a chemical reaction **(Figure 4.40, p. 176)**. If you can prevent a chemical reaction from reaching its activation energy, the reaction may either stop or slow down. Inhibitors increase the activation energy by slowing down the polymerization process. Catalysts decrease the activation energy — thus speeding up the

Activation Energy — Amount of energy that must be added to an atomic or molecular system to begin a reaction.

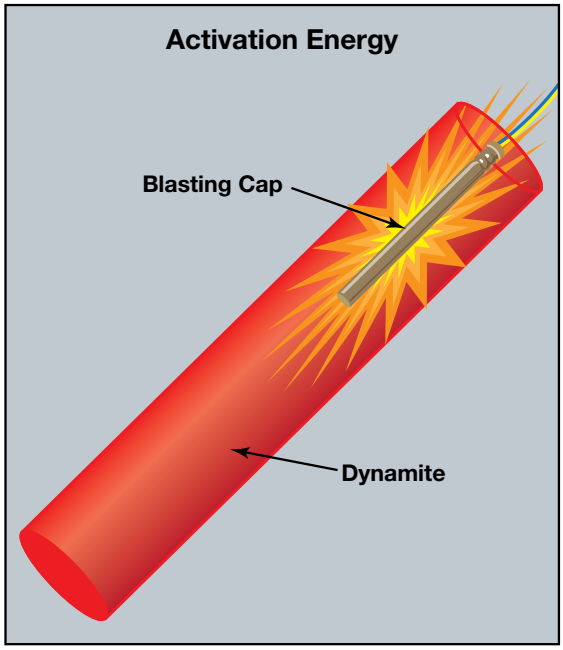


Figure 4.40 A blasting cap provides the activation energy needed to initiate the chemical reaction in dynamite that causes it to explode.

reaction. A chemical reaction may be altered by changing the temperatures of the chemicals involved. If cooling occurs, the reaction will likely slow down. If you increase the temperature of a chemical compound, the reaction rate will increase as well. A rough rule of thumb is that for every 50°F (10°C) a compound's temperature is increased, the reaction rate will double. The same philosophy can be used with pressure as well. An increase in pressure will increase the reaction.

Particulate size can also affect a chemical reaction. When discussing particle size, the smaller the particle, the faster the reaction and vice versa, based on the total surface of the particles. For example, when comparing sawdust versus a log in a fireplace, the coal dust in quantity may explode based on the overall surface area where in the case of the log, the reaction will not be an explosion, but rather a fire.

The state of matter can also have an effect on a reaction as well. In most cases a solid will have a much slower reaction rate than a liquid. Similarly, gases may have faster reaction rates than liquids, depending on density and concentration.

Common Families of Hazardous Materials

Haz mat technicians need to be familiar with the properties and behavior of common families of hazardous materials. These include the following:

- Inorganic compounds
- Organic compounds
- Oxidizers
- Reactive materials
- Corrosives
- Chemical warfare agents
- Biological agents and toxins
- Explosives and incendiaries
- Pesticides and agricultural chemicals

Inorganic Compounds

Inorganic chemistry is a branch of chemistry that is concerned with the properties and behavior of inorganic compounds. This field can cover all chemical compounds except the many organic compounds. Many inorganic compounds can be considered ionic compounds that are joined by ionic bonding.

Organic Compounds

There are predominately two types of organic compounds: hydrocarbons and hydrocarbon derivatives. Hydrocarbons contain only two elements, carbon and hydrogen, while the derivatives contain carbon, hydrogen, and one or more additional elements. The following section will describe in detail hydrocarbons and their derivatives along with the chemical bonding for each.

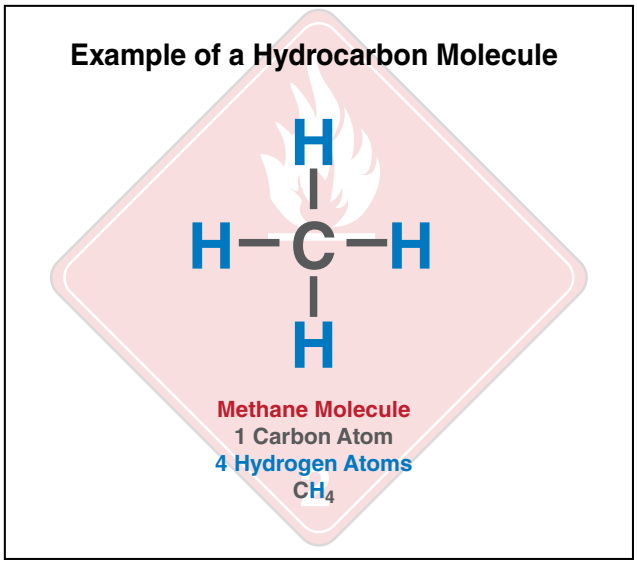


Figure 4.41 Hydrocarbons such as methane consist solely of hydrogen and carbon atoms. They are either flammable or combustible, depending on their flash point.

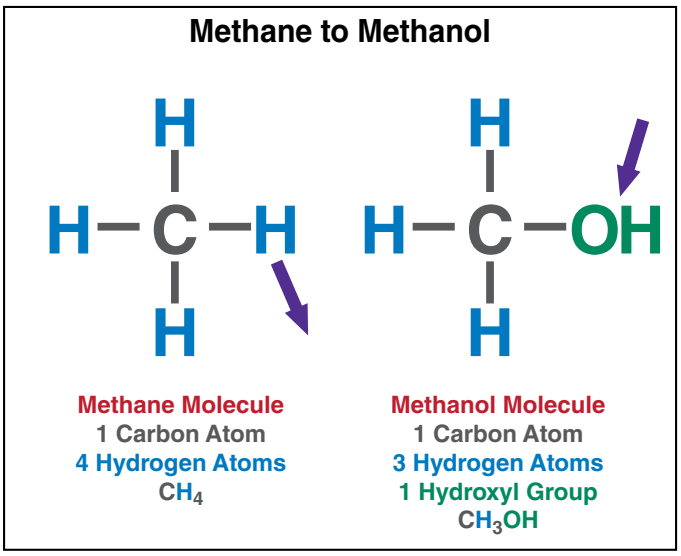


Figure 4.42 Methanol is a hydrocarbon derivative formed when a methane molecule loses one hydrogen atom and gains a hydroxyl group instead.

Hydrocarbons and Their Derivatives

Hydrocarbons are compounds that consist solely of hydrogen and carbon **(Figure 4.41)**. Regardless of how much hydrogen and carbon are present or how those elements are bonded to one another, if the compound contains just those two elements, it is a hydrocarbon.

As the name implies, *hydrocarbon derivatives* are compounds derived from hydrocarbons. The difference between methane (CH_4) and methanol (CH_3OH) is that the original methane compound loses one hydrogen atom (H) and gains a hydroxyl group (OH) in its place **(Figure 4.42)**. There are so many kinds of hydrocarbon derivatives that going into detail is beyond the scope of this text. **Table 4.9, p. 178,** introduces some of the hydrocarbon derivatives and the hazards associated with them.

All hydrocarbons, regardless of the type of bonds they contain, have the following common characteristics. Knowing this makes it possible for hazardous materials technicians to predict their behavior and hazards even before checking reference sources.

- All hydrocarbons are either flammable or combustible, depending on the flash point.
- All are toxic to some degree.
- All are insoluble in water and will float on the surface.

As indicated previously in this chapter, many of these properties are directly related to molecular size. For example, smaller compounds typically have lower flash points than larger ones. So methane (CH_4) will be more flammable than propane (C_3H_8), just as pentane (C_5H_{12}) is more flammable than octane (C_8H_{18}). These comparisons are most accurate when evaluating similar compounds (one alkane versus another).

Table 4.9
Hydrocarbon Derivatives and Their Hazards

Hydrocarbon Derivatives	Formula	Hazards
alpha-Naphthylamine	$C_{10}H_7N\ H_2$	• Combustible material • May form explosive mixtures with air when heated • Toxic if inhaled, ingested, or through skin contact
Ethyl Ether	$(C_2H_5)_2O$	• Extremely flammable liquid • Susceptible to peroxide formation that can form explosive mixtures
Ethyl Hexaldehyde	$C_8H_{16}O$	• Highly flammable liquid • Can form explosive mixtures with air • Fire can produce irritating, corrosive, or toxic gases • Can irritate the skin and eyes on contact • Can irritate the nose, throat, and lungs causing coughing and/or shortness of breath
Formaldehyde	CH_2O	• Flammable/combustible material • May form explosive mixtures with air • Can be toxic if inhaled/ingested • Can cause burns to the skin and eyes • Fire can produce irritating, corrosive, or toxic gases
Methyl Ethyl Ketone (also called Butanone)	$CH_3C(O)CH_2CH_3$	• Highly flammable material • Containers may explode when heated • Can be toxic if inhaled/ingested • May irritate or burn the skin and eyes • Fire can produce irritating, corrosive, or toxic gases

The types of bonds between carbon atoms also have a significant effect on chemical behavior. The bonds between carbon atoms are what distinguish the four types **(Figure 4.43)**.

These terms (*alkanes, alkenes, alkynes*, and *aromatics*) may be unfamiliar to the new technician, but they represent compounds whose names should be very familiar. Examples include methane, propane, ethylene, acetylene, and benzene. Selected hydrocarbons will be profiled in more detail later in this section.

The following are the four basic types of hydrocarbons:

- **Alkanes** — Most alkanes (single bonds) are relatively stable. They have only single bonds between carbon atoms. Examples are methane (CH_4) or Butane (C_4H_{10}).
- **Alkenes** — Alkenes (double bonds) are less stable than alkanes and are prone to polymerization. They have at least one double bond between carbon atoms. An example of an alkene would be ethylene (C_2H_4).

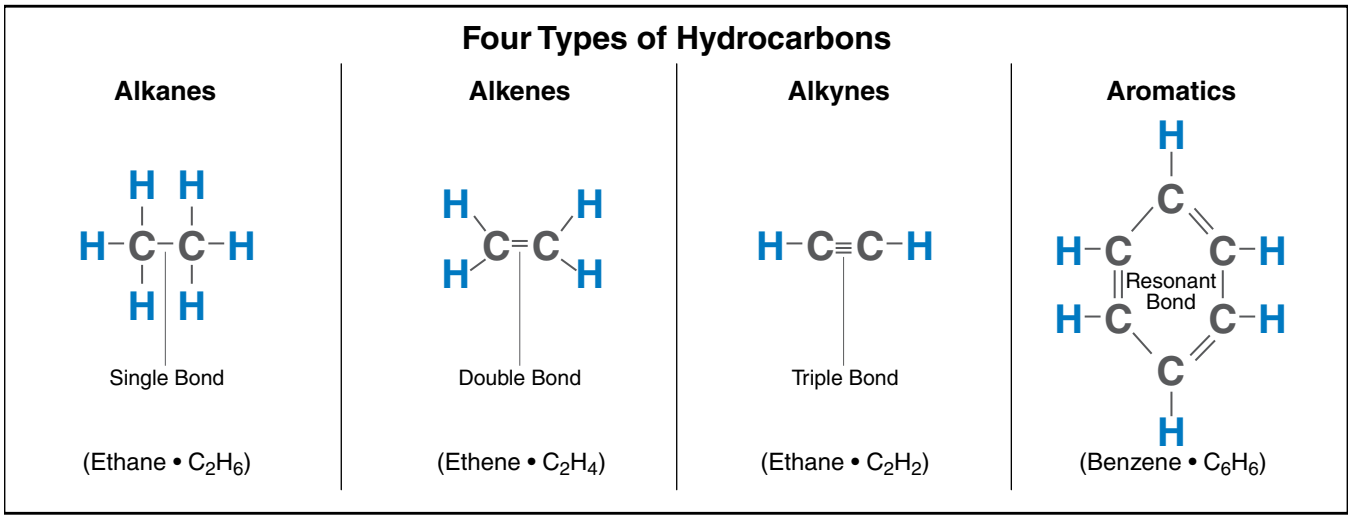


Figure 4.43 The four types of hydrocarbons (alkanes, alkenes, alkynes, and aromatics) are distinguished by the type of bonds between their carbon atoms.

- **Alkynes** — Alkynes (triple bonds) are highly unstable and have explosive potential. They have at least one triple bond between carbon atoms. An example of an alkyne would be acetylene (C_2H_2). Double and triple bonds are very reactive with triple bonds, more so than double bonds.
- **Aromatics** — Aromatics have a ring (cyclic) structure with resonant bonds. An example of an aromatic hydrocarbon would be benzene (C_6H_6). Most aromatics are very stable even though they appear to have three double bonds because the electrons actually resonate between the carbon atoms in the resonant bonds. As a group, they are also fairly toxic. Some are carcinogenic. The aromatics typically burn with sooty smoke that often gives the appearance of a spider web.

However, it is important to remember that these are only generalizations. The information does not necessarily apply to all compounds in each category. For example, while most aromatic hydrocarbons are stable, styrene (C_8H_8) contains a double bond between carbon atoms outside the resonant structure. Styrene will polymerize at normal temperatures if not mixed with an inhibitor. The bottom line is that there are enough common characteristics between the different hydrocarbons that hazardous materials technicians can use these generalizations for a quick assessment.

A halogenated hydrocarbon is one of the alkanes, alkenes, alkynes, or aromatics that contains a halogen (chlorine, bromine, iodine, fluorine). They are typically more toxic than the parent materials. Many of these materials do not have flash points because the halogen suppresses the flashing of these materials, but these same materials may have explosive ranges. When they combust they release toxic acid gases and potentially other extremely toxic materials such as phosgene.

WARNING!

Always check multiple reference sources to size up the hazards and identify characteristics that may not fit the general profile. Validate this research with appropriate monitoring.

Table 4.10
Aromatic Hydrocarbons and Their Hazards

Aromatic Hydrocarbons	Formula	Hazards
Benzene	C_6H_6	• Highly flammable liquid • Can form explosive mixtures with air • Fire can produce irritating, corrosive, or toxic gases • Can cause toxic effects if inhaled or absorbed through the skin • Can irritate or burn the skin and eyes
Biphenyl	$C_{12}H_{10}$	• Combustible • Emits toxic fumes under fire conditions • Irritating to eyes, nose, throat, and skin • Incompatible with oxidizers
Durene	$C_{10}H_{14}$	• Flammable/combustible • Emits irritating or toxic gases under fire conditions • Vigorous reactions to include explosions when in contact with strong oxidizers
Toluene	C_7H_8	• Highly flammable liquid • Insoluble in water • Vapors irritate eyes and upper respiratory tract • Vigorous reactions when in contact with alkyl chloride or other alkyl hallides

Aromatic Hydrocarbons and Their Derivatives

The five substances listed in **Table 4.10** are aromatic hydrocarbons. In general, aromatic hydrocarbons have benzene-like structures. Examples of aromatic hydrocarbons include benzene, toluene, xylene, styrene, and cumene.

Oxidizers

The oxidizer family of chemicals can be broken down to different families. Some are relatively stable while some can be very unstable. An oxidizer does not burn per se, but it can make a fire burn much hotter and faster **(Figure 4.44)**. For example, oxygen is an oxidizer but is not a flammable element. However, it can dramatically accelerate combustion. Oxidizers have the ability to burn continuously without air being present because they produce oxidizing capabilities and may need an air supply to support combustion. Oxidizers may also be explosive.

Inorganic peroxides can act as both an oxidizer and a corrosive. Hydrogen peroxide is an example of an inorganic peroxide. While the store-bought hydrogen peroxides are roughly 3% product with the remainder being water, commercial grade hydrogen peroxide can range from 30%-70% product. When hydrogen peroxide is in this concentration, it will have the ability to spontaneously combust if mixed with an organic material such as wood, leaves, or other Class A materials. Peroxides may have the ability to not only combust, but may even explode in the absence of air.

Organic peroxides are a unique element and typically contain both an O-O which supplies oxygen and a part that can act as a fuel in its molecular structure. For these materials, just a small amount of heat may be needed to create a fire or explosion.

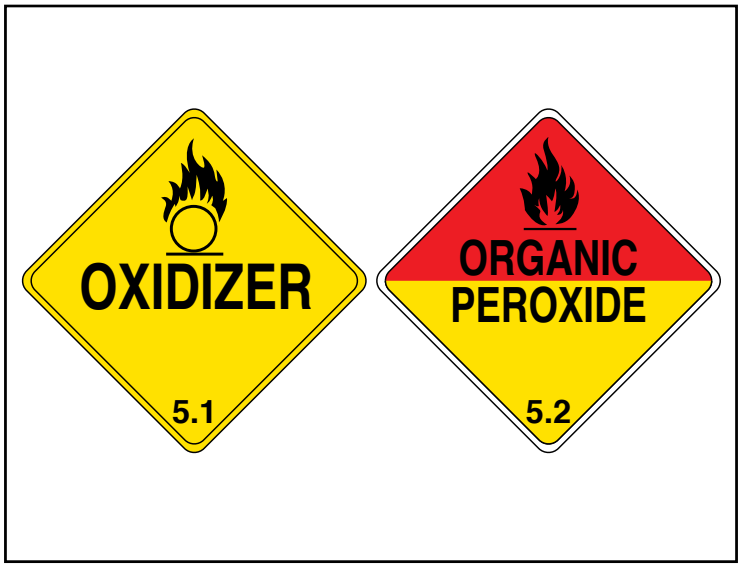


Figure 4.44 Oxidizers don't burn, but they can dramatically accelerate combustion.

Common uses for organic peroxides may include catalysts and/or initiators for a polymerization reaction. Organic peroxides may be liquids or solids and may be dissolved in a solvent. These solvents may be flammable. Organic peroxides are often shipped refrigerated and stored in cold storage cabinets.

Chlorates and perchlorates are unstable molecules containing excess oxygen. These elements are not flammable, but they will decompose rapidly when subjected to heat. When these elements decompose, they will release oxygen and support a rapid burning in any nearby combustible material.

Inorganic Peroxide — An inorganic compound containing an element at its highest state of oxidation (such as perchloric acid, $HClO_4$), or having the peroxy group, OO (such as perchromic acid).

Organic Peroxide — Any of several organic derivatives of the inorganic compound hydrogen peroxide.

WARNING!

Haz mat technicians should treat organic peroxides as a Class 1 explosive because of the instability and sensitively of organic peroxides.

Reactive Materials

Chemical reactivity describes a material's propensity to release energy or undergo change either on its own or in contact with other materials. Reactivity is the tendency of a material or combination of materials to undergo chemical change under the right conditions. Reactive materials, while dangerous, can serve a benefit in different processes. Chemical reactivity is a highly desirable trait that permits a wide variety of useful materials to be synthesized. It may also allow products to be made under moderate conditions of pressure and temperature, thus saving energy and reducing the risks of working with high pressure and temperature equipment.

Air-Reactive Material — Substance that ignites when exposed to air at normal temperatures. *Also called* Pyrophoric.

Air Reactive

Air-reactive materials (also called *pyrophoric materials*) ignite, decompose, or otherwise release energy when exposed to air. These reactions can be quite violent, with the added potential of container failure due to overpressurization.

Technically, pyrophoric materials are those that react in *dry* air, whereas those that react in *moist* air might be considered water-reactive instead. However, it should never be assumed that the word *pyrophoric* on a warning label, on a safety data sheet (SDS), or in hazardous materials reference sources is meant to exclude reactivity to moist air. Not everyone writing these documents will check the precise definitions of a word before using it, and not every dictionary will say the same thing. Hazardous materials technicians should assume that pyrophoric materials are also water-reactive until they have determined otherwise by checking at least three reference sources.

When materials are air-reactive but not water-reactive (white and yellow phosphorus, for example), they may be stored under water to prevent contact with air. But when materials are also so water-reactive that they will react with moisture in the air — for instance, sodium, potassium, and other alkali (Group I) metals — they must be stored under some other substance, such as an inert gas, mineral oil, or kerosene.

When pyrophoric materials are burning, any extinguishing agent that excludes air *should* be effective, which means that water can be used to fight the fire. However, because some pyrophoric materials are also water-reactive, it is essential that hazardous materials technicians check available reference sources to determine appropriate extinguishing agents for the substance(s) involved.

Water-Reactive Material — Substance that reacts in varying degrees when mixed with water or exposed to humid air.

Water Reactive

Water reactivity is the tendency of a material to react, or chemically change, upon contact with water. Reactions involving **water-reactive materials** can range from mild to severe, with some materials reacting explosively. The reactions and their by-products will vary depending on the materials involved. The following are some of the more common consequences of allowing these materials to come in contact with water **(Figure 4.45)**:

- **Flammable gases** — Hydrogen gas (H_2) is often created when hydrogen atoms that are liberated from water molecules are separated by the reaction. However, hydrogen is not the only flammable gas possible. For example, when calcium carbide (CaC_2) reacts with water, carbon and hydrogen combine to form highly flammable acetylene (C_2H_2) gas. Some of the other compounds that contain carbon, such as aluminum carbide ($A_{l4}C_3$) and beryllium carbide (Be_2C), evolve into methane gas (CH_4) upon contact with water.

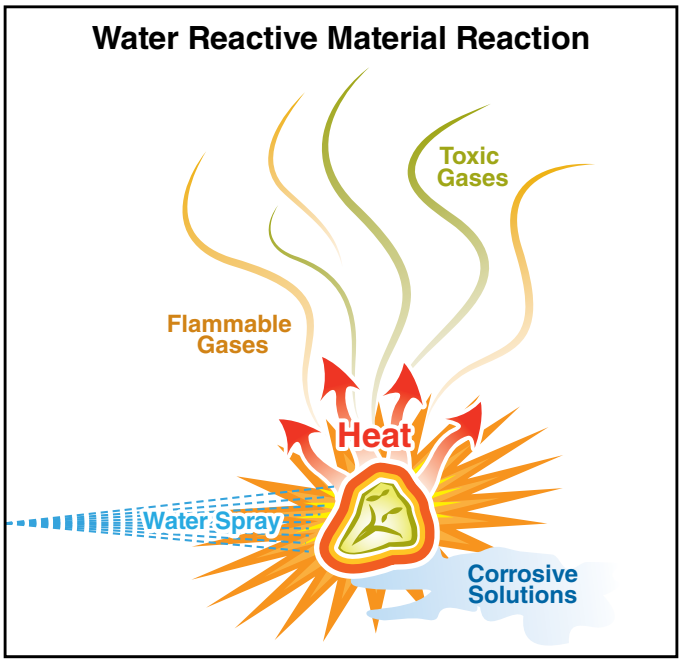


Figure 4.45 Chemical reactions involving water-reactive materials can release flammable gases, heat, corrosive solutions, and toxic gases.

- **Heat** — Water reactions are always exothermic, some very much so. A reaction that generates its own heat and flammable gases while liberating extra oxygen upon contact with water has all four parts of the fire tetrahedron in place. Fires should be expected. There is often enough heat to also ignite nearby combustibles. Because fires involving combustible metals can be significantly hotter than other fires, there is the added risk of causing a steam explosion if hazardous materials technicians attempt to use water as an extinguishing agent.
- **Corrosive solutions** — Many of the water-reactive materials are either metals or salts (compounds comprised of a metal element and one or more non-metal elements). When they react with water, metals frequently combine with oxygen and hydrogen from the water molecules to form highly caustic solutions, often recognized by the word *hydroxide* in the name. Examples include sodium hydroxide (NaOH) and potassium hydroxide (KOH) solutions. Some of the materials that are comprised of a metal element and chlorine, such as aluminum chloride ($AlCl_3$) and stannic chloride ($SnCl_4$), react with water to form hydrogen chloride (HCl), either in the form of an acid gas (if only small amounts of water are involved) or the acid gas in solution (if enough water is present).
- **Toxic gases** — Many of the reactions also produce gases that are irritating or toxic. For example, compounds made with nitrogen, such as lithium nitride (Li_3N), may evolve ammonia gas (NH_3), while those made with phosphorus, such as aluminum phosphide (AlP), may generate toxic phosphine gas (PH_3).

Figure 4.46 Class D extinguishers are designed for water-reactive metal fires.

When water-reactive materials are present, hazardous materials technicians must consider all the different ways that these substances may come in contact with moisture, including moisture in the air and moisture in the skin, in the eyes, or in the respiratory system. To overlook any of these less-obvious scenarios could put responders at risk for serious injury.

Fires involving water-reactive materials are some of the most challenging to handle. If the fire is still small, hazardous materials technicians may be able to control it with specially formulated dry powders, such as Pyrene G-1 or Met-L-X **(Figure 4.46)**. Sand can sometimes be used to extinguish a small fire involving combustible metals — but preferably if the sand is completely dry. If there is any moisture present, the burning metal will react with the water in the sand and intensify the problem.

Extinguishing Metal Fires

Ordinary extinguishing agents are *not* effective or safe to use on combustible metal fires. Dry chemical extinguishers will not put out the fire. Burning metals react readily with the oxygen in carbon dioxide (CO_2) extinguishers. The intense heat generated by these fires will cause Halon to break down more readily than it will in ordinary fires, evolving both highly reactive halogens (such as chlorine and fluorine) that serve as oxidizers and highly toxic gases, such as hydrogen fluoride (HF), hydrogen chloride (HCl), or hydrogen bromide (HBr).

To extinguish metal fires, use a Class D, dry powder extinguisher designed for this purpose. Do not confuse *dry powder* extinguishers with *dry chemical* extinguishers because the extinguishing agents are **not** the same.

When facilities are equipped with automatic flooding systems that fill the area with an inert gas such as argon, the fire can be effectively extinguished by excluding oxygen. If a system is already in place but has not been discharged, hazardous materials technicians may want to explore activating it as the safest means to mitigate the incident.

The best course of action for large fires involving water-reactive materials is typically to isolate the area, protect exposures, and allow the fire to burn until all of the fuel has been consumed. However, using water on such a fire is not *always* out of the question. For example, flooding amounts of water can be used to extinguish burning magnesium parts—*solid* parts such as castings and fabricated structures, not powder, dust, chips, and shavings—because copious amounts of water can eventually cool the fire enough to overcome the exothermic reaction. Hazardous materials technicians must *not* use water to fight fires involving water-reactive materials unless they know what they are dealing with, have thoroughly assessed all the risks, and are properly trained in extinguishing these fires. The dangers are too great.

Figure 4.47 Shock- and friction-sensitive materials can be triggered into a violent chemical reaction by very little activation energy.

Shock- and Friction-Sensitive

Shock- or friction-sensitive reactive materials are potentially explosive materials and can be extremely sensitive to heat or shock **(Figure 4.47)**. The chemicals may decompose violently if struck or heated. The most common example of a shock or friction-sensitive material is trinitrophenol, commonly known as *picric acid*. Other examples of shock or friction-sensitive materials include the following:

- Ammonium nitrate
- Ammonium perchlorate
- Calcium nitrate
- Nitroglycerin
- Organic peroxides

Light-Sensitive

Light-sensitive chemicals have the ability to change their composition if exposed to natural light. Quite often, these changes will lead to less stable substances that may be more dangerous than their original compound. Some examples of light-sensitive chemicals are:

- Ammonium dichromate
- Hydrogen peroxide
- Silver salts
- Mercuric salts

In addition, many monomers are catalyzed by light to promote polymerization — such as the methacrylates used as plastic fillings.

Temperature Sensitive

Some chemicals may decompose based on their temperature. If not stored properly, a chemical may break down and decompose. While some temperature reactions may be mild, others may be violent or even explosive. Many peroxides tend to be temperature-sensitive materials. Some chemicals may be very sensitive to high temperatures and some to low temperatures. Of course, the actual temperature that may affect a chemical is relative to the chemical itself. This critical information may be found in many chemical reference manuals. Terminology that must be understood by the haz mat technician follows:

- **Self-Accelerating Decomposition Temperature (SADT)** — Temperature above which the decomposition of an unstable substance continues unimpeded, regardless of the ambient or external temperature. SADT means the lowest temperature at which self-accelerating decomposition may occur for a substance in the packaging as used in transport.
- **Maximum safe storage temperature** — The maximum safe temperature at which a product can be stored. This temperature is well below the SADT.

Corrosives

As discussed in Chapter 3, corrosives are classified as either acids or bases based on their chemical behavior when in contact with water. Acids are those compounds that release hydronium ions $[H_3O]^{+1}$ when dissolved in water, a process sometimes referred to as **dissociation**. Bases (also called *caustics* or *alkalis*) release hydroxide ions $[OH]^{-1}$ when dissolved in water. Hazardous materials technicians cannot see the release of ions, but can detect them and distinguish between acids and bases by measuring the strength (pH) of a corrosive.

All corrosives, whether acid or base, have a variety of hazards. The profiles provided in this section give some good examples. However, one of the most significant differences between acids and bases is the way in which they damage human tissue. An acid in contact with the skin will cause the tissue to harden even as it eats away at that tissue, thereby limiting the damage to some degree. However, a base will soften and dissolve the tissue, creating far more penetrating and severe injuries. In both cases, the damage will continue until the corrosive is thoroughly flushed from the body. The extent of the injury is often not immediately obvious—something corrosive burns have in common with thermal burns.

Dissociation — In chemistry, a general process in which ionic compounds (complexes, or salts) separate or split into smaller particles, ions, or radicals, usually in a reversible manner. The dissociation of salts by solvation in a solution like water means the separation of the anions and cations; the dissociation of acids in a solution means the split-off of a proton H+.

Corrosives often produce immediate irritation, but it is not uncommon for pain to be delayed. This is particularly true with corrosives in solid form, which do not really start eating away at the tissue until they react with the moisture on the skin. Such a corrosive on dry skin might not be noticed until a person starts sweating or takes a shower later in the day.

Special Hazards of Chemicals and Weapons of Mass Destruction

Up to this point, we have concentrated on the chemistry of various chemical families and compounds. If a haz mat technician is called to intervene in an emergency situation, the technician should understand the makeup of the product and know how it will behave in this situation. Now that the haz mat technician has a background of the chemistry of a compound or a product, it is important to describe the special hazards of various chemical compounds. The following sections will explain the special hazards of chemicals that the responder may be exposed to during an emergency incident.

Chemical Warfare Agents

While many hazardous materials can be used as weapons, this chapter will focus on only five categories: nerve agents, blister agents (or vesicants), blood agents, choking agents, and riot control agents (irritants). The following sections will discuss these agents in greater detail.

Nerve Agents

Nerve agents are similar to organophosphate pesticides in their chemical makeup and in the way that they attack the nervous system and cause uncontrolled muscular contractions. However, they are 100 to 500 times more potent than the pesticide formulated materials. Exposure to even minute quantities can kill very quickly. Nerve agents are considered the most dangerous of the chemical warfare agents. The common ones are:

- Tabun (GA)
- Sarin (GB)
- Soman (GD)
- V agent (VX)

NOTE: "G" stands for Germany, the country where the first three agents were developed. "V" stands for *venom*.

Persistence — (1) Length of time a chemical agent remains effective without dispersing. (2) Length of time a chemical remains in the environment. (3) Length of time a chemical agent remains as a liquid; typically a liquid chemical agent is considered persistent if it remains for longer than 24 hours.

Although people will sometimes use the term *nerve gas*, the term is a misnomer. Nerve agents are liquids at ambient temperatures. Although nerve agents are generally clear and colorless, colors and odors can vary with impurities. Impure G agents may have a slight fruity odor. VX may have a slight sulfur odor.

G agents are described as volatile and nonpersistent. However, as emphasized in the last chapter, they are less volatile than water, which has a vapor pressure of 17.5 mmHg at 68°F (20 °C) **(Table 4.11)**. These agents are sometimes made more **persistent** by adding various thickeners. VX is a persistent, oily liquid that evaporates at about the same rate as motor oil. The vapors of all four agents are heavier than air.

Table 4.11
Nerve Agents and Their Characteristics

Nerve Agent (Symbol)	Descriptions	Symptoms (All Listed Agents)
Tabun (GA)	• Clear, colorless, and tasteless liquid • May have a slight fruit odor, but this feature cannot be relied upon to provide sufficient warning against toxic exposure • ***Probable Dispersion Method:*** Aerosolized liquid	***Low or moderate dose by inhalation, ingestion (swallowing), or skin absorption:*** Persons may experience some or all of the following symptoms within seconds to hours of exposure: • Runny nose • Watery eyes • Small, pinpoint pupils • Eye pain • Blurred vision • Drooling and excessive sweating • Cough • Chest tightness • Rapid breathing • Diarrhea • Increased urination • Confusion • Drowsiness • Weakness • Headache • Nausea, vomiting, and/or abdominal pain • Slow or fast heart rate • Abnormally low or high blood pressure ***Skin contact:*** Even a tiny drop of nerve agent on the skin can cause sweating and muscle twitching where the agent touched the skin ***Large dose by any route:*** These additional health effects may result: • Loss of consciousness • Convulsions • Paralysis • Respiratory failure possibly leading to death ***Recovery Expectations:*** • Mild or moderately exposed people usually recover completely • Severely exposed people are not likely to survive • Unlike some organophosphate pesticides, nerve agents have *not* been associated with neurological problems lasting more than 1 to 2 weeks after the exposure
Sarin (GB)	• Clear, colorless, tasteless, and odorless liquid in pure form • ***Probable Dispersion Method:*** Aerosolized liquid	
Soman (GD)	• Pure liquid is clear, colorless, and tasteless; discolors with aging to dark brown • May have a slight fruity or camphor odor, but this feature cannot be relied upon to provide sufficient warning against toxic exposure • ***Probable Dispersion Method:*** Aerosolized liquid	
Cyclohexyl sarin (GF)	• Clear, colorless, tasteless, and odorless liquid in pure form • Only slightly soluble in water • ***Probable Dispersion Method:*** Aerosolized liquid	
V-Agent (VX)	• Clear, amber-colored odorless, oily liquid • Miscible with water and dissolves in all solvents • Least volatile nerve agent • Very slow to evaporate (about as slowly as motor oil) • Primarily a liquid exposure hazard, but if heated to very high temperatures, it can turn into small amounts of vapor (gas) • ***Probable Dispersion Method:*** Aerosolized liquid	

Source: Information on symptoms provided by the Centers for Disease Control and Prevention (CDC).

Considering the very low vapor pressures, nerve agent vapors will not travel far under normal conditions. Therefore, the size of the endangered area may be relatively small. However, the vapor hazard can be significantly increased if the liquid is exposed to high temperatures, spread over a large area, or aerosolized.

Nerve agents usually enter the body through inhalation of the vapors. These agents are also toxic by eye absorption, skin absorption, or ingestion. Onset of signs and symptoms is very rapid for inhalation and eye exposure and can happen within minutes, sometimes seconds. Onset can take several minutes to several hours with skin absorption, although nerve agents do penetrate the skin rapidly and effectively. Speed of onset also varies with amount of exposure.

Because nerve agents are very similar to organophosphate pesticides, attacking the nervous system by inhibiting acetylcholinesterase, the signs and symptoms of exposure will be much like those of organophosphate poisoning, though usually more severe. The most significant signs of nerve agent poisoning are:

- Rapid onset of pinpoint pupils
- Muscular twitching
- Seizures
- Excess secretion of body fluids (runny nose, tearing, sweating, salivation, vomiting, urination, and defecation)

NOTE: Following inhalation exposure, these signs can appear almost immediately.

SLUDGEM and DUMBELS

Some people teach the symptoms of exposure to chemical warfare agents with the acronyms *SLUDGEM* or *DUMBELS*:

- ***S***alivation (drooling)
- ***L***acrimation (tearing)
- ***U***rination
- ***D***efecation
- ***G***astrointestinal upset/aggravation (cramping)
- ***E***mesis (vomiting)
- ***M***iosis (pinpointed pupils) or ***M***uscular twitching/spasms

  or
- ***D***efecation
- ***U***rination
- ***M***iosis or ***M***uscular twitching
- ***B***ronchospasm (wheezing)
- ***E***mesis
- ***L***achrimation
- ***S***alivation

Blister Agents/Vesicants

Blister agents (also known as *mustard agents* or *vesicants*) are extremely toxic chemicals that produce characteristic blisters on exposed skin. Common types of blister agents include mustard (H), distilled mustard (HD), nitrogen mustard (HN), Lewisite (L), and phosgene oxime (CX).

Mustards and *Lewisite* are oily liquids that have been described as anything from colorless to pale yellow to dark brown, depending on purity. Also depending on purity and concentration, mustards may be odorless or may smell like mustard, onion, or garlic. Lewisite reportedly smells like geraniums.

Pure *phosgene oxime* is a colorless crystalline solid, but phosgene oxime can also be found as a yellowish-brown liquid. It has an intense, irritating odor.

All of the blister agents are relatively persistent, which means that it can take several days or weeks for them to evaporate. The oily consistency also means that these agents will be more difficult to remove during decontamination than less viscous products.

Blister agents are extremely toxic and many are carcinogenic. The primary routes of entry are inhalation and absorption. Blister agents easily penetrate clothing and are quickly absorbed through the skin. Only a few drops on the skin can cause severe injury and 3 grams absorbed through the skin can be fatal.

Common signs and symptoms are irritation and burns to the skin, eyes, and respiratory tract; difficulty breathing; and blisters. If a large area of the skin is involved, significant amounts of the agent can be absorbed into the bloodstream, causing severe systemic poisoning.

A few notable differences between the effects produced by the three types of blister agents can help responders distinguish which one may be involved:

- Mustard causes tissue damage almost immediately after exposure, the clinical (noticeable) effects are delayed from two to twenty-four hours, with four to eight hours being the most common. (It is the only chemical warfare agent that does not produce symptoms within minutes of exposure.)
- Phosgene oxime causes immediate pain or irritation to the skin, eyes, and lungs. Another sign that distinguishes phosgene oxime from other blister agents is that the skin lesions look more like gray wheals (hives) than blisters. Phosgene oxime causes more severe tissue damage than do other blister agents.
- Lewisite's effects are felt within seconds to minutes after exposure. With Lewisite and phosgene oxime, the irritation to eyes, skin, and mucous membranes may initially resemble the effects of riot control agents. However, the pain is more severe and will not decrease upon moving the patient to fresh air, as would be the case with riot control agents.

Blood Agents

Blood agents interfere with the body's ability to use oxygen either by preventing red blood cells from carrying oxygen to other cells in the body or by inhibiting the ability of cells to use oxygen for producing the energy required for metabolism. The most common blood agents are hydrogen cyanide (AC) and cyanogen chloride (CK).

These substances are very volatile, nonpersistent, colorless liquids under pressure, although at higher temperatures, hydrogen cyanide is a colorless gas. Both produce an odor of bitter almonds or peach kernels, but at least 40% of the population is genetically unable to smell the odor. Hydrogen cyanide is also flammable.

The primary route of entry is inhalation. However, cyanide can also be absorbed through skin or eyes. Exposed patients experience rapid onset of respiratory difficulty, ranging from initial gasping and rapid breathing to subsequent respiratory arrest if exposed to higher concentrations. Other signs and symptoms often include: dizziness, nausea, vomiting, headache, and irritation of eyes, nose and mucous membranes.

Like nerve agents, blood agents can produce seizures. However, cyanide does not produce pinpoint pupils and excessive secretions, common with nerve agents. Another distinguishing characteristic sometimes seen with exposure to cyanide is abnormally red skin.

Specific treatment for hydrogen cyanide and cyanogen chloride includes amyl nitrite and sodium nitrite to draw the cyanide out of cells in the body and sodium thiosulfate to detoxify the cyanide and help remove it from the body. The three compounds (amyl nitrite, sodium nitrite, and sodium thiosulfate) are packaged together in cyanide antidote kits.

Choking Agents

Choking agents are those that primarily attack the respiratory tract (the nose, the throat, and particularly the lungs). While a number of common industrial chemicals can act as choking agents, the two most often cited in terrorism training are chlorine and phosgene. Each will cause the following:

- Irritation to the eyes, nose, and throat
- Coughing and choking
- Respiratory distress
- Nausea and vomiting
- Headache
- Tightness in the chest

Severe exposures can result in potentially fatal pulmonary edema.

Riot Control Agents/Irritants

Riot control agents (also known as *irritants, irritating agents*, or *harassing agents*) cause temporary incapacitation by irritating the eyes and respiratory system. Common agents include: pepper spray (OC), tear gas (CS or CR), mace (CN), and adamsite (DM).

Riot control agents are solids, dispersed either as a fine powder or as an aerosol (a powder suspended in a liquid.) Some are sold in small containers as personal defense devices containing either a single agent or a mixture. Some devices also contain a dye to visually mark a sprayed assailant. **Table 4.12** identifies the odors associated with these agents.

Riot control agents quickly incapacitate a person with severe irritation to the eyes, nose, and respiratory tract; difficulty keeping eyes open; sneezing; coughing; runny nose; and shortness of breath. Adamsite may cause nausea and vomiting. Exposure to riot control agents can also trigger asthma attacks or other secondary problems in some individuals.

The primary route of entry is inhalation, but these agents can also be absorbed through the skin and eyes. Onset of signs and symptoms usually occurs within seconds. The effects seldom persist more than a few minutes once patients are removed to fresh air, but they can last several hours, depending on the dose and duration of exposure. Decontamination can often be limited to flushing the eyes and washing the face or other parts of the body directly affected.

Biological Agents and Toxins

The biological agents most likely to be used as weapons of mass destruction are generally divided into four groups:

- **Bacteria** — *Bacteria* are single-celled living organisms capable of independent growth. They do not require a living host in which to replicate and many can be cultured in a lab. Some, like anthrax, have the ability to form spores

Table 4.12
Riot Control Agents and Their Characteristics

Riot Control Agent (Symbol)	Descriptions	Symptoms (All Listed Agents)
Chlorobenzylidene malononitrile (CS)	• White crystalline solid • Pepper-like smell	***Immediately after exposure:*** People exposed may experience some or all of the following symptoms: • ***Eyes:*** Excessive tearing, burning, blurred vision, and redness • ***Nose:*** Runny nose, burning, and swelling • ***Mouth:*** Burning, irritation, difficulty swallowing, and drooling • ***Lungs:*** Chest tightness, coughing, choking sensation, noisy breathing (wheezing), and shortness of breath • ***Skin:*** Burns and rash • ***Other:*** Nausea and vomiting Long-lasting exposure or exposure to a large dose, especially in a closed setting, may cause severe effects such as the following: • Blindness • Glaucoma (serious eye condition that can lead to blindness) • Immediate death due to severe chemical burns to the throat and lungs • Respiratory failure possibly resulting in death Prolonged exposure, especially in an enclosed area, may lead to long-term effects such as the following: • Eye problems including scarring, glaucoma, and cataracts • May possibly cause breathing problems such as asthma ***Recovery Expectations:*** If symptoms go away soon after a person is removed from exposure, long-term health effects are unlikely to occur.
Chloroacetophenone (CN, mace)	• Clear yellowish brown solid • Poorly soluble in water, but dissolves in organic solvents • White smoke smells like apple blossoms	
Oleoresin Capsicum (OC, pepper spray)	• Oily liquid, typically sold as a spray mist • ***Probable Dispersion Method:*** Aerosol	
Dibenzoxazepine (CR)	• Pale yellow crystalline solid • Pepper-like odor • ***Probable Dispersion Method:*** Propelled	
Chloropicrin (PS)	• Oily, colorless liquid • Intense odor • Violent decomposition when exposed to heat	

Source: Information on symptoms provided by the Centers for Disease Control and Prevention (CDC).

that can survive for long periods of time in conditions that would otherwise kill the bacteria. Bacteria can also produce extremely potent toxins inside the body. Examples of bacteria include anthrax, brucellosis, cholera, plague, and tularemia.

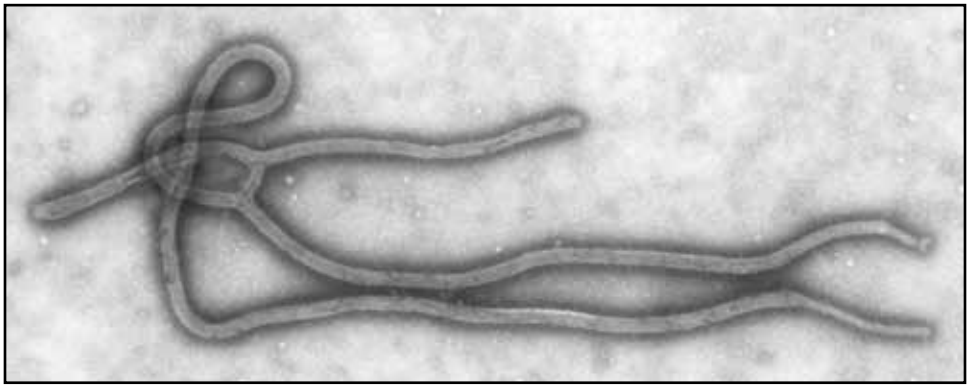


Figure 4.48 Viruses such as this Ebola virus are not capable of independent growth.

- **Viruses** — *Viruses* are living organisms that are much smaller than most bacteria **(Figure 4.48)**. Unlike bacteria, viruses are not capable of the basic metabolic functions necessary for independent growth. They require living cells in which to replicate. Examples of viruses include smallpox, Venezuelan equine encephalitis (VEE), and viral hemorrhagic fever (VHF).

- **Rickettsia** — *Rickettsia* are microorganisms that have many of the characteristics of bacteria. However, like viruses, they grow only within living cells. Q fever is an example of a rickettsia.
- **Toxins** — *Toxins* are nonliving chemical compounds—potent poisons produced by a variety of living organisms including bacteria, plants, and animals. They produce effects similar to those caused by chemical agents. Biological toxins are far more toxic than most industrial chemicals. Examples of toxins are botulinum toxin (botulism), ricin, saxitoxin, staphylococcal enterotoxin B, and trichothecene mycotoxins **(Figure 4.49)**.

Figure 4.49 Ricin, a biological toxin, is made from castor beans.

Biological agents and toxins can enter the body through most normal routes of entry. Much depends on the particular agent, how it is disseminated, and whether exposure is to the agent itself or the resulting disease in an infected person.

Toxins are not contagious at all. Some bacteria and viruses are contagious, but many are not. Three in particular that can be transmitted from one person to another to the degree that they require more than universal precautions are pneumonic plague, smallpox, and viral hemorrhagic fevers.

Explosives and Incendiaries

According to the Institute of Makers of Explosives, 2.51 million metric tons of explosives were produced in the United States in 2002. The largest consumption of explosives was for mining operations. However, it is the remaining 11% used for construction and miscellaneous purposes that is most likely to catch responders off guard because their presence is often unanticipated. Blasting agents and oxidizers based on ammonium nitrate accounted for 98% of U.S. industrial explosives sales.

Explosive — (1) Any material or mixture that will undergo an extremely fast, self-propagation reaction when subjected to some form of energy. (2) Material capable of burning or bursting suddenly and violently.

An **explosive** is any substance or article that is designed to function by explosion or that, by chemical reaction within itself, is able to function in a similar manner. Explosives range from being very sensitive to shock, heat, friction, or contamination, to being relatively insensitive, needing an initiating device to function.

This section addresses both common explosives (such as dynamite, TNT, and black powder) and improvised explosives devices (such as pipe bombs and mail bombs). Improvised explosives devices are often referred to as *IEDs*.

Understanding the Danger

It has been emphasized several times already, but it is worth repeating: One reason explosives are so dangerous is that they contain both an oxidizer and a fuel component in their structures **(Figure 4.50)**. For example, trinitrotoluene ($C_6H_2CH_3(NO_2)_3$), commonly known as TNT, begins as toluene (C_7H_8), which provides the fuel component. Three hydrogen atoms are replaced with three nitro groups (NO_2)—strong oxidizers. With two sides of the fire triangle already complete, all it takes is the introduction of energy in the form of heat, shock, or friction to cause a reaction.

Emergency responders need to be particularly cautious with older explosives, which can be even more unstable than those recently manufactured and explosives that have already been stressed by heat, shock, or friction. It is never safe to assume that explosives that survived flame impingement or a transportation accident, for example, are unscathed. Explosives have been known to detonate hours later, with little to no provocation.

Figure 4.50 Explosives contain both an oxidizer and a fuel component in their chemical structures.

Danger at Any Division

The six divisions of explosives identified in U.S. *Code of Federal Regulations, Title 49,* were established based on how explosives are expected to behave *under normal conditions of transport*. They do not necessarily reflect how these materials will behave when exposed to fire.

When six firefighters were killed fighting a fire involving ANFO (ammonium nitrate and fuel oil)—a common blasting agent—in Kansas City, Missouri, in 1988, it was common to think of these "very insensitive" Division 1.5 materials as posing little risk to firefighters. In fact, Division 1.5 explosives are described as being "so insensitive that there is very little probability of initiation or of transition from burning to detonation under normal conditions of transport." But "normal conditions of transport" does not include being exposed to the heat of a fire or being shocked by the impact of a transportation accident.

Many emergency responders have been killed or injured because they underestimated the hazard potential of relatively insensitive explosives. However, when explosives are threatened by fire, there is little difference between the six divisions. While the degree of risk varies, all Class 1 materials can be just as deadly if they explode.

Types of Explosives

Explosives are classified first as either low explosives or high explosives based on their detonation velocity. Low explosives are those that **deflagrate** (very rapid combustion at a rate slower than the speed of sound—1142 feet per second [348 mps]). Examples include black powder, smokeless powder, and solid rocket fuel. Low explosives have more of a "propelling" effect than a "shattering" effect, so they are used primarily for propulsion. Low explosives can be initiated by a simple flame or acid/flame reaction. They can also be initiated by shock or friction, but do not require the shock of a blasting cap.

High explosives are those that **detonate** (instantaneous combustion, with speeds ranging from 3,300 to 29,900 feet per second [1 006 to 9 114 mps]) with a shattering effect. In general, high explosives must be initiated by the shock of a blasting cap. High explosives are further categorized (primary or secondary) based on their sensitivity to shock, friction, flame, heat, or any combination of these factors.

Primary high explosives are extremely sensitive and very hazardous to handle. They are sometimes called *detonators* or *initiation devices* because they are mostly used to initiate secondary explosives. Examples of primary high explosives include blasting caps, safety fuses filled with black powder, mercury fulminate, lead styphnate, and lead azide.

Deflagration — (1) Chemical reaction producing vigorous heat and sparks or flame and moving through the material (as black or smokeless powder) at less than the speed of sound. A major difference among explosives is the speed of the reaction. (2) Can also refer to intense burning; a characteristic of Class B explosives. (3) An explosion involving a chemical reaction in which the reaction (energy front) proceeds at less than the speed of sound.

Detonation — Supersonic thermal decomposition that is accompanied by a shock wave in the decomposing material; high explosives decompose extremely rapidly (almost instantaneously).

Secondary explosives are much less sensitive, but far more powerful than primary explosives. They are sometimes called *main charge explosives* because they do the bulk of the work after being initiated by a shock from a primary explosive. Examples of secondary explosives include dynamite, nitroglycerin, TNT, cylconite (RDX), and pentaerythrital tetranitrate (PETN).

Pesticide — Any substance or mixture of substances intended to be used to control, repel, or kill pests such as insects, mice and other animals, unwanted plants (weeds), fungi, or microorganisms like bacteria and viruses.

Pesticides and Agricultural Chemicals

Many chemicals are toxic, but most were not intended to kill the way that **pesticides** are. Even though pesticides are designed to kill specific target organisms (e.g., insects, rodents, or weeds), many pesticides can be very toxic to both humans and the environment.

Some pesticides are so toxic (based on chemical composition, concentration, or both) that they are available only to trained and licensed applicators. However, the majority can be found in occupancies throughout the community, including commercial and agricultural warehouses, farms and farm supply stores, nurseries and greenhouses, supermarkets, hardware and discount stores, and homes. Pesticides are also transported throughout the community in everything from large rail cars to small pickup trucks driven by pest control workers.

Pesticides are sometimes referred to as "crop protection chemicals" because the term does not have the same negative connotation as the word *pesticide*. But changing the name does not change the toxicity or other hazards associated with these materials.

Pesticide is an umbrella term for a family of chemicals designed to kill specific target organisms. **Table 4.13** identifies some of the different types of pesticides.

Other terms are used to categorize pesticides based on how they are designed to function. **Table 4.14** provides some examples.

Radiation

Incidents involving radioactive materials are uncommon because of the strict requirements governing their use and transportation. The concept of radioactive materials is often frightening to the general public. What is more frightening is the belief that terrorists could use nuclear devices as a weapon of mass destruction. While this section does not focus on radioactive materials used as weapons of mass destruction, all of the information certainly applies to terrorist events as well.

A *radioactive material* is defined as any material having a specific activity greater than 0.002 microcuries per gram (Ci/g). (Units of radiation measurement are covered in the next section.) Examples of radioactive materials include cobalt, uranium hexafluoride, and medical isotopes such as barium.

In reality, most incidents involving radioactive materials present minimal risks to emergency responders, but it is still necessary to take appropriate precautions to prevent unnecessary exposures.

Non-Ionizing

Non-ionizing radiation refers to any type of electromagnetic radiation that does not carry enough energy to ionize an atom or a molecule. Non-ionizing radiation will not completely remove an electron from an atom. There is only sufficient energy to excite the electron into a higher energy state.

Table 4.13
Types of Pesticides and Their Target Organisms

Type of Pesticide	Target Organisms
Algicides	Algae
Antimicrobials	Microorganisms (such as bacteria and viruses)
Biocides	Microorganisms
Fungicides	Fungi (including blights, mildews, molds, rusts)
Herbicides	Weeds
Insecticides	Insects and other arthropods
Miticides (Acaricides)	Mites (acarids)
Molluscicides	Snails and slugs
Nematocides	Nematodes (worm-like organisms that feed on plant roots)
Ovicides	Eggs of insects and mites
Rodenticides	Mice and other rodents

Table 4.14
Pesticide Categories and Functions

Type of Pesticide	Functional Design
Antifouling Agents	Kill or repel organisms that attach to underwater surfaces, such as boat bottoms.
Attractants	Attract pests (for example, to lure into a trap)
Defoliants	Cause leaves or other foliage to drop from a plant (e.g., to facilitate harvesting)
Desiccants	Promote drying of living tissues (e.g., unwanted plant tops)
Disinfectants and Sanitizers	Kill or inactivate disease-producing microorganisms on inanimate objects
Fumigants	Produce gas or vapor to destroy pests in buildings or soil
Insect Growth Regulators	Disrupt growth process of insects
Pheromones	Disrupt the mating behavior of insects
Plant Growth Regulators	Alter expected growth, flowering, or reproduction rate of plants (excludes fertilizers and other plant nutrients)
Repellants	Repel pests rather than destroy them (e.g., insect repellant)

Visible light, microwaves, and radio waves are some examples of non-ionizing radiation. The light from the sun that reaches the earth is primarily composed of non-ionizing radiation, but most of the ionizing radiation from the sun is filtered out by the earth's atmosphere.

Ionizing

Alpha, beta, gamma, and neutron are the four primary types of ionizing radiation. All radioactive materials give off at least one type of radiation. Many give off two or three **(Figure 4.51, p. 196)**:

- **Alpha particles** — Relatively large particles that can travel only a few inches in air and are stopped by shielding as light as a thin sheet of paper. They cannot penetrate intact skin. However, they may enter the body through inhalation, ingestion, or contamination of an open wound. Alpha particles are an internal hazard only.
- **Beta particles** — Much smaller than alpha particles, and far more penetrating. They can travel several yards in the air. They can also penetrate intact skin, damaging the skin and possibly internal organs. Beta particles can be inhaled or ingested like alpha particles. It takes heavier shielding to stop beta radiation such as wood or metal.
- **Gamma rays** — Electromagnetic waves of high energy and short wavelength. Gamma radiation has strong penetrating power, able to travel considerable distances and through heavy objects. It travels at the speed of light. It, also,

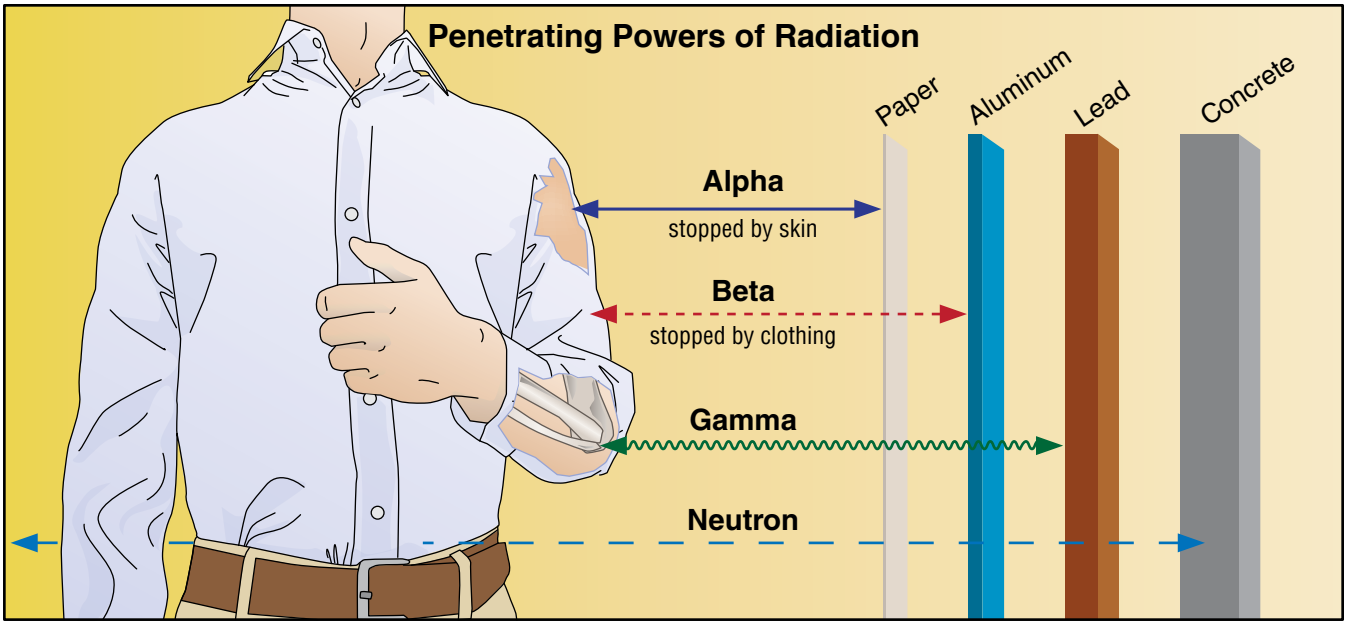


Figure 4.51 The three primary types of radiation are alpha particles, beta particles, and gamma rays. Neutron radiation and X-rays are unlikely to be involved in haz mat incidents. **Source:** *Modified from U.S. Environmental Protection Agency.*

can penetrate intact skin, causing skin burns and severe internal damage. Dense shielding, such as lead, concrete, or several feet of water, is required to stop gamma radiation.

- **Neutron particles** — Considerably larger than beta particles but smaller than alpha particles. Neutron radiation is normally associated with nuclear power plants but is becoming more common in medical treatment. It has very strong penetrating power and presents health hazards similar to that of other forms of radiation.

One other form of radiation bears mentioning: X-rays. However, the chances of encountering them at a hazardous materials incident are remote, so they are considered much less of a threat than alpha, beta, and gamma radiation. X-rays are similar to gamma rays, though not quite as hazardous. X-rays are of little concern to emergency responders since they are produced primarily by machines; they are rarely a by-product of natural radioactive decay.

Radioactive Decay

Radioactive decay is the spontaneous breakdown of an atomic nucleus resulting in the release of energy and matter from the nucleus. A radioisotope has an unstable nucleus that does not have enough energy to hold it together. Radioisotopes strive to be stable so they are constantly undergoing changes to try and maintain this stability. During this process they will release energy and matter from their nucleus and quite often may transform into a new element. This process is called *transmutation* **(Figure 4.52)**.

Half-Life — Time required for half the amount of a substance in or introduced into a living system or ecosystem to be eliminated or disintegrated by natural processes; period of time required for any radioactive substance to lose half of its strength or reduce by one-half its total present energy.

Half-Life

Half-life is the measure of how long it takes for one half of a given amount of radioactive material to decay (or change to a less hazardous form). For example, as uranium 238 decays, it changes first to thorium 230, which becomes radium 226, which decays to radon 218, which changes to bismuth 214, which finally becomes the stable element lead 206. This change occurs because as uranium

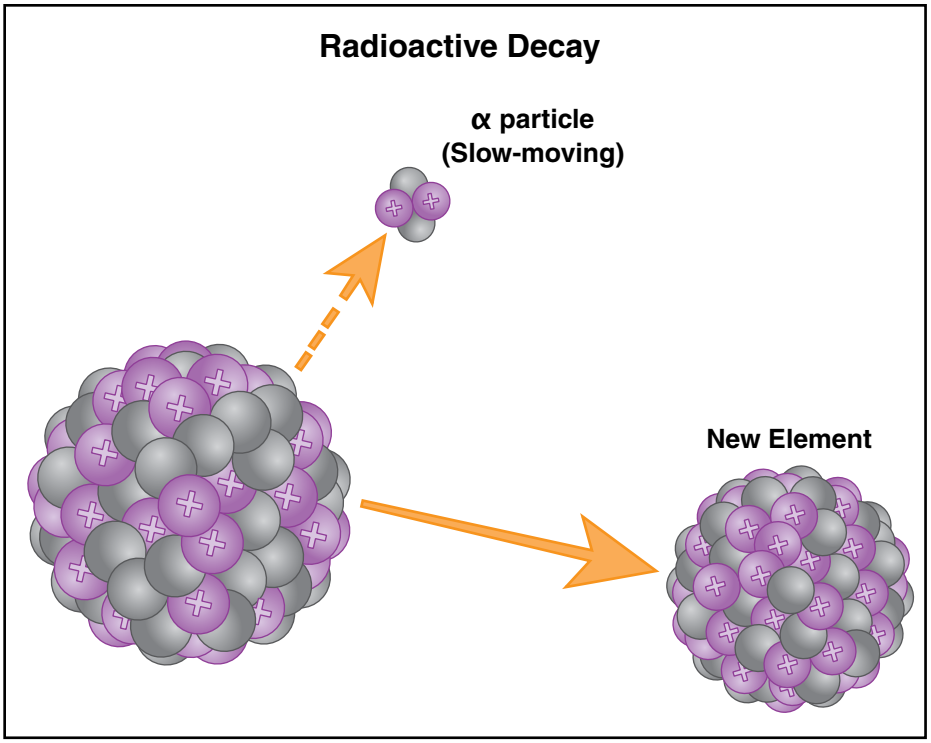


Figure 4.52 Radioactive decay is the spontaneous breakdown of an atomic nucleus resulting in the release of energy and matter from the nucleus.

238 decays, it "throws off" both neutrons and protons from the nucleus of the atom. The half-life of U238 is 4,468 million years. As a rule of thumb, a radioactive isotope decreases to less than 1% of its original value after seven half-lives.

Knowing a material's half-life can help hazardous materials technicians determine how long an area must be sealed off and whether the incident can be allowed to self-mitigate. If a radioactive material's half-life is only a few days, it may be best to simply seal off the site for a couple of weeks until the hazard is no longer present. However, where a material's half-life is extended, it will probably be necessary to bring in a cleanup company to mitigate the hazard. The majority of radioactive materials have extremely long half-lives, from several thousand to several billion years.

Activity

The energy of radiation gives it the ability to penetrate matter. Higher energy will be able to penetrate a higher volume and denser matter than lower level radiation. The strength of a radioactive source is called its activity. More accurately, the activity of a radioactive source can be defined as the rate at which a number of atoms will decay and emit radiation in one second **(Figure 4.53)**.

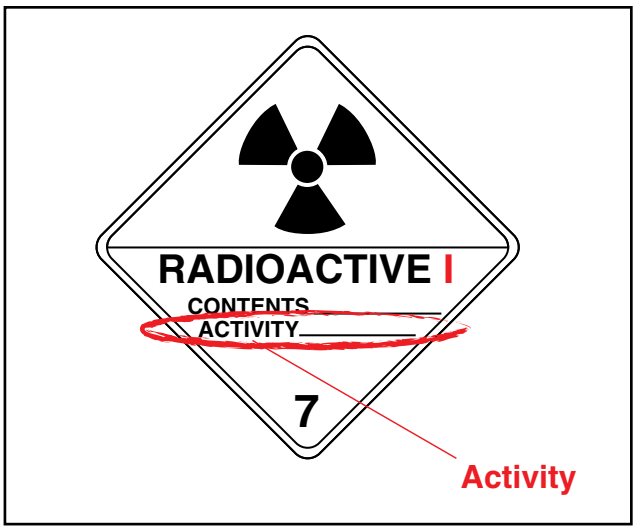


Figure 4.53 The activity of a radioactive source is listed on its radioactive label and represents the rate at which a number of atoms will decay and emit radiation in one second.

The International System (SI) unit for activity is the Becquerel (Bq), which is the quantity of radioactive material in which one atom transforms per second. The Becquerel tends to be a very small unit. The curie (Ci) is also used as the unit for activity of a particular source material. The curie is a quantity of radioactive material in which 3.7×10^{10} atoms disintegrate per second. The gamma curie can be defined as the activity of material in which the numbers of gamma-ray photons are emitted per second.

Chapter Summary

The haz mat technician is not expected to be a chemist, but a solid understanding of the chemistry principles that have been introduced in this chapter will benefit the emergency responder. Understanding how a chemical is composed and constructed will give the responder an advantage when making critical decisions during a haz mat response.

Dealing with a single chemical or compound may be challenging enough for the haz mat technician, but what could happen if another medium is introduced to a chemical product? This chapter covered the various types of reactions that may occur if a product comes in contact with heat, air, or another chemical. Reactions may run the gambit from docile to violent to explosive, so the haz mat tech must understand not only the terminology, but the philosophies as well.

The principles addressed in this chapter are not all encompassing, but the foundation has been laid for understanding the behaviors of a chemical at the structure level.

Review Questions

1. What is an atom made up of? **(p. 146)**
2. What is the periodic table of elements? **(p. 146)**
3. What are the four significant families of elements? **(p. 147)**
4. What is an example of matter that can exist in different states? **(p. 157)**
5. What is the difference between an ionic bond and a covalent bond? **(pp. 166-168)**
6. How do endothermic reactions, polymerization, and synergistic reactions compare with one another? **(pp. 171-174)**
7. What are the four basic types of hydrocarbons? **(pp. 178-179)**
8. What are the basic categories used for chemical warfare agents? **(p. 186)**
9. What is the difference between ionizing and non-ionizing radiation? **(pp. 194-195)**