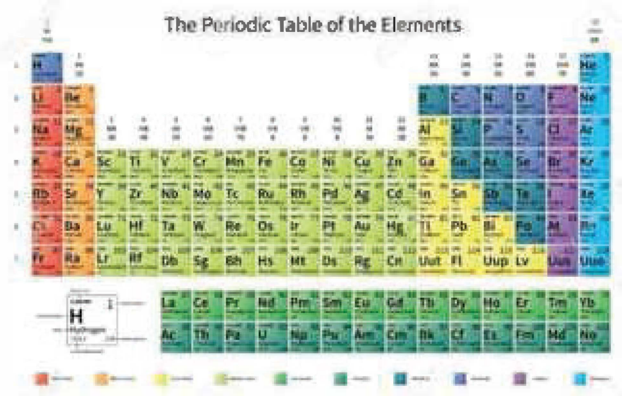
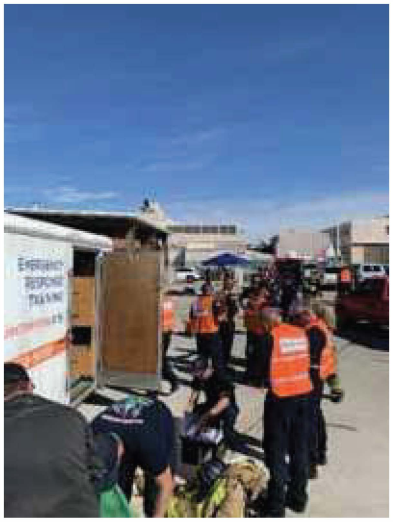
INDUSTRIAL EMERGENCY COUNCIL
Emergency Response Training

Hazardous Materials Technician 1A

Basic Chemistry





1301 Shoreway Road Suite 375 Belmont, CA 94002 (650) 508-9008 www.iectraining.org


CALIFORNIA SPECIALIZED
CSTI
TRAINING INSTITUTE

Table of Contents

Note: This Student Manual uses material from the Chemistry Library of the LibreTexts open source online textbooks. These textbooks are written and maintained by professors from various universities in the USA and Canada. https://chem.libretexts.org/

Chapter 1: Orientation and Administration

Course Overview

This course will give you a fundamental knowledge of basic chemistry. This foundation in basic chemistry is needed for the next phases of Hazmat Technician training. It will enable you to complete further training in hazardous materials response.

Understanding basic chemical concepts will give you the skills you will need to assess the hazards at a hazmat incident and analyze the risks of responding to that incident. Every major decision in a hazmat incident stems from this process.

Administrative Announcements

Course length: 32 hours.

Course completion requirements: attend at least 80% of the course, demonstrate the ability to perform assigned tasks and pass a written examination with a score of 70% or better.

Course management: the majority of the time in this course is spent on lecture. There may be some hands-on activities. The course manager will divide the class into groups of appropriate sizes to accomplish the assigned tasks in the most efficient manner. This may require you to periodically move to different training venues.

Facility policies: the course manager will advise you of all pertinent facility policies.

Course Objectives

Describe a hazard assessment and risk analysis process that will allow a Hazardous Materials Technician to analyze a hazardous materials incident to determine the complexity and potential outcomes of the incident.

Describe basic chemical and health hazard terms and principles. Explain their significance in the analysis process and in the behavior of a given hazardous material.

Describe resonant, ionic and covalent bonding and explain their significance in the analysis process and in the behavior of a given hazardous material.

Identify and describe the processes involved in chemical and physical change and explain their significance in the analysis process and in the behavior of a given hazardous material.

State the definition of DOT Hazard Classes and Divisions. Describe the major hazard(s) of each Class and/or Division.

Historical Perspective

The hazmat response system we have today is an integrated system of regulatory oversight, standardized training and standardized response resources and practices. A comprehensive regulatory process governs the production, transportation, storage, use and disposal of hazardous materials. Government agencies work with the private sector to ensure responders are adequately trained to safely mitigate hazmat incidents. The fire service has developed a standardized response organization, procedures and resources. The result is a response system that ensures that hazmat incidents are safely mitigated.

This has not always been the case.

The first fire service hazmat teams began to come online in the mid-1970s. Regulation of hazmat production, storage, use, transportation and disposal was fragmentary and stove piped until the late-1980s. Standardized training, equipment and procedures didn't become common until the early 1990s.

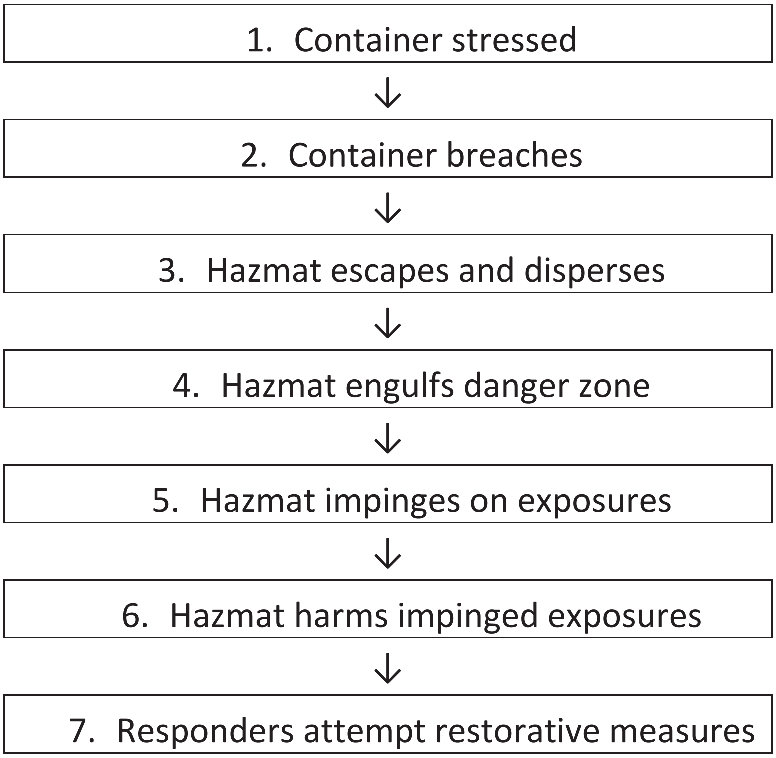
Prior to this, responders didn't have adequate training in how to deal with hazmat incidents. Hazmat response was largely the province of industry experts who would arrive on scene to assist emergency responders. Before these subject matter experts arrived emergency responders were largely on their own.

Ludwig Benner, a chemical engineer, joined the National Transportation Safety Board (NTSB) in 1970. As he investigated several major accidents involving hazardous materials he found that emergency responders were often victims in these incidents. He noticed that responders saw hazmat incidents as "an unintended, undesired *event…"* rather than a process that consisted of sequential and interconnected elements. The hazmat training at that time reflected that view. Most hazmat training consisted of descriptions of hazard classes and recognition clues along with various brief case studies. The training programs educated responders about what a hazardous material was and sometimes attempted to provide a "cookbook" for incidents involving specific materials. These programs didn't provide a systematic process for assessing hazards, analyzing risks and making decisions accordingly.

As Benner began to see hazmat incidents as a process rather than as a discrete event he realized there was a need to train responders accordingly. The process includes steps where responders can intervene to eliminate or reduce the hazards. This requires responders to assess the hazards and analyze the risks involved in the available response options. The potential outcomes are predictable and undesirable outcomes are often preventable.

General Hazardous Materials Behavior Model (GEBMO)

Based on his research, Benner developed a model he called the “General Hazardous Materials Behavior Model” (GEBMO). The GEBMO flowchart looked like this:



Hazmat Technician modules B-D will focus on steps 1-5 of the above. This course focuses on steps 6 and 7. Put another way, steps 6 and 7 bring up two questions:

1. How will this material hurt us?
2. What can we do about it?

This module of Hazmat Technician training is intended to help you understand the materials involved, predict their hazards and evaluate methods to reduce potential harm.

Responders can intervene at any step in GEBMO process to prevent or ameliorate harm. Whether or not they should intervene and at which step(s) they should intervene depends on their assessment of the hazards and risks. This module of Hazmat Technician provides the foundation for making those decisions.

OSHA Requirements

The OSHA Hazwoper regulation requires hazmat technicians to be able to do the following:

1. Know how to implement the employer’s emergency response plan.
2. Know the classification, identification, and verification of known and unknown materials by using field survey instruments and equipment.
3. Be able to function within an assigned role in the ICS.
4. Know how to select and use proper specialized chemical PPE provided to the hazardous materials technician.
5. Understand hazard and risk assessment techniques.
6. Be able to perform advanced control, containment, and/or confinement operations and rescue injured or contaminated persons within the capabilities of the resources and PPE available with the unit.
7. Understand and implement equipment, victim, and rescue personnel decontamination procedures.
8. Understand termination procedures.
9. Understand basic chemical and toxicological terminology and behavior.

This module of hazmat technician training will directly address items 5 and 9 of the above. Modules B-D will address the others. The remaining mandated competencies require a responder to understand the material presented in this course prior to being trained to meet those competencies. The other modules will build on the knowledge you gain here.

Chapter 2: Classification of Matter

Introduction

This course is designed to help responders assess and analyze the threat to human life, the environment, and property from incidents involving releases of hazardous substances. To accomplish this, a Hazmat Technician must understand basic chemistry. This module discusses the basic classification of matter and how it impacts the ability of a responder to perform risk analysis and assessment.

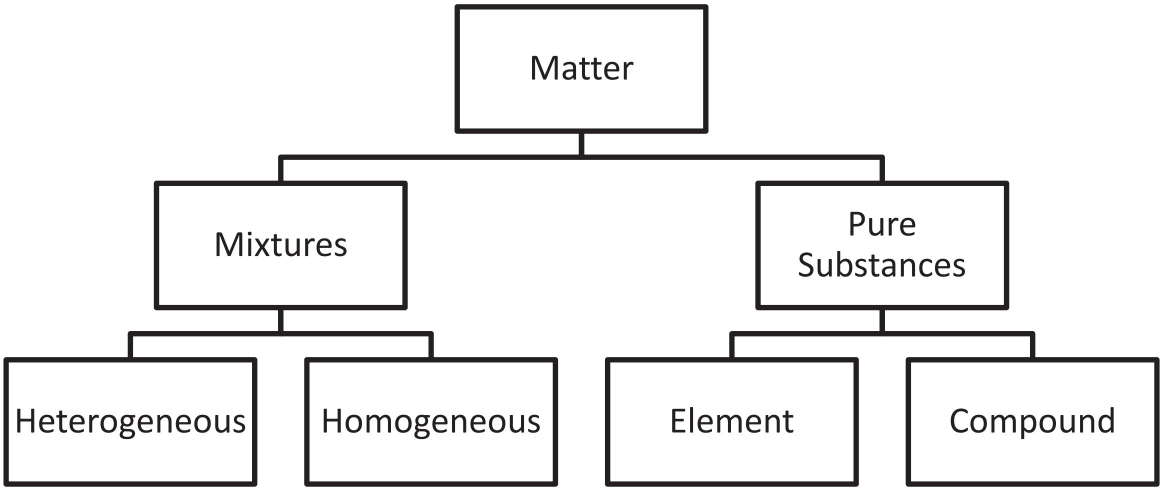
Matter

Matter, by definition, is anything that occupies space by having volume and has mass. (Mass: the quantity of matter it contains.) Matter can exist in four different states: solid, liquid, gas or plasma. Each state can be distinguished by certain characteristics:

- **Solid**: Particles (ions, atoms, or molecules) are closely packed together. The forces between particles are strong so that the particles cannot move freely but can only vibrate. As a result, solids are rigid, stable, possesses a definite shape and volume. The hazard of a solid can change depending upon its physical form. For example finely divided (powdered) Aluminum will burn explosively, while an Aluminum sauce pan presents no hazard at all. Solids can be transformed into liquids by melting and can change directly into gases through the process of sublimation.
- **Liquid**: The shape of a liquid is not definite but is determined by its container. Liquids flow and thus take the shape of their container. Liquids, like solids, are only slightly compressible. They have definite volumes (if the temperature and pressure are constant). As technicians, we will be concerned with characterizing liquids as either aqueous solutions, organic solvents, polar or non-polar, volatile, corrosive, etc.
- **Gas**: Has no fixed volume or shape. It expands to take both the shape and the volume of its container. Gases are readily compressible and capable of infinite expansion.
- **Plasma**: Like a gas, plasma does not have definite shape or volume. Unlike gases, plasmas are electrically conductive, produce magnetic fields and electric currents, and respond strongly to electromagnetic forces. They do not freely exist under normal conditions. Plasmas are commonly generated by either lightning or electric sparks. They are used in such things as fluorescent lights, neon lights and in plasma televisions.

Classification of Matter

Matter can be classified as either a pure substances or a mixture. A pure substance is defined as a homogeneous sample of matter, all specimens of which have identical compositions as well as identical chemical and physical properties. A pure substance may be an element.



Mixtures

A mixture consists of two or more elements or compounds that are physically mixed. However, these elements or compounds are not chemically bonded to one another and they retain their original properties. For example, the compounds salt and water combine to form the mixture salt water. Most mixtures can be separated into pure substances.

A mixture may be either homogeneous or heterogeneous. A homogeneous mixture is a mixture whose composition is uniform throughout and has no visible boundaries. Homogeneous mixtures are often called solutions. Solutions are normally transparent. A carbonated soft drink is a homogeneous mixture typically consisting of water, sugar, coloring, flavoring agents, and carbon dioxide, carbonate, or carbonic acid.

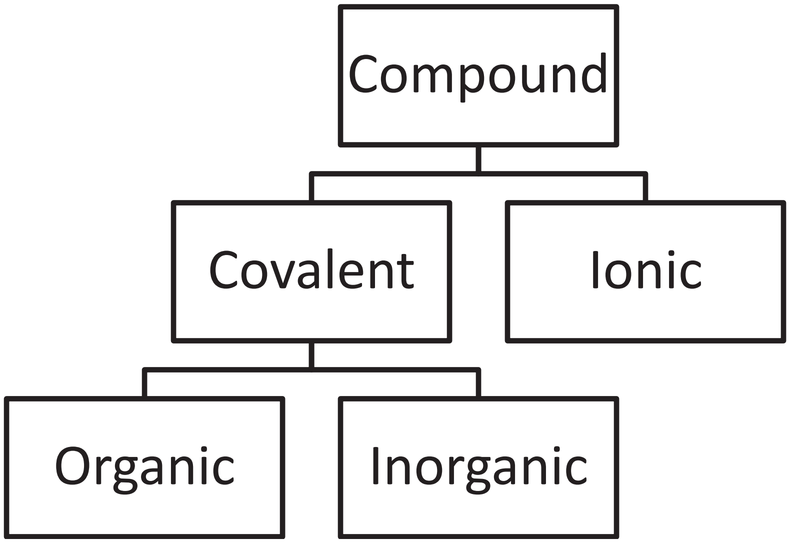
A mixture whose composition is not uniform is a heterogeneous mixture. Old waste paint that has settled and separated is an example of a heterogeneous mixture. Heterogeneous mixtures can be further divided into emulsions, suspensions or colloids. An emulsion is a heterogeneous mixture that includes two different liquids. A suspension consists of a solid suspended in a liquid. They are usually opaque and will separate over time. A colloid is a heterogeneous mixture composed of tiny particles suspended in another material. They are generally translucent and often won't separate over time. Milk is an example of a colloid.

Assessing the hazards at an incident entails assessing the hazards of each component of a mixture. It's important, therefore, to be able to recognize when an incident involves a mixture versus a pure substance.

Pure Substances

A pure substance can be made up of either a single chemical element or two or more elements bonded together. An element is a pure substance which is composed of a single type of atom. (The next chapter will go into more detail on elements.)

Compounds are made of multiple elements chemically bonded in a molecule. Two or more elements come together in specific amounts and form a compound. Properties of compounds are totally different from the properties of the elements comprising it. A compound that consists of two elements is called a binary compound. There is just one type of strong bond present: metallic, ionic or covalent. A compound made up of more than two elements is called a polyelemental compound. These substances have multiple types of chemical bonds.



A covalent bond is a chemical bond between non-metals that involves the sharing of electron pairs between atoms. Ionic bonding is a chemical bond between a metal and non-metal that involves the electrostatic attraction between oppositely charged ions.

Organic compounds always contain carbon. Nearly all organic compounds contain carbon-hydrogen or C-H bonds. Most inorganic compounds don't contain carbon. Inorganics include salts, metals, substances made from single elements and any other compounds that don't contain carbon bonded to hydrogen. (Some inorganic molecules contain carbon.) We will go into greater detail on this in later chapters.

Matter and Change

Matter can undergo a variety of changes. In general, these changes are classified as physical and chemical change. When matter undergoes a physical change it retains its fundamental identity. Chemical changes alter matter into another form with different properties from the original substance.

Physical Change

When the shape, size, appearance or state, of a substance is altered, but its chemical composition remains the same a physical change of matter takes place.

When a physical change occurs, only the phase or state of matter is modified. Physical changes occur when a substance transforms in physical state (solid to liquid to gas), but the chemical composition and identity remains the same. Physical changes are usually easily reversible. In a physical change, the state, shape or size of the object is changed.

Pressure, temperature or motion can bring about a physical change. Increasing pressure can cause a gas to become a liquid. The opposite occurs when pressure is decreased. Adding energy will cause the matter to increase in phase (e.g. a solid will become a liquid). Removing energy from a substance will cause it to decrease in phase (e.g. go from liquid to solid).

The amount of energy it takes for a substance to undergo a physical change can be measured and is commonly expressed in joules per gram (J/g) of the material.

Physical changes can be powerful enough to cause explosions. Any substance heated under confinement and capable of undergoing a physical change from a liquid to a gas can cause a mechanical explosion, a pressurized container failure – more commonly known of as a boiling liquid expanding vapor explosion (BLEVE).

There are six different types of physical change.

Process	Phase Change
Melting	Solid to liquid
Freezing	Liquid to solid
Vaporization	Liquid to gas
Condensation	Gas to liquid
Sublimation	Solid to gas
Deposition	Gas to solid

Chemical Change

A change in which the composition of a substance is altered is called as chemical change. As a result, the original properties get changed and one or more new substances are formed.

Chemical changes occur when one substance reacts with another substance to create a new compound. For example, Iron undergoes a chemical change when it combines with oxygen to form the reddish-brown compound iron oxide, commonly known as rust.

Chemical Change	Definition
Neutralization (Acid/Base)	A strong acid and strong base react with each other to form water and salt.
Oxidation/Reduction	A reaction that involves a transfer of electrons between two molecules.
Combustion	A chemical process in which a substance reacts rapidly with oxygen and gives off heat.
Decomposition	The process by which organic substances are broken down into simpler matter.
Polymerization	Relatively small molecules, called monomers, combine chemically to produce a very large chainlike or network molecule, called a polymer. Often an exothermic reaction, sometimes quite violent.
Replacement Reaction	The exchange of one group of atoms or a single non-hydrogen atom for another. An element reacts with a compound and takes the place of another element.

Chemical reactions generally involve a change in heat energy. Chemical reactions that release heat are called exothermic. Endothermic reactions are chemical changes in which heat is absorbed.

There are various indicators that a chemical change has taken place. They are:

- Change of odor.
- Change of color (for example, silver to reddish-brown when iron rusts).
- Change in temperature or energy, such as the production (exothermic) or loss (endothermic) of heat.
- Change of composition (paper turning to ash when burned).
- Light and/or heat given off.
- Formation of gases, often appearing as bubbles in liquids.
- Formation of a precipitate (insoluble particles).
- The decomposition of organic matter (e.g. rotting food).
- The change is difficult or impossible to reverse.

The rate at which chemical changes (reactions) occur is affected by heat, pressure, light, electricity and/or the presence of a catalyst. For example, platinum metal is used as a catalyst in a combustible gas indicator (CGI). It makes it possible for combustible gases/vapors to oxidize (i.e. burn) at lower temperatures. This allows a CGI to detect combustible gases without igniting them. Unwanted side reactions may be prevented with the introduction of other sacrificial substances that react more readily; for example adding BHT (butylated hydroxytoluene) to food to protect the food from oxidation. In many cases a chemical change won't occur at all without sufficient heat, pressure, light or electricity.

Catalysts

Catalysts are compounds that speed up a reaction rate but aren't otherwise used up in the reaction. Some reactions don't occur at appreciable rates without the presence of catalysts. Catalysts may be organic or inorganic, solid, liquid or gas. For example, the catalytic converters in vehicles reduce and oxidize vehicle emissions to chemically change them to less harmful gases. They use platinum, palladium and rhodium as catalysts to reduce the vehicle emissions.

Inhibitors

An inhibitor is a chemical compound, usually organic, that either retards the rate of a chemical reaction or prevents it from occurring. Inhibitors can make a chemical in storage more stable. For example, liquid organic peroxides are often inhibited from breaking down by diluting them approximately 25% with an alcohol or a ketone. Inhibitors may be added to other chemicals to prevent or retard corrosion, oxidation, or runaway polymerization reactions. Chemicals with inhibitors added often have limited shelf lives.

Summary

Matter is anything that occupies space and has mass. There are four states of matter: solid, liquid, gas and plasma. There are a number of different ways in which to classify matter. So far, we've been able to break matter down into pure substances or mixtures and to further divide pure substances into elements or compounds.

Hazardous materials incidents often involve physical or chemical changes. Physical changes occur when a substance transforms its physical state (solid, liquid, or gas). Chemical changes occur when one substance reacts with another to create a new compound. Later we will address how these physical or chemical changes can present additional dangers to response personnel. These will be addressed again in more detail later in the course as we learn how to recognize various chemicals.

Chapter Review

1. Check the box that matches the category that each substance belongs in.

Substance	Mixture	Pure Substance
Orange Juice	________	________
Gasoline	________	________
Aluminum Oxide	________	________
Sea Water	________	________
Water	________	________
Wine	________	________
Baking Soda	________	________
Air	________	________
Sugar	________	________

2. Compounds are made of (blank) element(s) chemically bonded in a molecule.
   A. One
   B. Multiple
   C. Similar
   D. Saturated

3. Chemical reactions that release heat are called:
   A. Endothermic
   B. Heterogeneous
   C. Exothermic
   D. Plasmic

4. What type of reaction occurs when monomers combine chemically to produce a very large chainlike or network molecule?
   A. BLEVE
   B. Decomposition
   C. Sublimation
   D. Polymerization

Chapter 3: Atomic Structure and the Periodic Table

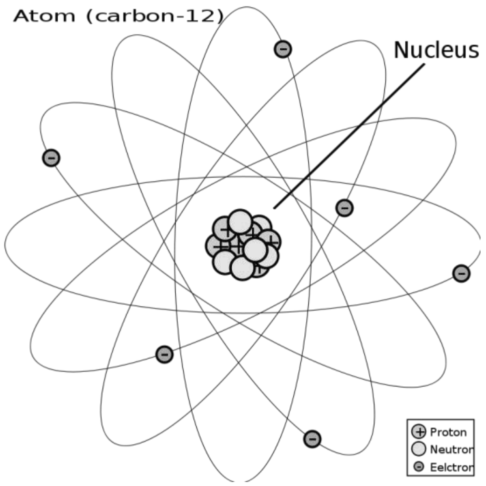
Introduction

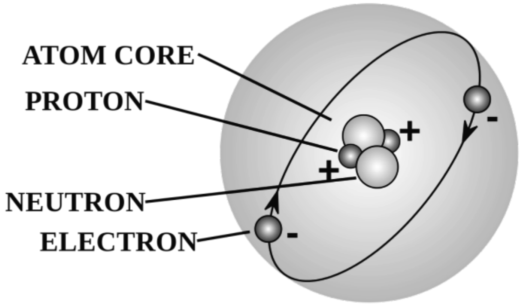
In this chapter you'll learn the basic building blocks of basic chemistry. We'll identify the names of elements, their chemical symbols, atomic number and show how they are organized on the periodic table.

Atomic Structure

Atoms are the basic building block of matter and can't be subdivided. They are smallest distinct unit of matter. They consist of protons, neutrons, and electrons. The nucleus, the center of an atom, contains the protons and neutrons. Electrons exist in "clouds," called orbitals, surrounding the nucleus. Atoms are electrically neutral. Atoms are made up of protons, electrons and neutrons.

- **Protons**: have a positive electrical charge and a mass of 1 atomic mass unit (amu). An amu equals 1.675 x10^{-24} grams. (An amu is one twelfth of the mass of a carbon-12 atom.) Every atom will have one or more protons in the nucleus. The number of protons in an atom is the atomic number for that element. The atomic number for an atom is unique to that atom. It determines the properties of that atom.
- **Electrons**: have a negative electrical charge and are almost weightless, having a mass 1/1840th that of a proton. Electrons are found in orbitals of different energy that surround the nucleus. Each orbital can hold a pair of electrons.
- **Neutrons**: have no electrical charge. They have a mass of 1 atomic mass unit. The number of neutrons plus the number of protons in the nucleus represent the atomic weight (mass) of the atom.





Elements

An element is a pure chemical substance composed of atoms with the same number of protons in the atomic nucleus.. There are currently 118 elements known, 98 of which occur naturally. The number of protons is what defines an element. Atoms of the same element can have differing numbers of neutrons, but they must have the same number of protons. The number of protons, neutrons and electrons in an atom determine its properties and identity.

Atoms of the same element that have a different number of neutrons are called isotopes of each other. They have different atomic weights due to the different number of neutrons in the nucleus. Different isotopes of the same element exhibit nearly identical chemical behavior. For example, carbon has 6 neutrons and 6 protons (C^{12}). Carbon^{14} (C^{14}) has 8 neutrons (2 extra). The C^{14} atom is unstable. Over time, it loses its extra neutrons and becomes C^{12}. The loss of those neutrons is called radioactive decay. That decay occurs at a known rate. Measuring the amount of C^{14} in a sample will determine how old that sample is. This process is called carbon dating.

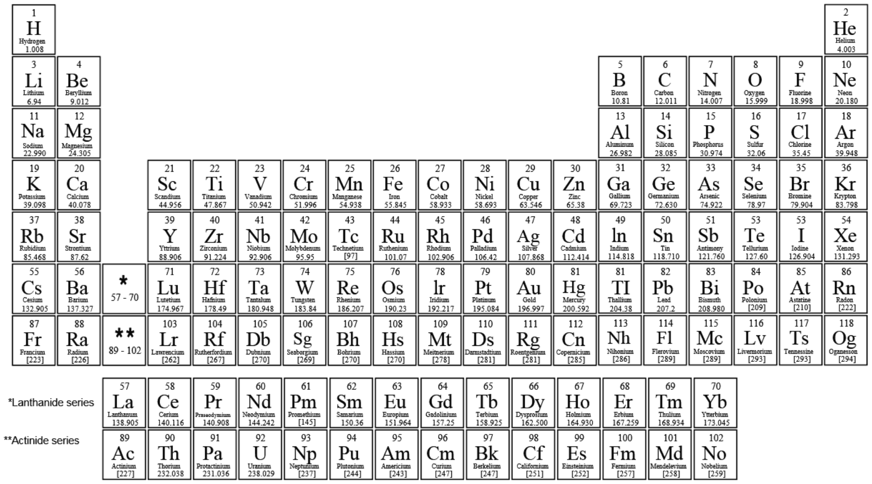
Alphabetic symbols are used as shorthand representations for the name of each element. According to International Union of Pure and Applied Chemistry (IUPAC) policy, “Elements can be named after a mythological concept, a mineral, a place or country, a property, or a scientist.” Elements have also been named after astronomical bodies, including planets, dwarf planets, a few asteroids, characters from Greek mythology, or words from other languages that describe a property they have (Barium derives from a Greek word meaning “heavy”). The original name may have been in a different language and as such the symbol doesn’t always stem from its current name. The symbol for Mercury is Hg and comes from the Latin word “Hydrargyrum” meaning “liquid silver.” Each of these symbols consists of a single uppercase letter or an uppercase letter followed by a lowercase letter. (Two uppercase letters written together indicate a compound rather than an element.)

Several gaseous elements (including halogens) occur naturally as diatomic molecules. In this form, two atoms of the element have a covalent bond between them. These include the elements: Hydrogen (H_2), Nitrogen (N_2), Oxygen (O_2), Fluorine (F_2), and Chlorine (Cl_2).

The noble gases, on the other hand, are often monatomic (single atoms). These include helium, neon, argon, krypton, xenon, and radon. Noble gases are unreactive gases so are often used to create an inert (unreactive) atmosphere.

The Periodic Table

The periodic table arranges all the known elements in a systematic array. Elements are arranged left to right and top to bottom in order of increasing atomic mass and atomic number. They are arranged in a manner that emphasizes the chemical relationships between the elements. The organization of the periodic table reveals recurring (“periodic”) chemical properties. The periodic table is a useful tool for predicting the behavior of an element.

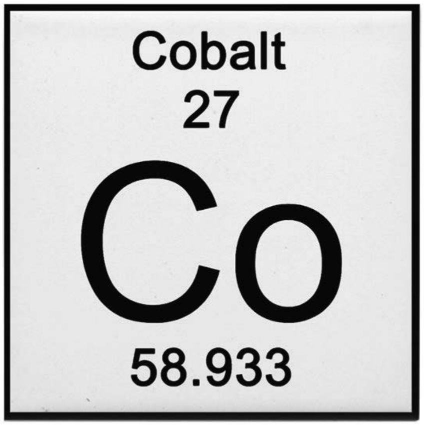


1 H Hydrogen 1.008																		2 He Helium 4.003
3 Li Lithium 6.94	4 Be Beryllium 9.012												5 B Boron 10.81	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
11 Na Sodium 22.990	12 Mg Magnesium 24.305												13 Al Aluminum 26.982	14 Si Silicon 28.085	15 P Phosphorus 30.974	16 S Sulfur 32.06	17 Cl Chlorine 35.45	18 Ar Argon 39.948
19 K Potassium 39.098	20 Ca Calcium 40.078		21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.630	33 As Arsenic 74.922	34 Se Selenium 78.97	35 Br Bromine 79.904	36 Kr Krypton 83.798
37 Rb Rubidium 85.468	38 Sr Strontium 87.62		39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium [97]	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.414	49 ln Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	53 Te Tellurium 127.60	53 I Iodine 126.904	54 Xe Xenon 131.293
55 Cs Cesium 132.905	56 Ba Barium 137.327	* 57 - 70	71 Lu Lutetium 174.967	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	78 lr Iridium 192.217	79 Pt Platinum 195.084	80 Au Gold 196.997	81 Hg Mercury 200.592	81 TI Thallium 204.38	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [209]	85 At Astatine [210]	86 Rn Radon [222]
87 Fr Francium [223]	88 Ra Radium [226]	** 89 - 102	103 Lr Lawrencium [262]	104 Rf Rutherfordium [267]	105 Db Dubnium [270]	106 Sg Seaborgium [269]	107 Bh Bohrium [270]	108 Hs Hassium [270]	109 Mt Meitnerium [278]	110 Ds Darmstadtium [281]	111 Rg Roentgenium [281]	112 Cn Copernicium [285]	113 Nh Nihonium [286]	114 Fl Flerovium [289]	115 Mc Moscovium [289]	116 Lv Livermorium [293]	117 Ts Tennessine [293]	118 Og Oganesson [294]

*Lanthanide series	57 La Lanthanum 138.905	58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.242	61 Pm Promethium [145]	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.045
**Actinide series	89 Ac Actinium [227]	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium [237]	94 Pu Plutonium [244]	95 Am Americium [243]	96 Cm Curium [247]	97 Bk Berkelium [247]	98 Cf Californium [251]	99 Es Einsteinium [252]	100 Fm Fermium [257]	101 Md Mendelevium [258]	102 No Nobelium [259]

The different rows of elements are called periods. The period number of an element signifies the highest energy level an electron in that element occupies (in the unexcited state). The number of electrons in a period increases as one traverses down the periodic table. An element’s position on the periodic table shows the electron configuration. Elements in the same column on the periodic table (called a “group”) have identical valance electron configurations and consequently behave in a similar fashion chemically. For instance, all the group 18 elements are inert gases.

Each square on the table is one of the 118 elements and information can be found in the square, such as we see in the example in for Cobalt: Name (Cobalt), Atomic Number (27), Symbol (Co), Atomic Weight (58.933). The atomic weights listed on the periodic table are average weights of the relative percentages of different isotopes found in naturally occurring samples of each element. Samples of elements from different places can have different atomic weights because they have different isotopic makeups. For example, boron from mines in Turkey has a lower atomic weight than boron found in California.



The size and weight of the atoms can be determined by their relative position on the table. As one moves from left to right in a row, the atoms become smaller. This is because they become more compact. These rows are called "periods" and as we move to the right in a period, an electron shell (K, L, M.) keeps adding one more electron until the shell is full, ending in a Noble Gas. As one moves from top to bottom on the periodic table, the atoms become heavier. Thus the largest elements are toward the bottom left and the smallest are near the upper right. Similarly, lighter elements are found toward the top of the table and heavier elements are located near the bottom. The lightest element is hydrogen, the smallest is fluorine and the largest is francium. The heaviest element you might be likely to respond to as a hazardous materials technician is Uranium. Depleted Uranium metal (U-238) has been used as counterweights in aircraft and race cars, and for radiation shielding in medical equipment. (The elements that are heavier than Uranium are man-made in nuclear reactors and linear accelerators. They don't occur naturally.)

The elements on the periodic table are divided into two main categories: metals and nonmetals. Metals are found to the left and below the stair casing line (a bold staggered line extending from the top of Group 13 to the bottom of Group 18, while non-metals are located to the right and above the stair casing line.

The dividing line between metals and non-metals is not hard and fast. The elements between metals and non-metals are often referred to as "Semimetals," "Post-transition metals" and "Metalloids." There is no official definition of these terms and they are often represented differently on different versions of the Periodic Table.

Metals are generally good conductors of heat and electricity; they have luster and are malleable. Subgroups of the metals include the precious metals, heavy metals, alkali and alkaline earth metals, and transition metals. Metals are fuels and will burn. They are considered electron rich and are called reducers or reducing agents. The ease with which they ignite depends on the type of metal and the exposed surface area. Metal blocks do not burn as well as metal turnings and finely divided metal dusts and powders. Metal powders can be spontaneously combustible (pyrophoric).

Solid nonmetals are often brittle or amorphous powders. A few of the nonmetals are flammable – carbon, phosphorous and sulfur. Five of them are strong oxidizers – oxygen, fluorine, chlorine, bromine and iodine. The nonmetals include chemically inert gases – nitrogen, helium, krypton, neon and argon. Non-metals positioned along the staircase line are the Metalloids or semimetals. These include germanium, silicon, arsenic and antimony. The metalloids have properties intermediate between a metal and a nonmetal. The silicon chip industry exploits this behavior as that one property of metalloids is their ability to act as a semiconductor.

Hydrogen is a non-metal, but can also at times behave as a metal. Which element hydrogen bonds with will determine its ultimate behavior. In certain covalent compounds it gives up an electron (polar covalent), but in ionic compounds it tends to gain an electron. The following is the generally accepted organization of the periodic table.

- **Alkali metals.** The alkali metals make up group 1 of the Table, and comprise Li through Fr. They have very similar behavior and characteristics. Hydrogen is group 1 but exhibits few characteristics of a metal and is often categorized with the nonmetals.
- **Alkaline earth metals.** The alkaline earth metals make up group 2 of the periodic table, from Be through Ra. The alkaline earth metals have very high melting points. They are oxides that have basic alkaline solutions.
- **Transition metals.** The transition elements are metals that have a partially filled *d* subshell and comprise groups 3 through 12 and the lanthanides and actinides.
- **Post-transition metals.** The post-transition elements are Al, Ga, In, Tl, Sn, Pb and Bi. As their name implies, they have some of the characteristics of the transition elements. They tend to be softer and conduct more poorly than the transition metals.
- **Metalloid.** (or “semi-metal” or “poor metal”). The metalloids are B, Si, Ge, As, Sb, Te, and Po. They sometimes behave as semiconductors (B, Si, Ge) rather than as conductors.
- **Lanthanides.** The lanthanides comprise elements 57 (lanthanum, hence the name of the set) through 71. They are grouped together because they have similar chemical properties. They, along with the actinides, are often called “the f-elements” because they have valence electrons in the *f* shell.
- **Actinides.** The actinides comprise elements 89 through 103. They, along with the lanthanides, are often called “the f-elements” because they have valence electrons in the *f* shell. Only thorium and uranium are naturally occurring actinides with significant abundance. They are all radioactive.
- **Nonmetals.** The term “nonmetals” is used to classify the elements H (also classed as a metal), C, N, P, O, S, and Se.
- **Halogens.** The halogen elements are a subset of the nonmetals. They comprise group 17 of the periodic table, from F through At. They generally very chemically reactive and are present in the environment as compounds rather than as pure elements.
- **Noble gases.** The noble gases comprise group 18. They are generally very stable chemically and exhibit similar properties of being colorless and odorless.

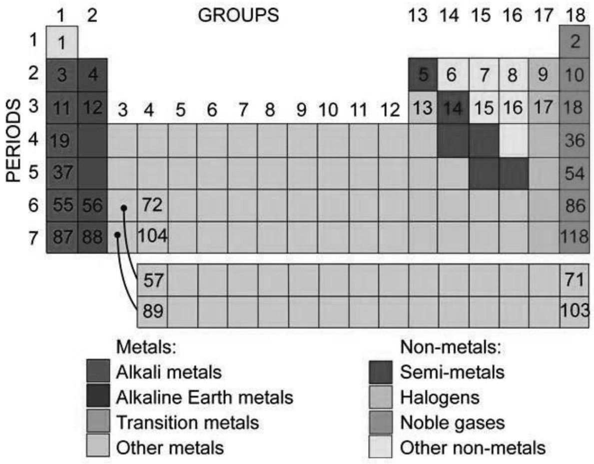
Periodic Table Groups

In chemistry, a group (also known as a family) is a column of elements in the periodic table of the chemical elements. There are 18 numbered groups in the periodic table, and the f-block columns (between groups 3 and 4) are not numbered. The elements in a group have similar physical or chemical characteristics of the outermost electron shells of their atoms (i.e., the same core charge), as most chemical properties are dominated by the orbital location of the outermost electron. There are three systems of group numbering. The modern numbering *group 1* to *group 18* is recommended by the International Union of Pure and Applied Chemistry (IUPAC). It replaces two older naming schemes that were mutually confusing. Also, groups may be identified by their topmost element or have a specific name. The following table shows all of the groups in the periodic table.

New IUPAC numbering	**Old IUPAC (European)**	**CAS (American)**	**Name**
Group 1	IA	IA	the alkali metals or lithium family
Group 2	IIA	IIA	the alkaline earth metals or beryllium family
Group 3	IIIA	IIIB	the scandium family (consisting of the rare earth elements plus the actinides)
Group 4	IVA	IVB	the titanium family
Group 5	VA	VB	the vanadium family
Group 6	VIA	VIB	the chromium family
Group 7	VIIA	VIIB	the manganese family
Group 8	VIII	VIIIB	the iron family
Group 9	VIII	VIIIB	the cobalt family
Group 10	VIII	VIIIB	the nickel family
Group 11	IB	IB	the coinage metals (not an IUPAC-recommended name) or copper family
Group 12	IIB	IIB	the zinc family
Group 13	IIIB	IIIA	the triels, boron group or boron family
Group 14	IVB	IVA	the tetrels, carbon group or carbon family
Group 15	VB	VA	the pnictogens or nitrogen family
Group 16	VIB	VIA	the chalcogens or oxygen family
Group 17	VIIB	VIIA	the halogens or fluorine family
Group 18	Group 0	VIIIA	the noble gases or helium family or neon family

The following are descriptions of the Groups that are of interest to hazmat responders:

- **Group 1: Alkali Metals** have one electron in the outer shell. The Alkali metals will lose one electron when they react with other elements. Alkali metals are reducing agents. They are water-reactive. The alkali metals include lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), and francium (Fr). Sodium is a silvery light metal that will float on water. It is so reactive with water, producing hydrogen gas, a lot of heat and leaving behind a caustic solution of lye, that it is stored under mineral oil to keep it away from the moisture in the air. Sodium is so soft it can be cut with a butter knife.
- **Group 2: Alkaline Earth** Metals have two electrons in the outer shell. The two valence electrons are not tightly bound to the nucleus so they tend to lose two electrons when combining with other elements. Alkaline earth metals are reducing agents. Some may be somewhat water-reactive. Alkaline earth metals include beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra). Calcium is a dull grey metal that is water reactive (substances that spontaneously undergo a chemical reaction with water). In water it produces hydrogen gas, heat and a caustic solution of Calcium Hydroxide (slaked lime). Calcium burns to form Calcium Oxide and while burning produces an intense white light called limelight. The alkaline earth metals are very reactive, although less so than the alkali metals. Because of their high reactivity, the alkaline earths are not found free in nature. However, all of these elements do occur naturally. They are common in a wide variety of compounds and minerals.
- **Group 7/17: Halogens** have seven electrons in the outer shell. It is the only element group that has elements existing in three of the four main states of matter at room temperature and pressure (solids, liquid, gas). The word *halogen* means “salt-producing”, because halogens reacted with metals produce many important salts. When forming compounds they tend to gain one electron. Halogens are powerful oxidizers also known for their toxicity and reactivity. The halogens include fluorine (F_2), chlorine (Cl_2), bromine (Br_2), iodine (I_2), and astatine (At_2). Iodine is a dark purple solid that sublimes readily at room temperature. When the gaseous iodine comes in contact with surfaces it re-deposits and leaves behind a brown stain. Iodine as a gas is a violet color and one of the few gases that can be seen with the naked eye. Tincture of iodine is this element dissolved in alcohol. Halogens are excellent disinfectants. Chlorine bleach and iodine tincture are two well-known examples.
- **Group 8/18: Noble Gases**, also known as the inert gases or rare gases, have eight electrons in the outer shell. Having this number of electrons makes this group of elements very stable, inert or unreactive. Because they have a complete valence shell they are the least reactive elements. They have low boiling points and are gases at room temperatures. The noble gases include helium (H), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), and radon (Rn). Argon is heavier than air and is used to fill incandescent light bulbs and double pane windows. Argon is colorless, odorless, tasteless and non-toxic. These gases may displace oxygen and act as a simple asphyxiant. Argon and nitrogen releases have caused deaths in confined spaces through asphyxiation.



Radioactive Atoms

Radioactive elements are atoms that have excess nuclear energy and are therefore unstable. They are subject to spontaneous degeneration of the nucleus accompanied by the emission of alpha particles, beta particles, or gamma rays. All elements with atomic numbers greater than 83 are radioactive. Naturally occurring radioactive elements include radium, thorium, and uranium. Several radioactive elements not found in nature have been produced by the bombardment of stable elements with subatomic particles in a cyclotron. Some atoms have a different weight than normal due to an excess or deficiency of neutrons in the nucleus. Radioactive elements are those heavier than bismuth (atomic number 83). Examples include radium (atomic number 88) and uranium (atomic number 92). Isotopes of elements lower on the periodic table can also be radioactive.

Transition Metals

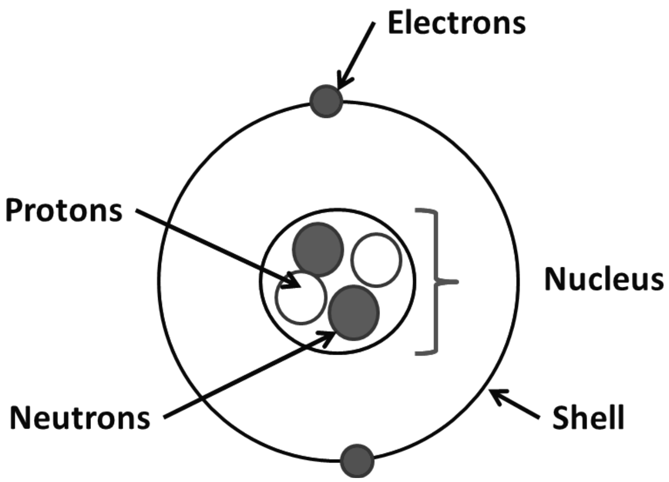
Transition Metals is a collective term for a group of elements found in the center of the periodic table. Transition Metals are Group 3 to Group 11. They include the elements chromium, manganese, iron, cobalt, nickel and copper. These elements are very hard, with high melting points and boiling points. They can form colored solutions and compounds. Iron, cobalt, and nickel are transition metals. They are the only elements known to produce a magnetic field.

These metals behave as though they have different numbers of electrons in their outer shell. Iron will react as if it has two electron or three electrons in the outer shell. This behavior is termed “multiple valence states”.

Iron forms Iron II and Iron III compounds, also called ferrous and ferric compounds. Ferric Chloride ($FeCl_3$) (Iron III Chloride) is a yellow solid used in sewage treatment. In this compound, Iron acts as though it had three electrons in its outer shell. Ferrous Chloride ($FeCl_2$) (Iron II Chloride) is a green solid used as a reducing agent in organic synthesis. In this compound, Iron acts as though it had two electrons in its outer shell. The transition metals are sometimes referred to as heavy metals. Heavy metals, such as lead and chromium, are known for their toxicity. When certain transition metals react they form compounds with brilliant colors. Their color can be an aid in the identification of these substances. Chrome compounds may be bright orange, cobalt – pink, copper – aqua, nickel – green, and manganese – brilliant purple.

Outer Shell Electrons

The number of outer-shell electrons may be determined by the group number at the top of each column. For example, sodium (Na), located in Group 1 on the periodic table, has one electron in its outer shell, while radon (Rn), located in Group 18, has eight electrons in its outer shell.



The number of electrons in the outer shell are called the valence electrons and are the key factor when it comes to bonding. The shell closest to the nucleus holds a maximum of two electrons. The outer shell can hold a maximum of eight (8) electrons. The exceptions are hydrogen (H) and helium (He), which are so small that they each have only one shell and can hold a maximum of two electrons in that one shell.

Ionization Energy

The ionization energy is the energy required to remove an electron from its orbital around an atom to a point where it is no longer associated with that atom (i.e. ionize the atom). The greater the ionization energy, the more difficult it is to remove an electron. The ionization energy may be an indicator of the reactivity of an element. (Ionization energy is sometimes referred to as “ionization potential” which is an outdated and inaccurate term.)

The ionization energy of an element increases as one moves across a period in the periodic table because the electrons are held tighter by the higher effective nuclear charge.

The ionization energy of the elements increases as one moves up a given group because the electrons are held in lower-energy orbitals, closer to the nucleus and therefore are more tightly bound (harder to remove).

The ionization energy of a substance will influence decisions about monitoring instruments, in particular, photoionization detectors (PID). A PID ionizes a gas or vapor with ultraviolet (UV) light. The lamps these instruments use to generate the UV light have different energy outputs. Each bulb can only ionize gases/vapors that have ionization energies that are lower than the rating for that bulb. This will determine what gases/vapors the instrument can detect. Responders will have to select lamps appropriate for the substance(s) involved. (Note: we will cover this subject in more detail in the next module.)

Summary

Atoms are the basic building blocks of all materials. Understanding atomic structure, particularly the outer-shell electron configuration, is essential to accurately predict the behavior of hazardous materials. The periodic table is a useful tool for determining whether an element is a metal or nonmetal and for determining the element's size and weight. Most importantly, the elements are organized into families based on their behaviors. This chapter presented four families: alkali metals, alkaline earths, halogens, and the noble gases. The reactivity of an element is due to the behavior of the outer shell electrons.

Chapter Review

1. Complete the following table.

Part of the Atom	Location	Charge	Weight
Protons			
Neutrons			
Electrons			

2. Use a periodic table to complete the following chart.

Name of Element	Atomic Number	Atomic Weight*
Lithium		
Carbon		
Calcium		
Nitrogen		
Selenium		
Potassium		
Magnesium		
Chlorine		
Iron		

*Round to the nearest whole number.

3. Fill in the name of the periodic table group that each of the following elements belongs in.

Name of Element	Group*
Lithium	
Bromine	
Calcium	
Neon	
Potassium	
Magnesium	
Chlorine	
Argon	

*Choices: Alkali Metals, Alkali Earth Metals, Halogens & Noble Gases

4. The different rows of elements are called: _______________________

5. A column of elements in the periodic table is called a: _______________________

6. Isotopes of atoms have a different number of: _______________________

7. Elements that have excess nuclear energy and are unstable are called: _______________________

8. A gas consisting of two atoms of an element with a covalent bond between them: _______________________

Chapter 4: Chemical Bonding

Introduction

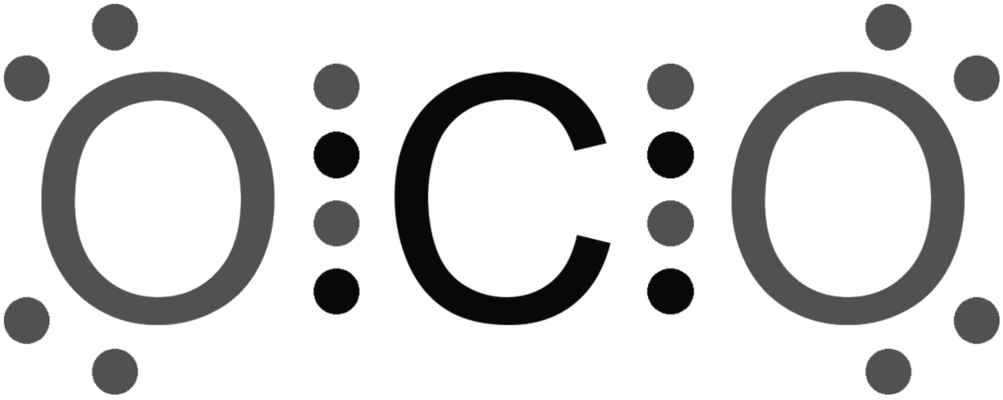
Chemical bonding is the lasting attraction between atoms. When atoms bond, they form chemical compounds. Molecular bonds are formed when constituent atoms come close enough together so the outer (valence) electrons of one atom are attracted to the positive nuclear charge of its neighbor. As the independent atoms approach one another, there are both repulsive forces (between the electrons in each atom and between the nuclei of each atom), and attractive forces (between the positive nuclei and the negative valence electrons). When a chemical reacts it's either breaking or forming bond(s). Since chemical bonds store energy, energy is released when bonds are broken during a chemical reaction.

The "Octet/Duet" Rule

Elements can exist by themselves or they can combine chemically to form a new substance. Two or more atoms bonded together chemically are called a "molecule." If the atoms are of the same element, the molecule is considered "diatomic" (i.e. two atoms). If the atoms are different, the molecule is called a "compound."

Atoms of Main Group elements react to try to achieve a completely full valence shell. (Main Group elements are those elements in groups 1, 2 and 13 through 18 of the periodic table. These groups contain the most naturally abundant elements, comprise 80 percent of the earth's crust and are the most important for life. Economically those elements and their compounds are the most produced chemicals.) A full valence shell for these elements is considered to contain either eight electrons or, in the case of hydrogen and helium, only two electrons. This is called the "octet/duet" rule.

The figure below illustrates this rule for carbon dioxide. Each oxygen atom shares four electrons with the central carbon atom to give each atom eight electrons in their valence shell.

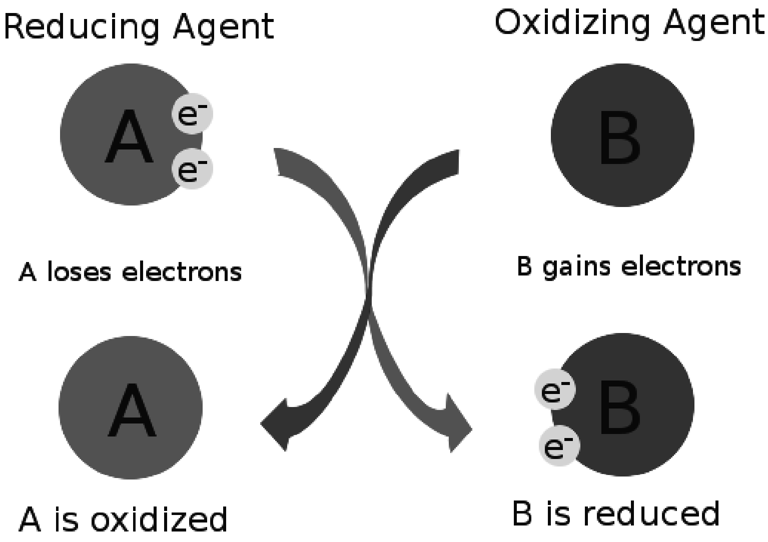


Atoms are electrically neutral when they have the same number of protons and electrons. When an atom reacts with another atom it gains, loses, or shares electrons to achieve a full outer shell. If an atom gains or loses electrons, the resulting imbalance of protons and electrons creates a charged atom known as an ***ion***. Positively charged ions are ***cations***, while negatively charged ions are ***anions***.

Metal atoms (electron donors) always lose electrons from their outer shell. These atoms will gain a positive charge in the process of losing electrons, thus becoming cations. Nonmetal atoms (electron acceptors) can acquire electrons to achieve a full outer shell. These atoms will gain a negative charge in the process, thus becoming anions.

Oxidization/Reduction

Reduction is the complete transfer of one or more electrons to a molecular entity. Oxidization is the reverse process. It's the complete, net removal of one or more electrons from a molecular entity. These reactions are common and vital to some of the basic functions of life, including photosynthesis, respiration, combustion, and corrosion (rusting).



Reducing and Oxidizing Agents

Reducing agents cause the oxidation state of other substances to become more negative by releasing electrons to them. They are electropositive, meaning that they will readily lose electrons to achieve an octet, becoming positively charged as a result. Those reducing agents which are metals will form a *cation* when they react. Reducing agents include elements such as carbon, lithium, hydrogen, magnesium, phosphorous, aluminum and sodium.

Strong reducing agents easily lose (or donate) electrons. The energy required to add or remove electrons is measured in volts. That property is called the oxidation potential. An atom with a relatively large atomic radius tends to be a better reductant and so has a higher oxidation potential. In such species, the distance from the nucleus to the valence electrons is so long that these electrons are not strongly attracted. These elements tend to be strong reducing agents. Good reducing agents tend to consist of atoms with a low electronegativity, the ability of an atom or molecule to attract bonding electrons, and species with relatively small ionization energies serve as good reducing agents too. The elements with the highest oxidation potential are lithium, sodium and magnesium.

Oxidizing agents cause the oxidation state of other substances to become more positive by accepting their electrons. They are electronegative. Oxidizers readily grab electrons to achieve an octet, becoming negatively charged as a result. They form anions when they react. Oxidizing agents include oxygen, chlorine, fluorine, iodine and bromine. The elements that are the most electronegative are the strongest oxidizers. This would include fluorine (the most electronegative element), oxygen and chlorine.

In general, Halogens are oxidizing agents and Alkali Metals are reducing agents.

As an example, oxygen is an oxidizing agent. It normally has only six electrons in the outer shell; it is electron-deficient. Oxygen will react with a reducing agent, accepting two electrons, to form an octet with eight electrons in the outer shell. Because it gains two electrons it becomes an anion with a charge of (-2). The new name for the negatively charged anion is "-oxide." For example, when iron is oxidized it becomes iron oxide (rust).

Oxidization Potential

Oxidization Potential is the tendency for a species to be *oxidized* at standard conditions. The energy change is measured in the volts required to add or remove electrons to or from an element or compound. "Potential" means the voltage which is associated with the tendency for that reaction to occur.

Reduction Potential

The reduction potential is the likelihood that a species will be reduced. It is a measure of the tendency of a chemical species to acquire electrons and thereby be reduced. Like oxidization potential, reduction potential is measured in volts (V), or millivolts (mV). Each species has its own intrinsic reduction potential; the more positive the potential, the greater the species' affinity for electrons and tendency to be reduced. (The term is sometimes used interchangeably with the term oxidation potential.)

Combustion

Combustion (also known as burning) is a reduction/oxidization reaction. It occurs between a fuel and an oxidizing agent that produces energy, usually in the form of heat and light. It is a high-temperature exothermic redox chemical reaction between a fuel (the reductant) and an oxidant. (The oxidant is usually atmospheric oxygen.)

Fire

Fire is the result of combustion. It is the rapid oxidation of a material in the exothermic chemical process of combustion, releasing heat, light, and various reaction products. Combustion in a fire produces a flame, and the heat produced can make combustion self-sustaining. Flames consist primarily of carbon dioxide, water vapor, oxygen and nitrogen. Fire produces oxidized, often gaseous products, in a mixture termed as smoke. Solid fuels, such as wood and coal, first undergo endothermic pyrolysis to produce gaseous fuels whose combustion then supplies the heat required to produce more of them.

Smoldering

Smoldering is the slow, low-temperature, flameless form of combustion, sustained by the heat evolved when oxygen directly attacks the surface of a solid fuel. It is a typically incomplete combustion reaction. Solid materials that can sustain a smoldering reaction include coal, cellulose, wood, cotton, tobacco, peat, duff, humus, synthetic foams, charring polymers (including polyurethane foam) and dust. Common examples of smoldering phenomena are the initiation of residential fires on upholstered furniture by weak heat sources (e.g., a cigarette, a short-circuited wire) and the persistent combustion of biomass behind the flaming fronts of wildfires. The fundamental difference between smoldering and flaming combustion is that smoldering occurs on the surface of the solid rather than in the gas phase.

Spontaneous Combustion

It is a type of combustion which occurs by self-heating (increase in temperature due to exothermic internal reactions) followed by thermal runaway (self-heating which rapidly accelerates to high temperatures). Spontaneous combustion begins if sufficient oxidizer, such as oxygen, and fuel are present to maintain the reaction into thermal run-away. The heat is unable to escape (hay, straw, peat, etc. are good thermal insulators), and the temperature of the material rises and finally ignites.

Organic materials undergoing bacterial composting can generate enough heat to reach the point of combustion. It often occurs with substances with a relatively low ignition temperatures. A substance with a relatively low ignition temperature (hay, straw, peat, etc.) begins to release heat. This may occur in several ways, either by oxidation in the presence of moisture and air, or bacterial fermentation, which generates heat.

Reducing Agent	Oxidizing Agent	End Result
Magnesium	Oxygen	Magnesium Oxide
Sodium	Chlorine	Sodium Chloride
Hydrogen	Fluorine	Hydrogen Fluoride

Chemical Bonds

The atoms in all substances that contain more than one atom are held together by interactions between electrically charged particles (protons and electrons). An electrostatic interaction between oppositely charged species (positive and negative) results in a force that causes them to move toward each other, like the attraction between opposite poles of two magnets. In contrast, electrostatic repulsion, the electrostatic interaction between two species that have the same charge results in a force that causes them to repel each other. Atoms form chemical compounds when the attractive electrostatic interactions between them are stronger than the repulsive interactions. The attractive interactions between atoms are called chemical bonds.

The number of electrons, particularly those in the outer shell, can predict the type of bond the atom will form. For example, sodium (Na) has one electron in its outer shell. To have a filled outer shell, sodium has two choices: (1) lose one electron to eliminate the outer shell, thereby exposing the next shell, which is filled, or (2) gain seven electrons to completely fill the outer shell. Atoms will typically take the simplest option, the one requiring the least amount of energy. In this case, the choice for sodium is clear; it takes far less energy to lose one electron than to gain seven. The opposite is true with fluorine. It has seven electrons in its outer shell. It’s far easier for fluorine to gain one electron than to give up seven.

For elements such as carbon, with four electrons in the outer shell, the choice becomes less clear. Carbon would either have to give up four electrons or gain four electrons to achieve a filled outer shell. Yet, carbon does neither. Carbon will share electrons instead and achieve a filled outer shell *without* actually gaining or losing any electrons.

The difference of electronegativity or ionization energies between two reacting elements also affects the type of bond. For example, the difference of ionization energies and electronegativity between Na and. Cl causes sodium to remove the electron from its outermost orbital and chlorine accepts the electron, resulting in an ionic bond. In cases where there is no difference in electronegativity, the sharing of electrons produces a covalent bond.

There are four major forms of bonding which occur during an atom’s quest for a filled outer shell: *ionic*, *covalent, metallic and resonant*. Understanding the type of bond in a compound is helpful in predicting the hazard of that material because each of the bonds behaves differently.

Chemical Formulas and Bonds

Elements are represented by chemical symbols. Chemical formulas for compounds are made up of the symbols for the elements present, the number of those atoms present and the types of bonds present. There are various methods of showing formulas of compounds.

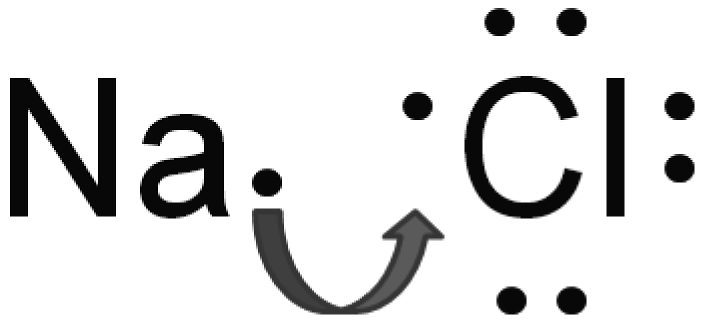
The method most familiar to responders is the called the “molecular formula” which indicate the numbers of each type of atom in a molecule.A molecular formula will be made up of the symbols for the elements present along with integers indicating the number of those atoms present. These integers will be shown as subscript numbers. If no number is used it means that there is only one of that particular atom. For example: Methane (CH_4) consists of four hydrogen atoms bonded to one carbon atom. (It is a covalently bonded organic compound.)

Ionic Bonds

Ionic bonding is the complete transfer of valence electron(s) between atoms with different ionization energies and electron affinities. This transfer of electrons is known as electrovalence in contrast to covalence. Ionic compounds are formed through an ionic bond between a metal element and a nonmetal element. The attractive forces between ions are isotropic—the same in all directions—meaning that any particular ion is equally attracted to all of the nearby ions of opposite charge. This results in the ions arranging themselves into a tightly bound, three-dimensional lattice structure. This structure determines the properties of ionic compounds.

Ionic bonds are formed by the *transfer* of electrons between a metal and a nonmetal. It is a type of chemical bond that generates two oppositely charged ions. In ionic bonds, the metal loses electrons to become a positively charged cation, whereas the nonmetal accepts those electrons to become a negatively charged anion. Ionic bonds require an electron donor, often a metal, and an electron acceptor, a nonmetal.

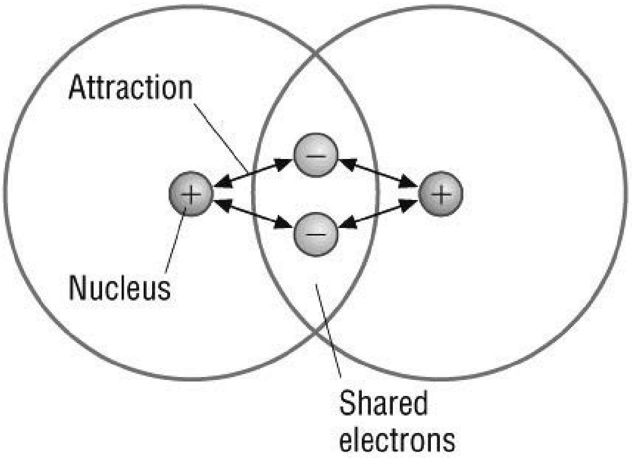
Metals are electron-rich; they donate electrons, acquiring a net positive charge to become a *cation*. Nonmetals are electron-deficient; they accept electrons, acquiring a negative charge to become an *anion*. Oppositely charged ions attract in a proper ratio to produce a neutral salt molecule. The result of this attraction is a compound, which is generally water-soluble. Ionic bonding commonly occurs in metal salts. (A “salt” is a chemical compound consisting of an assembly of cations and anions.) A common example is when sodium combines with chlorine to form sodium chloride (table salt).



Type Atom	Action of Electrons	Ion Formed	Charge
Metals	Lose electrons	Cation	Positive
Nonmetals	Gain electrons	Anion	Negative

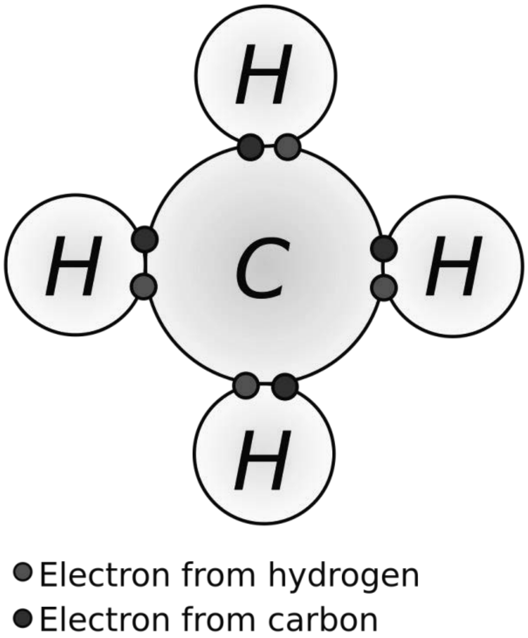
Covalent Bonds

Covalent bonds are formed by the *sharing* of electrons primarily between two or more nonmetal elements with similar electro negativities. (Electronegativity is the relative ability of an atom to draw electrons in a bond toward itself.) They form when the ionization energy of the atom is too large and the electron affinity of the atom is too small for ionic bonding to occur. This type of bonding generally occurs between two atoms of the same element or of elements close to each other in the periodic table. Covalent bonding occurs primarily between nonmetals; however, it can also be occur between nonmetals and metals.

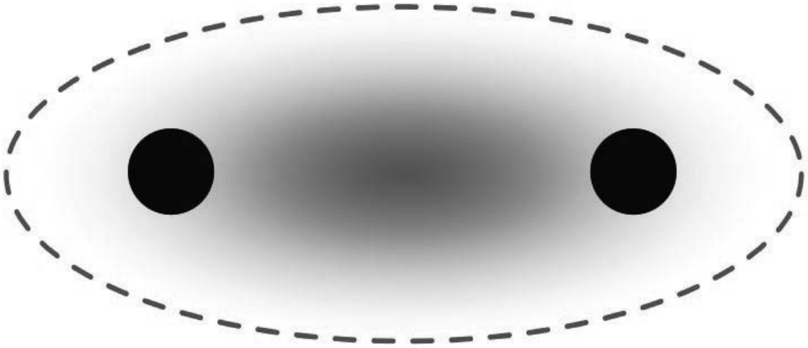


The two nonmetal atoms overlap their outer shell electrons. This allows each atom to attain the equivalent of a full outer shell to achieve a stable electronic configuration. The electrons located between the two atoms are shared in a manner that binds the atoms in a fixed orientation and makes the electrons appear to belong to *each* atom at the same time. Relatively high energies are required to break covalent bonds. Compounds with covalent bonds are generally not water-soluble.

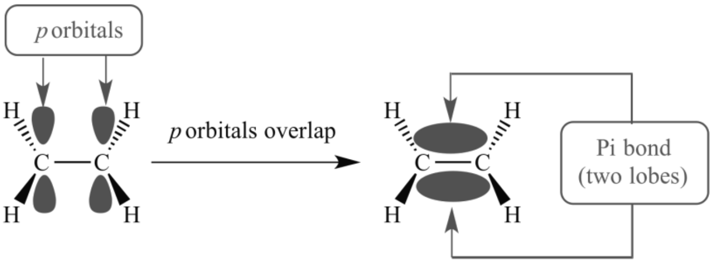
The figure below shows the sharing of electrons between one carbon atom and four hydrogen atoms to form four covalent bonds. Covalent bonds are represented by a dash between two atoms in a structural formula.



If the atoms share one pair of electrons that is called a single bond. A single bond consists of a single sigma bond. Sigma bonds (σ bonds) are the strongest type of covalent chemical bond since the atomic orbitals directly overlap between the nuclei of two atoms.



If they share two pairs we call that a double bond. Double bonds involve four bonding electrons instead of two like a single bond. They can be described in terms of overlapping atomic orbitals, except that, unlike a single bond (which consists of a single sigma bond), a carbon–carbon double bond consists of one sigma bond and one pi bond. (A triple bond consists of one sigma bond and two pi bonds.)



Pi bonds (π bonds) are covalent chemical bonds where two lobes of an orbital on one atom overlap two lobes of an orbital on an adjacent atom. They are perpendicular to any sigma bond(s) between the same atoms. A pi bond has two orbital lobes, one above and one below the plane of the sigma bond. The orbital lobes are a region of space in which you can find the two electrons which make up the bond. Those two electrons can live anywhere within that space. This double bond (one sigma bond and one pi bond) is stronger than a single covalent bond even though pi bonds are weaker than sigma bonds.

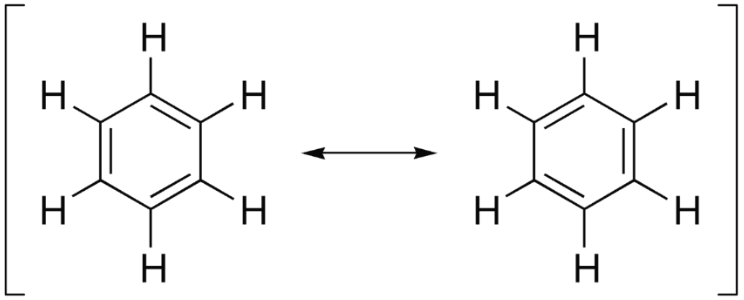
Pi bonds make atoms move closer together, and the combination of sigma and pi bonds creates a stronger and more stable connection between two atoms. The electrons from pi bonds are much more likely to react with other atoms because they are less strongly bonded together. Because of their molecular geometry carbon atoms can have various hybrid orbitals and form single, double and triple bonds with other atoms. This accounts for the ability of organic molecules to form an infinite variety of compounds.

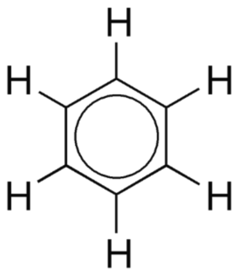
The formation of a pi bond requires that molecules adopt a specific orientation. As a result, the presence of pi bonds introduces rigidity into molecules. In molecules that have multiple bonds and more than one resonance structure, such as C_6H_6, the pi bonds are delocalized. In other words, the pi bonds are spread among several atoms. This results in the formation of what are known as “resonant” bonds.

Resonant Bonds

Resonant bonds are a special type of covalent bond formed by the *sharing* of electrons between multiple nonmetal elements. Unlike covalent or ionic bonds, the electrons in resonant bonds are less localized in a molecule. The relative positions of the atoms don’t change, only the electron locations change.Molecules with resonant bonds are usually extremely stable.

The most common example of this type of bonding is found in aromatic hydrocarbons. The six-sided benzene ring (C_6H_6) is the most well-known. When the six carbon atoms are formed into the hexagon shape, the position of the electrons cannot be represented by one diagram. The electrons forming the bonds in this structure are shared equally by all six carbons in the ring. The ring does not have three double bonds as the structure on the left suggests. In actuality the structure can be said to “resonate” between two structures and it is more accurately represented by the structure on the right wherein the position of the electrons are represented by a circle inside the six sided ring. The electrons rotate between the six carbons very rapidly and are shared in a manner that makes the electrons appear to belong to *each* atom at the same time. This rapid movement is called resonation. The result is a compound with strong “aromatic” bonds. These molecules are called aromatic because of their peculiar odor. The parent member of this cyclic family is benzene. Other members of the aromatic hydrocarbon family, which is frequently called the BTX family, are toluene and xylene.





When we speak of “resonant” bonding in this course, we will be referring to the six sided carbon structure known also as the benzene ring. It is a very stable structure and acts nothing like the double bonds that can undergo oxidation and polymerization.

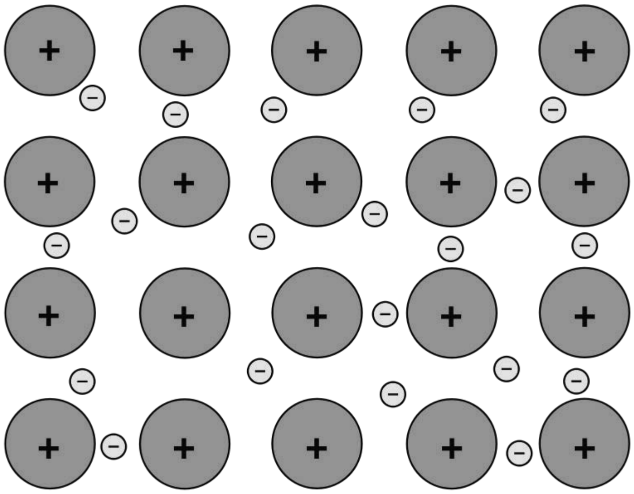
Metallic Bonding

In the metallic bond, there is no transfer or sharing of electrons. The elements form a tightly packed homogeneous mixture where the atoms of one element replace or occupy interstitial positions (or intervening spaces) between the atoms of the other element.

The electrons overlap with neighboring atoms and can move freely within their molecular orbitals so each electron becomes detached (“delocalized”) from its parent atom. Metals have low ionization energies, thus they do not have a tight hold on their outer shell electrons. The metal is held together by the strong forces of attraction between the positive nuclei and the delocalized electrons. These outer shell electrons easily move around as they do not “belong” to any one atom. They are part of the whole metal crystal. The negatively charged electrons act as “cement” that hold the positively charged metal ions in their relatively fixed positions. An example of the metallic bond is the combining of zinc and copper to create brass. In this course, we will often refer to these as alloys or metallic solid mixtures.

Because the atoms in metals have a strong attractive force between them much energy is required to overcome it. Metals are insoluble in water or organic solvents unless they undergo a reaction with them. (Typically this is an oxidation reaction that robs the metal atoms of their itinerant electrons, destroying the metallic bonding.) However metals may be readily soluble in each other while retaining the metallic character of their bonding. Gold, for example, dissolves easily in mercury, even at room temperature.

In metallic bonding, bonding electrons are delocalized over a lattice of atoms. By contrast, in ionic compounds, the locations of the binding electrons and their charges are static. The freely-moving or delocalization of bonding electrons leads to common metallic properties such as luster (surface light reflectivity), electrical and thermal conductivity, ductility (capacity to deform permanently in response to stress) and high tensile strength.



Chemical Formulas and Structures

There are a variety of methods of drawing chemical formulas and structures. The basic methods of showing structures of molecules are: empirical formula, molecular formula, and structural formula.

Empirical Formula

The empirical formula is the simplest type of formula. It identifies the ratio of the whole number of elements in a compound showing the atomic symbols with their appropriate subscripts. It gets its name because it often comes from experimental or empirical data.

Molecular Formula

A molecular formula shows the atomic composition of a molecule. It identifies the number and type(s) of atoms present in a molecule. The chemical symbols of elements from the periodic table represent which elements are present in the molecule. A subscript numbers after the symbol shows how many of those atoms are present. (Note: no subscript number means a subscript of 1.)

]

Structural Formula

Although the molecular formula tells you how many atoms of each element are present in a compound it does not indicate the way the atoms are arranged or bonded to each other. A structural formula shows the chemical bonds. This is important information because two molecules may share the same number and type of atoms yet have different structures and bonds. Molecules with the same atomic composition (molecular formula) but different structures and bond will have different physical and/or chemical properties. (Note: structural formulas can be shown as 2D or 3D formats.)

Structural formulas show the arrangement of chemical bonds between atoms. Specifically, they will display which atoms are chemically bonded to what other atoms with what kind of chemical bond.

Drawing Structures

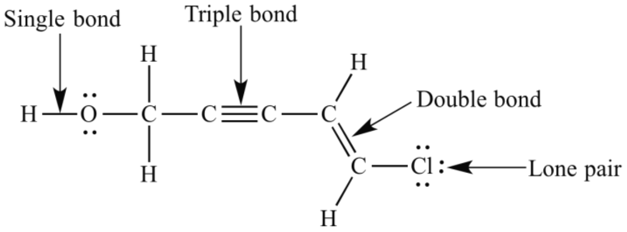
A graphic representation is often very helpful when trying to understand chemical bonding or trying to predict chemical hazards.

Bond Line Structures

Bond-line structure (sometimes called bond-line formula, skeletal structure or skeletal formula) are a representation of molecular structure in which covalent bonds are represented with one line for each level of bond order. A single bond is represented with a single line, a double bond is shown by two parallel lines, and a triple bond by three parallel lines. The position of carbon atoms may be shown with letters, or may be implied (in certain circumstances).

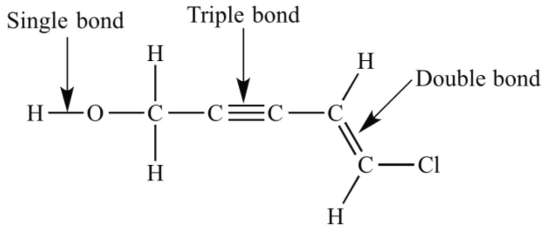
Lewis Structure

Similar, but not identical to a bond line structure. It’s a representation of the molecular structure in which all electron pairs are shown. A line between two atoms represents a single covalent bond. Two lines between two atoms represent a double bond, and three lines a triple bond. Lone electron pairs (unshared electron pairs) are indicated by a pair of dots next to an atom. A Lewis dot structure uses dots instead of lines for all electrons.



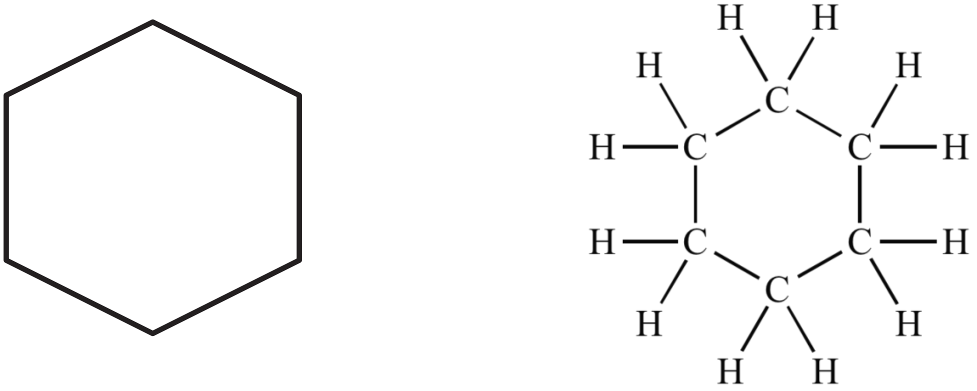
Kekulé Structure

This is a Lewis structure in which bonded electron pairs in covalent bonds are shown as lines. The most well-known Kekulé structures were originally designed to show the resonance contributors of benzene.



Structure of Cycloalkane Molecule

(Formula C_6H_{12})


Bond Line Structure

Lewis Structure

Ionic Compounds

Ionic compounds are composed of positive and negative ions that are joined by ionic bonds. They consist of anions and cations held together by strong electrostatic forces. In ionic compounds the ions are arranged into a tightly bound, three-dimensional lattice structure. This structure defines the properties and behavior of ionic compounds.

There are some characteristics common to all ionic compounds. Ionic compounds are stable solids (and often crystalline) at standard temperature and pressure. They resist evaporation. They are (with exceptions) water-soluble. Since the ionic bond has a strong electrical attraction ionic compounds are often hard and have high melting/boiling point. They tend to be brittle. Solid ionic compounds don’t conduct electricity but ionic solutions may.

Many ionic compounds are known as “salts” which is a chemical compound consisting of an assembly of cations and anions. A salt is an ionic compound that can be formed by the neutralization reaction of an acid and a base. (Salt is the general term for any ionic substance that does not have OH− as the anion or H+ as the cation.) They are composed of related numbers of cations (positively charged ions) and anions (negative ions) so salts are electrically neutral (without a net charge). The component ions can be inorganic, such as chloride (Cl−), or organic.

Molten salts and solutions containing dissolved salts (called electrolytes) are able to conduct electricity. In the solid state they are generally nonflammable. Because of the strong ionic bonds, salts tend to melt at higher temperatures than other solid molecules.

Naming Ionic Compounds

Under the International Union of Pure and Applied Chemistry (IUPAC) system ionic compounds are named according to their composition, not their structure. Many industrial chemicals have several names associated with them. These names may be common names, archaic chemical names or the IUPAC names. They are universally accepted in chemical references, formal chemistry courses, and scientific and forensic laboratories. Common names, however, may be used widely throughout industry, in commerce, among workers, and among the public.

Salts are named starting with the cation, followed by the anion. Salts typically have an “-ide,” “-ite” or “-ate” ending. Salts typically occur only in specific ratios so the Greek prefixes such as “mono-,” “di-” and “tri-” are rarely used in naming salts. For example, aluminum chloride always occurs in a 1:3 ratio. Therefore, chemists refer to AlCl3 simply as aluminum chloride rather than aluminum trichloride.

Formula	**Common Name**	**Old Chemical Name**	**IUPAC Name**
NaCl	Table salt	Halite	Sodium chloride
KOH	Potash or lye	Potassium hydrate	Potassium hydroxide
CaO	Lime	Quick lime	Calcium oxide
$NaHCO_3$	Baking soda	Sodium bicarbonate	Sodium hydrogen carbonate
KNO_3	Saltpeter	Niter	Potassium nitrate
FeS_2	Fool’s gold	Iron pyrite	Iron sulfide

Types of Salts

Some of the major classifications of salts that we'll emphasize in this course are: binary, metal cyanide, metal oxide, metal hydroxide, metal peroxide, and metal oxysalt, sulfide salts, and ammonium salts. The metal (italicized) always proceeds the nonmetal. The type of salt is indicated (bold type) by the nonmetal component. The hazard of a salt compound may come from the cation or the anion or both. In the compound lead carbonate the hazard comes from the toxic heavy metal – lead, the cation. In the compound sodium cyanide the hazard comes from the cyanide anion. It is important to analyze both parts of a salt compound for hazards.

Type	Name	Structural Formula
Binary	*Sodium* **Chloride**	$NaCl$
Metal (binary) Oxide	*Sodium* **Oxide**	Na_2O
Metal Hydroxide	*Calcium* **Hydroxide**	$Ca(OH)_2$
Metal Peroxide	*Lithium* **Peroxide**	Li_2O_2
Metal Cyanide	*Potassium* **Cyanide**	KCN
Sulfide Salt	*Sodium* **Sulfide**	Na_2S
Metal Oxysalt	*Sodium* **Bromate**	$NaBrO_3$
Ammonium Salt	*Ammonium* **Nitrate**	$N_2H_4O_3$

Binary Salts

Binary salts are comprised of a metal ion and a simple nonmetal ion, the nonmetal being some other element other than oxygen. Names of binary salts begin with the metal cation, followed by the nonmetal anion with the suffix "-ide".

Name	Formula	DOT Hazard Class
Sodium chloride	$NaCl$	none
Calcium carbide	CaC_2	4.3
Potassium hydride	KH	4.3

Metal Oxide Salts

Metal oxide salts are the metallic compounds formed with metal and oxygen in the form of oxide ion (O2-). Metallic oxides are basic in nature and often exist as solids at room temperature. Generally, metal oxide bonds are strong so they are insoluble in water. They can produce salts with acids. A metal oxide salt has a metal ionically bonded to oxygen. The name of the metal oxide salt begins with the metal cation, followed by the word "oxide". Most metal oxides are fairly inert. Rust (iron oxide) is an example of a metal oxide. Iron oxide is very inert, not water soluble and non-toxic. Metal oxide salts containing metals from Group 1 Alkali Metals or Group 2 Alkaline Earth Metals on the Periodic Table are, however, reactive and create bases or caustic solutions in water (a solution of the metal hydroxide). Metal oxides are not oxidizers.

Name	Formula	DOT Hazard Class
Sodium oxide	Na_2O	8
Calcium oxide	CaO	8
Potassium oxide	K_2O	5.1

Metal Hydroxides

Metal hydroxide salts are any combination of a metal and a hydroxide (OH) group. They consist of a metal cation ionically bonded to a complex ion, made of oxygen and hydrogen. This complex ion is referred to as a hydroxide, and is often written as "OH". The hydroxide anion has covalent bonding between the oxygen and the hydrogen atoms and acts as a single unit. The soluble Metal Hydroxides are strong bases or caustics. The name of the metal hydroxide salts begin with the metal cation first, followed by the word "hydroxide". A common example is sodium hydroxide (NaOH).

Name	Formula	DOT Hazard Class
Sodium hydroxide	$NaOH$	8
Potassium hydroxide	KOH	8
Calcium hydroxide	$Ca(OH)_2$	8

When the hydroxide ion is bonded to an alkali metal, it becomes a strong caustic with a high pH (greater than 12). These alkali metal hydroxides are some of the most destructive chemicals you may ever encounter. They react with water. They attack body fats in a reaction called saponification or necrosis. They react, attack, corrode and dissolve many substances including metals. Many of these salts are deliquescent (absorb atmospheric moisture to become liquid).

Metal Peroxides

Metallic peroxides are metal-containing compounds with the metal ionically bonded to a peroxide group. The O−O group is called the “peroxide group” (or peroxo group). The peroxide group consists of two covalently bonded oxygen (O_2) atoms. Names of peroxide salts begin with the metal cation, followed by the word “peroxide”. They are commonly referred to as peroxides.

The relatively weak oxygen-oxygen bond is characteristic of peroxide molecules. Peroxides tend to spontaneously change to form more stable products. The weakness of the O−O bond means peroxides are prone to decomposition initiated by several mechanisms including heat, mechanical shock or friction.

Name	Formula	DOT Hazard Class
Sodium peroxide	Na_2O_2	5.1
Potassium peroxide	K_2O_2	5.1
Calcium peroxide	CaO_2	5.1

Metal peroxide salts are highly unstable, water reactive compounds which can produce explosive reactions under the right conditions. They are strong oxidizers and can react with fuels.

Metal Cyanides

A metal cyanide is a compound that contains one carbon atom and one nitrogen atom joined with a triple bond. The complex ion is abbreviated as “CN”. The names of metal cyanides begin with the metal cation, followed by the word “cyanide.” For the salts such as sodium cyanide and potassium cyanide, these compounds are highly toxic. Hydrocyanic acid, also known as hydrogen cyanide, or HCN, is a highly volatile liquid that is produced on a large scale industrially. The most toxic form of cyanide is free cyanide. HCN is highly soluble in water. Both HCN gas and liquid are colorless and have the odor of bitter almonds, although not all individuals can detect the odor. Cyanide is very reactive, forming simple salts with alkali earth cations and ionic complexes of varying strengths with numerous metal cations.

Name	Formula	DOT Hazard Class
Sodium cyanide	NaCN	6.1
Potassium cyanide	KCN	6.1

Metal cyanides are very toxic. Always avoid contact with acids. Mixing metal cyanides and acid solutions produces hydrogen cyanide, a very toxic and flammable gas. Avoid inhalation.

Sulfide Salt

Sulfide is used to describe any of three types of chemical compounds that contain sulfur. Sulfides, also spelled sulphides, come in three classes: organic sulfides, inorganic sulfides and phosphine sulfides. Organic sulfides are compounds in which sulfur is bonded to two organic groups. Inorganic sulfides are ionic compounds or salts which contain a negatively charged sulfide ion. Phosphine sulfides occur when the sulfur atom reacts with organic phosphines. Examples of sulfides include zinc, copper, silver and mercury. Metal sulfides are binary salts. They are a combination of a metal cation and sulfur (nonmetal).

Name	**Formula**	**DOT Hazard Class**
Sodium sulfide	NaS	4.2
Hydrogen sulfide	H_2S	2.3

Metal sufides in contact with an acid form toxic hydrogen sulfide gas. Hydrogen sulfide has the odor of rotten eggs and can be detected in relatively small amounts.

Metal Oxysalts

Metal oxysalts are three-part salts made up of a metal cation, another element (most often a nonmetal) and oxygen. You will recognize a metal oxysalt by the name. It will end in either "-ate" or "-ite". Some will have a prefix "hypo-" or "per-". Examples include:

Names of oxysalts begin with the metal cation first. The complex ion is then named in three parts: the prefix, the root and the suffix. The root is derived from the nonoxygen nonmetal in the anion. A prefix of "hypo" is added to indicate a very low oxygen content, while "per" indicates excessive oxygen content. The suffix "ite" indicates an anion with a low or very low oxygen content, while the suffix "ate" indicates a normal or high oxygen content.

Oxy-Radicals Chart

-1 Charge	**-2 Charge**	**-3 Charge**
ClO_3 chlorate	CO_3 carbonate	PO_4 phosphate
BrO_3 bromate	SO_4 sulfate	BO_3 borate
IO_3 iodate	CrO_4 chromate	AsO_4 arsenate
NO_3 nitrate		
MnO_3 manganate		

Common Oxysalts

Name	**Formula**	**DOT Hazard Class**
Sodium chromate	Na_2CrO_4	6.1
Potassium nitrate	KNO_3	5.1
Sodium hypochlorite	NaClO	8

Most of these salts readily dissolve in water with no heat generation, gas liberation or caustic reaction. Magnesium Sulfate MgSO4 is often found in bath salts. Calcium Sulfate CaSO4 is also known as Plaster of Paris or gypsum. Sodium sulfate is also known of as Glauber's salt and is used in the manufacture of detergents. Some of the oxysalts must be kept away from heat and fuels, because they are powerful oxidizers. The chlorates and nitrates are oxidizers.

Covalent Compounds

As discussed earlier in this chapter, covalent bonds between *atoms* are very strong and take a lot of energy to break. However, the forces that hold one covalently bonded *molecule* to its neighbor are much weaker. It takes a far lower temperature to provide enough energy to break these intermolecular forces. As a result, many covalent compounds are gases or liquids at standard temperature and pressure. (Unlike compounds with ionic bonds that are usually solids at standard temperature and pressure.) Also, covalent bonding allows molecules to share electrons with other molecules, creating long chains of compounds.

General Properties of Covalent Compounds

- Most covalent compounds have relatively low melting points and boiling points.
- Covalent compounds tend to be soft and relatively flexible.
- Covalent compounds tend to be more flammable than ionic compounds.
- When dissolved in water, covalent compounds don't conduct electricity.
- Many covalent compounds don't dissolve well in water.

(Note: there are *always* exceptions!)

This chapter will focus on two subcategories of covalent compounds; *organic* covalent compounds and *inorganic* covalent compounds. Organic compounds are those that contain the element carbon covalently bonded to hydrogen and may have other non-metals in their structure such as nitrogen, oxygen, sulfur and phosphorous. Organic compounds make up the majority of substances involved in hazmat incidents (80% according to USDOT).

Organic compounds can be further subdivided into two groups: hydrocarbons and hydrocarbon derivatives. We will discuss those organic compounds in subsequent chapters.

Examples of Organic Covalent Compounds

Hydrocarbons		Hydrocarbon Derivatives	
Name	**Formula**	**Name**	**Formula**
Methane	CH_4	Methyl Chloride	CH_3Cl
Propane	C_3H_8	Dimethyl Ketone (acetone)	CH_3COCH_3
Butane	C_4H_{10}	Butanol	$CH_3(CH_2)_2CH_2OH$

Inorganic Covalent Compounds

In this course we will divide inorganic covalent compounds into five categories: Binary Non-Salts, Non-Metal Oxides, Binary Acids, Oxy Acids and Inorganic Cyanides.

Binary Non-Salts

Binary Non-Salts are defined as a non-metal (not hydrogen) bonded to a non-metal (not oxygen). The difference between these and binary salts is that there is no metal or cation in these compounds – the entire compound is covalently bonded.

There are two main subcategories within the binary non-salt category: Non-Metal Hydrides and Non-Metal Halides.

Non-Metal Hydrides are compounds with a covalent bond between a non-metal (not carbon) and hydrogen. Several of them are toxic and many will burn. They include ammonia, silane, arsine, phosphine and diborane.

Examples of Inorganic Compounds: Non-Metal Hydrides

Name	Formula	Physical State
Anhydrous ammonia	NH_3	Gas
Arsine	AsH_3	Gas
Diborane	B_2H_6	Gas
Phosphine	PH_3	Gas
Silane (silicon tetrahydride)	SiH_4	Gas

Ammonia (NH_3) is a corrosive gas that readily dissolves in water producing ammonium hydroxide solution with a pH of ~11. This solution, often called aqueous ammonia, is used in floor wax strippers, window washing fluids and oven cleaners. Ammonia gas is used industrially to make fertilizes and explosives. Ammonia (NH_3) gas can also burn. It has a flammable range of 16-25% and is remembered in the hazardous materials response arena as the gas that caused the deadly explosion at the cold storage facility in Shreveport, Louisiana. It is widely used as a refrigerant gas and has the powerful pungent irritating odor of smelling salts. (Note: DOT doesn't classify anhydrous ammonia as "flammable" because it doesn't meet the DOT definition of "flammable" because the LEL is too high. And, no the cold storage industry didn't bribe DOT to do this. Reason: the cold storage industry isn't covered by DOT regulations.)

Arsine (AsH_3) is made from arsenic and hydrogen. It is very toxic, slightly soluble and has a flammable range of 5-78%. It is reported to have the smell of garlic. It is used in the semiconductor industry. Gallium arsenide, a semiconductor used to make infrared LED's, laser diodes and solar cells, is an example of a compound made from arsine gas.

Diborane (B_2H_6) is a very toxic, water-reactive, pyrophoric gas with a flammable range of 0.8-88%. It is used to vulcanize rubber and is also used as a rocket propellant. It has a repulsive, sweet odor and is one of the products of the chemical reaction between sulfuric acid and sodium borohydride.

Phosphine (PH_3) is a very toxic gas. It has caused deaths at illicit methamphetamine labs when it is inadvertently produced in the Red P/Iodine method during the "cook" phase of manufacture. If the reaction mixture is overheated or boiled dry the deadly phosphine gas will be produced. Phosphine gas (PH_3) has a foul odor reported as decaying fish. It is used as a fumigant and rodenticide and can be delivered in a cylinder as a compressed liquefied gas or can be produced when an inorganic compound such as aluminum phosphide or zinc phosphide reacts with water. It is used to kill gophers and to fumigate stored grains. Phosphine gas (PH_3) is also flammable, with a flammable range of 1.8-98%. It can spontaneously combust in air and when it burns, it produces a dense white cloud of phosphorous pentoxide (a Non-Metal Oxide).

Silane (SiH_4) is a pyrophoric gas. Trace impurities in silane can cause an extremely violent reaction that will destroy the system it is contained in. It is used to manufacture semiconductors and is used in many high-tech applications, including the manufacture of solar panels.

Non-Metal Halides

Non-Metal Halides are compounds with a covalent bond between a non-metal and one of the halogens. These compounds are often used as intermediates in the synthesis of other organic compounds. As a group, they are unstable compounds and will react with moisture to release one of the binary halide acids, such as hydrogen chloric acid (HCl) or hydrogen fluoric acid (HF).

Examples of Inorganic Compounds: Non-Metal Halides

Name	Formula	Physical State
Nitrogen Triiodide	NI_3	Solid
Sulfur Dichloride	SCl_2	Liquid
Sulfur Tetrafluoride	SF_4	Gas
Boron Trichloride	BCl_3	Gas
Boron Trifluoride	BF_3	Gas
Phosphorous Pentachloride	PCl_5	Solid
Phosphorous Trichloride	PCl_3	Liquid

Nitrogen triiodide (NI_3) is an extremely unstable, friction sensitive, contact explosive. A tickle from a feather will set it off with a loud crack and the release of purple iodine gas.

Sulfur tetrafluoride is a corrosive gas that reacts with water and releases HF gas, which in water makes hydrofluoric acid.

Phosphorus pentachloride is a clear solid that reacts with water and releases HCl gas, which in water produces hydrochloric acid.

Non-Metal Oxides

Non-Metal Oxides are compounds formed as the result of the oxidation of certain non-metals. The products of combustion from any fire will contain some of these non-metal oxides, depending on the chemical makeup of the fuel that is burning. When the non-metal carbon burns, it forms carbon monoxide and carbon dioxide. When the non-metal phosphorous burns, it forms phosphorous pentoxide. Burning fuels containing nitrogen creates NO_x, the different oxides of nitrogen. Nitrogen dioxide is one of these noxious gases. Burning fuels containing the element sulfur produce sulfur dioxide, one of the So_x gases.

Examples of Inorganic Compounds: Non-Metal Oxides

Name	Formula	Physical State
Carbon Monoxide	CO	Gas
Carbon Dioxide	CO_2	Gas
Phosphorous Pentoxide	P_2O_5	Solid
Nitrogen Dioxide	NO_2	Gas
Sulfur Dioxide	SO_2	Gas
Sulfur Trioxide	SO_3	Gas

The Non-Metal Oxides will generally dissolve in water to create an acid. They are often referred to as the NMAP's – the Non-Metallic Acid Precursors. Carbon Dioxide produces carbonic acid (seltzer water). Phosphorous pentoxide is also called phosphoric acid anhydride and in solution makes phosphoric acid. Sulfur trioxide dissolved in water produces sulfuric acid.

Carbon monoxide, the product of the *incomplete* combustion of carbon, is a toxic, flammable gas with a flammable range of 12.5-74%. When it burns, it produces carbon dioxide gas, the product of the *complete* combustion of carbon. Carbon dioxide is used as an extinguishing agent for ordinary combustibles. It is considered inert and is not nearly as toxic as carbon monoxide. Carbon dioxide in solid form is called dry ice and sublimes to produce the heavier than air gas CO_2.

Phosphorous pentoxide (P_2O_5), is a white solid that reacts vigorously with water. It is considered a "Dangerous-when-Wet" material and an acid anhydride producing phosphoric acid in water. When it reacts with water it releases oxygen gas and produces a lot of heat. Phosphorous pentoxide is also considered an oxidizer because its reaction with water releases oxygen gas. Burning red phosphorous will billow clouds of thick white smoke which consists of the aerosolized white solid phosphorous pentoxide.

Nitrogen dioxide (NO_2) is a reddish-brown gas produced when nitrogen burns. Automobile internal combustion engines burn a certain amount of nitrogen and release NO_x in their exhaust. This pollutant gas, nitrogen dioxide, gives the atmosphere a brown haze appearance and dissolves in water to produce acid rain or nitrous acid. Nitrogen dioxide gas is also produced when concentrated nitric acid reacts with a metal or when the acid is decomposed by heat. This gas (NO_2), in addition to being an acid precursor, is also an oxidizer and can support combustion just like an enriched oxygen atmosphere would. Nitrogen dioxide gas is one of the few gases visible to the naked eye. If this gas is inhaled, it will dissolve in moisture produced by the mucous membranes, creating nitrous acid.

Sulfur dioxide (SO_2) is a choking, acid gas that is used industrially as a preservative for dried fruits. It is produced when substances that contain sulfur burn. At one time it was used as a refrigerant gas in home refrigerators. In the event of a leak in a refrigerant system; the leaking SO_2 gas could be bubbled through a rigged up scrubber made with a bucket of a basic solution such as baking soda (sodium bicarbonate $NaHCO_3$) and water.

There are many more Inorganic Covalent Compounds which do not fall into one of the three groups discussed above. Some of them are highlighted here.

Binary Acids

Binary Acids are defined as a hydrogen atom attached to a halogen atom. These compounds are gases in their pure form and end with an –ide ending. Examples include hydrogen chloride (HCL), hydrogen fluoride (HF) and hydrogen bromide (HBr). These gases, when dissolved in water, ionize the H atom and form the binary acids, which are corrosive liquids that off-gas toxic gases. These materials will be further discussed in the chapter on corrosives.

Oxy Acids

Oxy Acids are defined as hydrogen bonded to an oxy radical. These are similar to the oxy salts that were presented in the last chapter, except there is hydrogen instead of a metal or cation attached to the oxy radical. The radicals are utilized in a similar manner for naming the entire compound, however, instead of –ate and –ite, there is now –ic and –ous. There are oxy acids that use the per- and hypo- prefix. These compounds are corrosive and are oxidizers.

Inorganic Cyanides

Inorganic cyanides are extremely toxic substances. They are defined as a non-metal (not H) attached to a cyanide radical (CN). Hydrogen cyanide (HCN) is technically an organic compound, since hydrogen is bonded to carbon. In this category, there are compounds such as ClCN and BrCN. When naming inorganic cyanides, the term "cyanogen" is utilized more often than the term "cyanide."

Other Inorganic Compounds

There are some inorganic compounds that do not fall nicely into one of the groups discussed above. One example is phosgene, which is the common name for carbonyl chloride ($COCl_2$). The name starts with the prefix "phos-," but there is no phosphorus in the formula. Do not confuse phosgene ($COCl_2$) with phosphine (PH_3). Phosgene was used in World War I as a chemical warfare agent. It is very toxic, causing suffocation. It has the odor of fresh mown hay or cut grass. Phosgene does not burn. It reacts slowly in water to form hydrochloric acid and carbon dioxide, and is only slightly soluble. It is very heavy, and stays close to the ground.

Other Inorganic Compounds

Name	Synonym	Formula	Physical State
Water	Dihydrogen Monoxide	H_2O	Liquid
Carbon Tetrachloride	Carbon Tet	CCl_4	Liquid
Phosgene	Carbonyl Chloride	$COCl_2$	Gas
Hydrogen Peroxide		H_2O_2	Liquid

Naming Inorganic Covalent Compounds

Many of these compounds have multiple names associated with them. They are frequently named with Greek prefixes to indicate the number of each type of atom. The most common prefixes are "mono-" (1), "di-" (2), "tri-" (3), and "tetra-" (4).

Summary

The properties of a compound are largely dictated by the type of bonding. Compounds differ by the type of bond from which they are formed, namely, ionic, covalent, resonant or metallic.

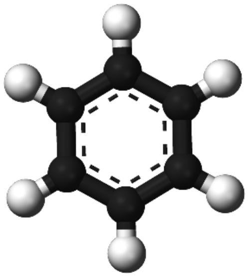
Information Sheet 6.1

Salt	Composition	Naming	Example	Common Hazards
Binary Salts	Metal + Nonmetal (not listed below)	Metal + nonmetal root - ends in “ide”	CaC_2 Calcium carbide	Toxic. May be water-reactive. May produce flammable or toxic gas with water
Metal Cyanides	Metal + cyanide (CN)	Metal + “cyanide”	NaCN Sodium cyanide	Highly toxic. Reacts with acids to produce toxic, flammable hydrogen cyanide gas
Metal Oxides	Metal + oxygen (O)	Metal + “oxide”	Na_2O Sodium oxide	Water-reactive. Produces heat and a caustic solution when mixed with water
Metal Hydroxides	Metal + hydroxide(OH)	Metal + “hydroxide” (or alkali, caustic or base	NaOH Sodium hydroxide	Strong caustic. Water-reactive
Metal Peroxides	Group 1 or 2 metal + peroxide (O_2)	Metal +”peroxide”	Na_2O_2 Sodium peroxide	Strong oxidizer. Water-reactive. Produces caustic solution, heat and oxygen when mixed with water
Metal Oxysalts	Metal + element + oxygen	Metal + oxyradical “per” or “hypo” prefix “ate” or “ite” suffix	$NaNO_3$ Sodium nitrate	Very strong oxidizers

Chapter Review

1. What type of chemical bond is formed by the *sharing* of electrons primarily between two or more nonmetal elements with similar electro negativities?
   A. Ionic
   B. Covalent
   C. Metallic
   D. Resonant

2. What type of chemical bond does this chemical structure have?



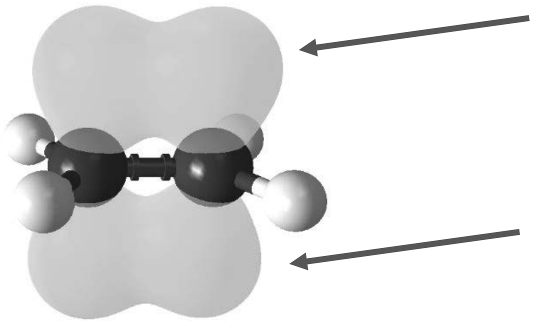
   A. Ionic
   B. Covalent
   C. Metallic
   D. Resonant

3. A full valence shell for elements (with the exception of hydrogen and helium) is considered to contain (blank) electrons.
   A. 2
   B. 4
   C. 6
   D. 8

4. Match the type of salt with the molecular group it contains.

Metal Peroxide	OH
Metal Hydroxide	CN
Metal Oxide Salt	O-O
Metal Cyanide	O2-

5. What types of bonds are the arrows pointing at?



6. The names of Binary Acids end with: ___________________

7. The names of Metal Oxysalts end with: __________________

8. The names of Metal Peroxides end with: __________________

9. The names of Oxy Acids end with: __________________

10. Positively charged ions are called: __________________

11. Negatively charged ions are called: __________________

12. What type of chemical bond involves the complete transfer of valence electron(s) between atoms?
    - E. Ionic
    - F. Covalent
    - G. Metallic
    - H. Resonant

Chapter 5: Hydrocarbons and Isomers

Introduction

Organic chemistry is the study of organic compounds. There is no universally agreed upon precise definition of "organic" compounds. The International Union of Pure and Applied Chemistry (IUPAC) defines organic compounds as a structure that contains at least one carbon atom. In general, most definitions of organic compounds include compounds that have carbon-hydrogen bonds.

Organic compounds include a vast number of compounds, both naturally occurring and manmade, that are key components of the endless varieties of substances that we use every day; everything from Acetylene to Vitamin D.

Organic compounds that contain only carbon and hydrogen are called hydrocarbons (IUPAC definition). They are the simplest of the organic compounds. The fuels we use every day are hydrocarbons. The natural gas (methane) that cooks our food, the gasoline and diesel that fuels our cars and trucks, the propane that lights up our barbecues and the wax that keeps our candles lit — are all hydrocarbons.

Hydrocarbon Bonding

Carbon atoms bond with other carbon atoms with covalent bonds. Because covalent bonds allow carbon atoms to bond by sharing electrons they can almost endlessly bond to other carbon atoms. These covalent bonds can be single, double or triple bonds. They can form complex molecules, long or short chains, and 4, 5 or 6 sided ring structures. It also forms covalent bonds with many other non-metal elements, especially hydrogen, nitrogen, oxygen, sulfur and phosphorous. (Note: Not all carbon-containing compounds are classified as organic. For example, carbonates and cyanides, and simple oxides, such as CO and CO2 aren't classed as "organic" even though they contain carbon.)

This type of carbon bonding is called "catenation" which is the bonding of atoms of the same element into a chain. These chains can be open ended or closed. Closed end carbon chains bond in the form of a ring (called a "cyclic" compound). Catenation allows organic molecules to form compounds with an endless variety of sizes, shapes, structures and properties. This is why there is such a vast array of organic compounds in existence.

The properties of organic compounds are determined by the type and structure of these chain structures.

Naming Hydrocarbons

Because the number of organic substances is essentially infinite it's impossible to come up with a system of single, unique names for hydrocarbons. The International Union of Pure and Applied Chemistry (IUPAC) put forth a recommended system for naming hydrocarbons. Their system assigns a basic designation for a hydrocarbon compound based on the name of a parent structure. This basic name is then modified by prefixes and suffixes. These more precisely convey the structural changes from the parent structure. Their system still allows the use of traditional names which are widely used in industry and academic circles (e.g. acetic acid, benzene and pyridine).

The simple hydrocarbons are named using a prefix that stands for the number of carbons in the structure, and a suffix that denotes the type of bonds in the compound.

Naming Compounds

Number of Carbons	**Prefix**	**Suffix "ane" type of bond: single bonds**
1	Meth-	Methane
2	Eth-	Ethane
3	Prop-	Propane
4	But-	Butane
5	Pent-	Pentane
6	Hex-	Hexane
7	Hept-	Heptane
8	Oct-	Octane
9	Non-	Nonane
10	Dec-	Decane

Classifying Hydrocarbons

Functional Groups

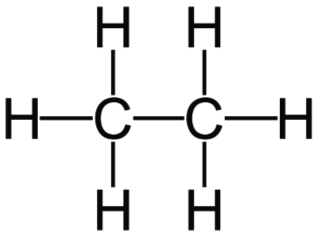
Hydrocarbons are classified by their functional group. A functional group is a molecular module attached to the parent structure of a molecule. They are specific groups of atoms or bonds within molecules that determine the properties and behavior of those molecules. The same functional group will undergo the same or similar chemical reaction(s) regardless of the size of the molecule it is a part of. The atoms of functional groups are linked to each other and to the rest of the molecule by covalent bonds. The functional groups we'll discuss in this chapter are only for hydrocarbons. These contain only carbon and hydrogen, but they vary in the number and order of double bonds. (We'll discuss functional groups that contain other elements in subsequent chapters.)

The concept of functional groups is central in organic chemistry. They can have a decisive influence on the chemical and physical properties of organic compounds. They also determine the chemical reactivity of an organic molecule.

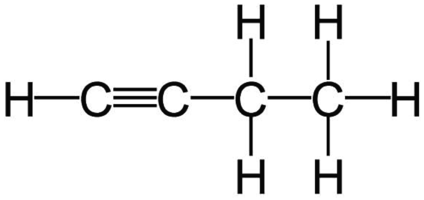
Saturated vs. Unsaturated

Unsaturated hydrocarbons are hydrocarbons that have double or triple covalent bonds between adjacent carbon atoms. Saturated hydrocarbons are hydrocarbons having only single covalent bonds between their carbons. Those with at least one carbon-to-carbon double bond are called alkenes and those with at least one carbon-to-carbon triple bond are called alkynes.

Saturated Hydrocarbon



Unsaturated Hydrocarbon



Hydrocarbons are generally classified into four groups. They are: Alkanes, Alkenes, Alkynes and Aromatics (also called "arenes").

Alkanes

Alkanes are organic compounds that consist entirely of single-bonded carbon and hydrogen atoms arranged in a tree structure. The number of carbon and hydrogen atoms will determine the properties of the molecule. The properties will change predictably according to the number of carbon and hydrogen atoms present. Alkanes lack any other functional groups.

Alkanes are *saturated* hydrocarbons. The carbon-carbon bonds are single (sigma) bonds. In the IUPAC naming system alkanes have names that end in "ane."

Alkanes are the simplest and least reactive hydrocarbon species. The main sources of alkanes are crude oil and natural gas. They are commercially very important, being the principal constituent of various fuels and lubricating oils. Other alkanes (such as hexanes) are used as solvents. They are generally colorless and odorless.

Examples of Alkanes.

Name	Formula	Comments
Methane Ethane	CH_4 C_2H_6	Commonly referred to as natural gas, with methane as the major constituent.
Propane Butane	C_3H_8 C_4H_{10}	Both propane and butane are gases at ambient temperature. Liquefied Petroleum Gas (LPG) is primarily made up of propane and butane.
Pentane Hexane	C_5H_{12} C_6H_{14}	These hydrocarbons are liquids at room temperature. As mixtures, they are referred to as petroleum ether. They evaporate readily.

Alkenes

Compared to an alkane with the same number of carbons, an alkene has fewer hydrogen atoms in its structure and at least one carbon-to-carbon double bond. For this reason the alkenes are unsaturated hydrocarbons. Alkenes will have one or more sets of double bonds between carbon atoms somewhere in their carbon skeleton. (Alkenes are sometimes called olefins.) The presence of the double bonds makes alkenes more reactive than alkanes.

In the IUPAC naming system, these hydrocarbons with double bonds have names that end in “ene.” Their formulas will fit into CnH_2n, where n is equal to the number of carbons in the compound. Alkenes use the same set of prefixes as the alkanes.

The physical properties of alkenes and alkanes are similar. They are colorless, nonpolar, combustible, and almost odorless. Like the alkanes, the boiling points of alkenes increase as the molecular mass increases. The simplest alkenes are gases at room temperature. Alkenes are virtually insoluble in water, but dissolve in organic solvents.

Alkenes are oxidized with a large number of oxidizing agents. In the presence of oxygen, alkenes burn with a bright flame to produce carbon dioxide and water. Catalytic oxidation yields epoxides. Reaction with ozone breaks the double bond, yielding two aldehydes or ketones. Polymerization and oxidization of alkenes yields polymers of high industrial value such as the plastics polyethylene and polypropylene.

Examples of Alkenes

Name	Formula	Uses
Ethylene (ethene)	C_2H_4	Production of polyethylene plastic, production of ethylene oxide (a sterilant gas)
Propylene (propene)	C_3H_6	Production of polypropylene plastic, production of acetone, phenol and isopropyl alcohol
Butylene (butene)	C_4H_8	Production of plastics

Alkynes

An alkyne is an unsaturated hydrocarbon containing at least one carbon—carbon triple bond. Alkynes tend to have higher boiling points than alkanes or alkenes. Like other hydrocarbons, alkynes are generally hydrophobic but tend to be more reactive. They show greater tendency to polymerize than alkenes do.

In the IUPAC naming system, these hydrocarbons have names that should end in “yne” but there are some exceptions. One prominent exception is acetylene, one of the most common alkynes. Under the IUPAC naming convention is should be called “ethyne.” Another example is ethylene (C_2H_2). Under the IUPAC system it should be called “ethyne” since it follows the formula structure for alkynes (C_nH2_{n-2}). In cases like this the traditional names will vary from the IUPAC standard. In situations like this you may not always see the “yne” ending used.

Examples of Alkynes

Name	Formula	Uses
Ethyne (acetylene)	C_2H_2	Welding gas
Propyne (methylacetylene)	C_3H_4	Component of MAPP gas used for welding
Butyne (dimethylacetylene)	C_4H_6	Used in the synthesis of organic compounds

The alkanes, alkenes and alkynes lumped together are called *aliphatic* compounds to differentiate them from the *aromatic* compounds.

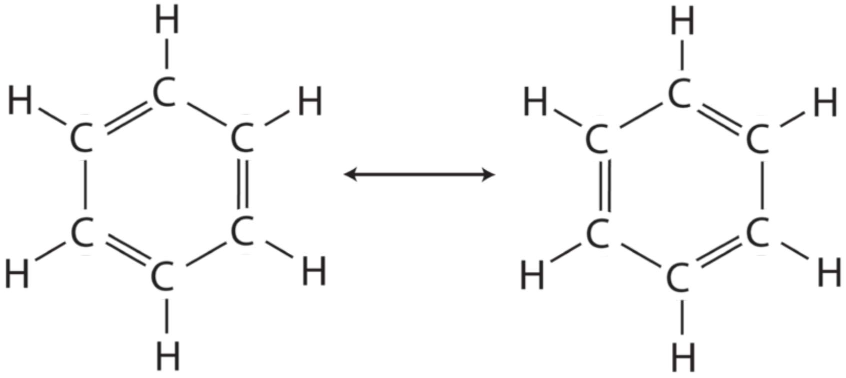
Aromatics (also called "Arenes")

Aromatic hydrocarbons have a 6-sided ring structure with resonant bonding. All 6 carbons share 6 electrons in a double-donut shaped orbital. Many aromatic compounds are naturally occurring and display unusual stability.

Note: These compounds were originally classified as "aromatic" because they were obtained from naturally occurring substances that had a pleasant or fragrant odor. The term aromatic has since come to mean any compound structurally derived from benzene.

Benzene, C6H6, has the simplest structure of the aromatic hydrocarbons. It was the first "aromatic" discovered and was named as such. Each carbon atom in the hexagonal cycle has four electrons to share. One goes to the hydrogen atom, and one each to the two neighboring carbons. This leaves one electron to share with one of the same two neighboring carbon atoms, thus creating a double bond with one carbon and leaving a single bond with the other, which is why the benzene molecule is drawn with alternating single and double bonds around the hexagon.

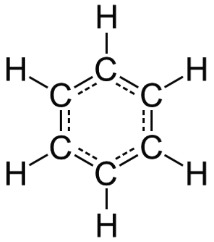
Benzene Bonding



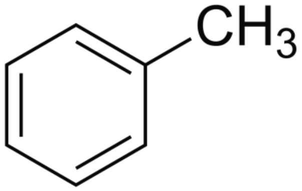
The parent member of this cyclic family is benzene. Other members of the aromatic hydrocarbon family include toluene and xylene, which is frequently called the BTX family (or when ethylbenzene is included, it is called BTEX). They burn with a strong sooty yellow flame because of the high carbon–hydrogen ratio. The flame color takes on an orange/red color. Aromatic ring structures are found in countless organic compounds. The small to medium size compounds with aromatic rings are flammable or combustible liquids, sometimes called aromatic solvents.

The BTX Family of Hydrocarbons

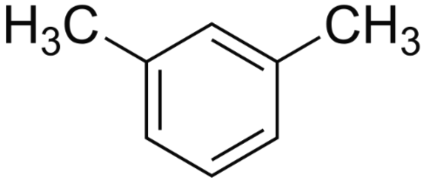
Benzene



Toluene



Xylene



Aromatic Hydrocarbons BTX

Name	**Formula**	**Uses and Hazards**
Benzene	C_6H_6	Solvent flammable liquid, toxic carcinogen
Toluene	C_7H_8 or $C_6H_5CH_3$	Solvent flammable liquid
Ethylbenzene	C_8H_{10} or $C_6H_5C_2H_5$	Production of Styrene, paints flammable liquid
Xylene	C_8H_{10} or $C_6H_4(CH_3)_2$	Paint solvent flammable liquid

Toxicity of Hydrocarbons

Hydrocarbons are a heterogenous group of organic substances that are primarily composed of carbon and hydrogen molecules. Because of their diverse structures and properties it's all too easy to over-generalize about their toxicity. They do, however, have some common attributes regarding toxicity. Many are readily absorbed through the skin. Skin contact and ingestion should be avoided. Inhalation is a very common route of exposure.

Hydrocarbons can be classified as being aliphatic, in which the carbon atoms are arranged in a linear or branched chain, or aromatic, in which the carbon atoms are arranged in a ring structure. Halogenated hydrocarbons are a subgroup of aromatic hydrocarbons, in which one of the hydrogen molecules is substituted by a halogen group. The most important halogenated hydrocarbons include carbon tetrachloride, trichloroethylene, tetrachloroethylene, trichloroethane, chloroform, and methylene chloride. Unlike the aromatic or aliphatic hydrocarbons, the halogenated hydrocarbons tend to cause a wider range of toxicity.

The toxicity and route of entry of hydrocarbons is directly related to their physical properties. The chemical properties of the individual hydrocarbon determine the specific toxicity, while the dose and route of entry affect which organs are exposed to the toxicity.

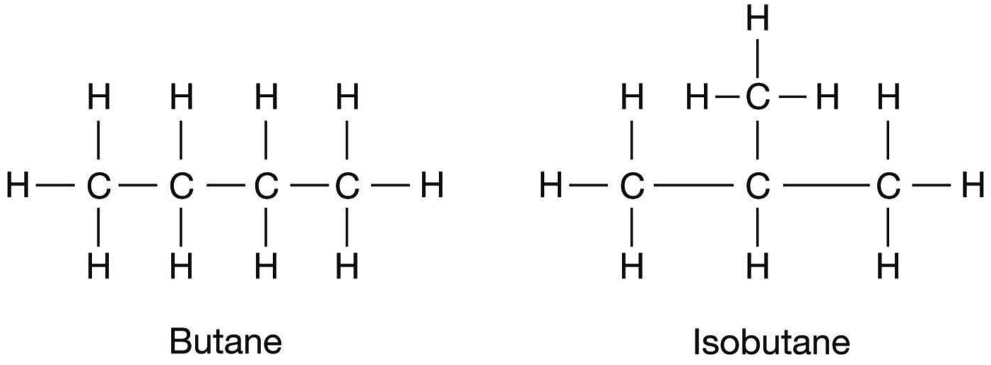
Toxicity from hydrocarbon ingestion can affect many different organs, but the lungs are the most commonly affected. Organ systems that can be affected by hydrocarbons include the pulmonary, neurologic, cardiac, gastrointestinal, hepatic, renal, dermatologic, and hematologic systems. Because many hydrocarbons are volatile and have low viscosity they are easily inhaled making the pulmonary system is the most commonly involved system.

Many hydrocarbons have properties that can cause specific toxic effects. Certain hydrocarbons are highly lipophilic (they easily dissolve in fats, oils, lipids) and can make their way across the blood-brain barrier to directly affect the central nervous system. Some hydrocarbons can cause elevated heart rates. The chlorinated hydrocarbons, in particular carbon tetrachloride, are capable of damaging the liver. Certain aromatic hydrocarbons (especially benzene) can lead to an increased risk of blood cancers.

In general, aromatic hydrocarbons tend to be the most toxic. The aromatic ring structure is so stable that is tends not to break down readily in the environment. As such, aromatic hydrocarbons are considered *persistent and bioaccumulative*. They are lipid soluble substances that are stored in fat tissue. Acute (one-time) exposures of toluene and xylene have an anesthetic effect. Chronic exposures to benzene, toluene, and xylene (BTX) can cause liver and kidney damage. Of these three aromatics, benzene is the most toxic and is a known carcinogen.

Isomers

An isomer is a molecule with the same molecular formula as another molecule, but with a different chemical structure. That is, isomers contain the same number of atoms of each element, but have different arrangements of their atoms. Isomers do not necessarily share similar properties, unless they also have the same functional groups. Two isomers of butane are shown below.



Because butane and isobutane have the same molecular formula (C_4H_{10}), but different structural formulas, they are considered to be *isomers* of one another.

Summary

The key to evaluating the hazards of a hydrocarbon is recognizing its structure and composition. There are four types of hydrocarbons: alkanes, alkenes, alkynes, and aromatics. Each has different characteristics. Isomers have the same molecular formula, but different molecular structures. These structures give isomers different characteristics and different hazards than their hydrocarbon counterparts. This chapter also addressed how to name hydrocarbons, their structures, and the hazards associated with each type.

Chapter Review

1. Fill in the number of carbon atoms a molecule with the following prefixes contain.

Suffix	Number of Carbons
Hept	______________
But	______________
Eth	______________
Pent	______________
Meth	______________
Dec	______________
Non	______________
Prop	______________
Oct	______________
Hex	______________

2. Fill in the blank.

An isomer is a molecule with the same molecular formula as another molecule, but with a different chemical (_______________________).

Aromatic hydrocarbons have a (__________________)-sided ring structure with resonant bonding.

Saturated hydrocarbons are hydrocarbons having (__________________) covalent bonds between their carbons.

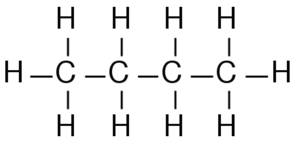
The parent member of BTX family is benzene. Other members of the BTX family include (_________________) and (__________________).

Carbon atoms bond with other carbon atoms with (__________________) bonds.

3. Check the appropriate box to identify which group each substance belongs in. alkane, alkene, alkyne

Substance	Alkane	Alkene	Alkyne
Ethylene			
Acetylene			
Methane			
Propane			
Propylene			
Butane			
Hexane			
Butylene			
Butene			

4. What type of hydrocarbon is this substance?



$$\begin{array}{ccccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array}$$

A. Aromatic
B. Unsaturated
C. Saturated
D. Olefilic

5. In general, what types of hydrocarbons tend to be the most toxic?
A. Saturated
B. Alkane
C. Catenated
D. Aromatic

Chapter 6: Hydrocarbon Derivatives

Introduction

In the previous chapter we discussed functional groups (an atom or group of atoms attached to the parent structure) and how they can affect the physical and chemical behavior of the hydrocarbons they are attached to. The atoms of functional groups are linked to each other and to the rest of the molecule by covalent bonds. The functional group defines the characteristic physical and chemical properties of a given family of organic compounds.

The functional groups for hydrocarbons we discussed in the previous chapter contain only carbon and hydrogen. In this chapter we'll go over functional groups that contain other elements such as nitrogen, sulfur, oxygen, phosphorous and halogens such as chlorine. The atom (or group) that replaces one or more hydrogen atoms attached to a parent structure are called "substituent" atoms (or groups).

The backbone of an organic compound is formed from chains, branches and rings of covalently bonded carbon atoms. Organic compounds that consist of carbon and at least one other element that is not hydrogen are called Hydrocarbon Derivatives. These other non-metals can be attached to the carbon skeleton either alone or as a distinct functional groups such as -NO_2, (the nitro group), or –COOH, (the carboxyl group). There are about a dozen of these groups that are commonly found in a wide variety of organic structures.

Functional groups are responsible for the characteristic chemical reactions of the molecules they are attached to. The same functional group will undergo the same or similar chemical reaction(s) regardless of the size of the molecule it is a part of. The type of derivative and how it's bonded to the hydrocarbon molecule determines the behavior of that compound. If you're familiar with the common hydrocarbon derivatives you can predict the likely behavior and properties of these substances.

Functional groups can be organized into groups based on their formulas. They are commonly divided into groups that contain the element oxygen as the only other non-metal and those that contain other non-metals such as sulfur and nitrogen. The groups are further divided by general structure; for example, the carbonyls, which all have a double bond between carbon and oxygen within their structures. (Note: formulas of hydrocarbon derivatives will often use the letter "R" to denote an attached hydrogen, or a hydrocarbon side chain of any length. It may sometimes refer to any group of atoms. It is simply a placeholder.)

This course will cover the following Hydrocarbon Derivatives:

Hydrocarbon Derivatives Containing Oxygen	
Ethers	Alcohols
Organic Peroxides	Carbonyls (see below)
Epoxides	Others

Carbonyls	
Aldehydes	Carboxylic Acid Derivatives
Ketones	Esters
Carbamates	Amides

Hydrocarbon Derivatives Containing Nitrogen	
Nitros	Amines
Nitriles	Amides
Isocyanates	Carbamates

Hydrocarbon Derivatives Containing Halogens	
Haloalkanes	Fluoroalkanes
Chloroalkanes	Bromoalkanes
Iodoalkanes	

Hydrocarbon Derivatives Containing Oxygen

Ethers

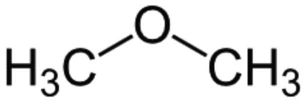
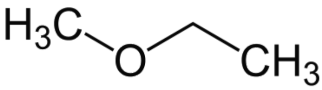
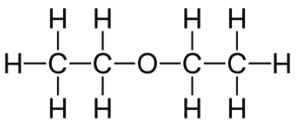
Ethers are organic compounds that have an oxygen atom bonded to two alkyl or aryl groups. The carbon groups are generally named first, followed by “ether.” In the official IUPAC nomenclature system, the shorter of the two chains becomes the first part of the name with the -ane suffix changed to -oxy, and the longer alkane chain becomes the suffix of the name of the ether. (For example CH3-CH2-CH2-O-CH3 is methoxypropane.) The small straight chain ethers are extremely volatile and flammable. The simplest ether, dimethyl ether CH3OCH3 is a flammable gas used as a propellant in aerosol canisters and as a substitute for LPG gas.

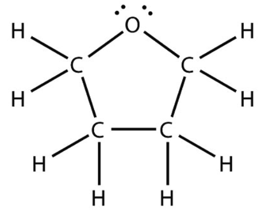
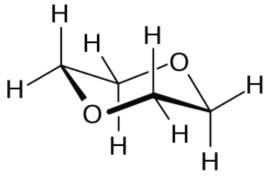
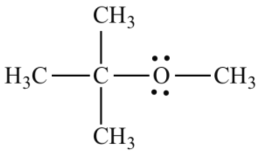
Diethyl ether burns very clean with a tall yellow organic flame. This is the most common liquid ether and is commonly called just “ether”. Diethyl ether is normally stored in amber glass bottles, aluminum cans, steel drums or tanks packaged under nitrogen. Cans of ether are sold as a starting fluid for automobiles. Heating a can or a bulk container of ether may result in a container failure (BLEVE or Boiling Liquid Expanding Vapor Explosion). Diethyl ether has a limited shelf life. It has slow oxidation potential and can add another oxygen atom into its chemical makeup to become an organic peroxide (diethyl peroxide). Antioxidants, such as ethanol or BHT, are added to ether to keep it from oxidizing. If you see crystals on or in an old container of ether, they could be crystals of diethyl peroxide, which could be very unstable. Never open a can of ether if it is past its expiration date. The crystals could form along the threads of the cap and could decompose energetically due to friction created when the cap is twisted open. Diethyl ether is practically insoluble in water and will appear to float on water. Its solubility is 69 grams per liter of water. The ether functional group in a straight chain compound is a “non-polar” functional group. This “non-polarity” is the reason why the smaller straight chain ethers are so volatile and do not dissolve well in water. High exposure to diethyl ether can have an anesthetic effect on the body. Chronic exposure could cause liver damage and irritate the skin, eyes and upper respiratory system. The formula for diethyl ether is $C_2H_5OC_2H_5$, but may be written as $(C_2H_5)_2O$ because the hydrocarbon chains are the same on both sides of the oxygen atom. It has also been called “ethyl ether,” “ether,” or “hospital ether.”

Methyl tertiary butyl ether (MTBE) was used as an oxygenate additive for gasoline and jet fuel. It is extremely flammable, burns very clean and is a suspected carcinogen. MTBE will appear to float in water but enough of it dissolves in water, about 4% by weight, so it became a groundwater contamination concern. It has now been replaced with ethanol for the purpose of fuel oxygenation.

The cyclic ether THF (tetrahydrofuran) is a common solvent in varnishes and PVC glue. It is considered to be a “polar ether”. The oxygen atom sticks out away from the plane of the molecule to make the resultant compound a “polar solvent” It is miscible with water. THF also has the tendency to form explosive peroxides when it is exposed to the oxygen in the air. It is also stored with antioxidants.

Examples of Ethers

Common Name *Official Name*	DOT Hazard Class	Condensed Formula	Structural Formula
Dimethyl ether *methoxymethane*	Flammable gas	CH_3OCH_3	
Methyl ethyl ether *methoxyethane*	Flammable gas	$CH_3OC_2H_5$	
Ether (diethyl ether) *ethoxyethane*	Flammable liquid	$C_2H_5OC_2H_5$	 $\begin{array}{ccccccccccccc} & & H & & H & & & & H & & H & & \\ & & \mid & & \mid & & & & \mid & & \mid & & \\ H & - & C & - & C & - & O & - & C & - & C & - & H \\ & & \mid & & \mid & & & & \mid & & \mid & & \\ & & H & & H & & & & H & & H & & \end{array}$

Tetrahydrofuran (THF) *oxolane*	Flammable liquid	$(CH_2)_4O$	
Dioxane 1,4-Dioxacyclohexane	Flammable liquid	$C_4H_8O_2$	
Methyl tertiary butyl ether MTBE	Flammable liquid	$CH_3OC(CH_3)_3$	 $H_3C-\overset{CH_3}{\underset{CH_3}{C}}-\ddot{O}-CH_3$

Organic Peroxides

Organic peroxides are organic compounds containing the peroxide functional group (ROOR'). The formula may appear as R-O-O-R or R-O_2-R. The naming of the organic peroxides typically starts by naming the carbon groups first, followed by "peroxide," or by using the term "peroxy" in between the names of the two carbon groups. If one of the substituent groups is just a hydrogen, then the term "hydroperoxide" or "hydroperoxy" is used.

Organic peroxides are extremely unstable. While these materials are generally placarded for transportation as "organic peroxide" versus "explosive," they have much in common with explosives. They contain both a fuel component and an oxidizer component in the same formula. Because they already contain two of the three sides of the fire triangle (*fuel, oxygen*, heat), all that is needed is heat or friction to cause them to burn with rapid, explosive combustion. Extreme care must be taken in handling these compounds. The most important parameter in dealing with organic peroxides is to control the temperature. Organic peroxides range from non to moderately soluble in water.

MEKP, methyl ethyl ketone peroxide is an oily liquid commonly used as a plastics hardener/catalyst. In this application it is mixed in with solvents, such as phthalates, MEK and xylene at around 30% by weight. It is only slightly soluble and sinks in water. In pure form it is considered a shock sensitive high explosive.

Benzoyl peroxide is a white crystalline solid. It will decompose explosively at 221°F. Benzoyl peroxide is well known for its use as the active ingredient in acne treatment. It is also used to bleach flour, hair and teeth, for polymerizing polyester and many other uses.

Organic peroxides are widely used in the plastics industry to initiate the polymerization process as activators, cross-linking agents, accelerators and hardeners. They are also used for room temperature curing of polyester resins, paints and varnishes.

Peroxyacetic acid CH_3COOOH is an example of a compound that is an organic peroxide and an organic acid. In fact peroxyacetic acid is the compound formed when acetic acid oxidizes. Peroxyacetic acid is also called peracetic acid, acetic peroxide and acetyl hydroperoxide to name just a few synonyms. It is a pungent, colorless liquid. It is considered a strong oxidizer and it has a flashpoint of 105°F so it also meets the definition of a flammable liquid. It is also a corrosive and a very toxic compound with an oral lethal dose as low as 1 teaspoon for a 150 lb person. It will decompose violently releasing acrid smoke fumes when its temperature reaches 230°F.

TATP or triacetone triperoxide is one of the explosive compounds used by the Shoe Bomber, the Underwear Bomber, Vest Bombers and in the July 7th London Train bombings. It is an organic peroxide easily made by mixing together acetone, hydrogen peroxide and an acid such as sulfuric acid. It is a shock and friction sensitive explosive. In the incidents cited it was used to make improvised blasting caps or as a primary explosive. It is a white solid that explodes with a detonation velocity of 5250 meters per second.

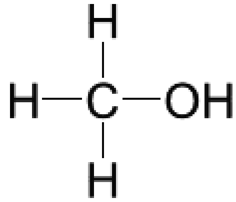
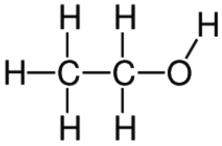
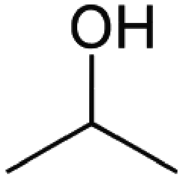
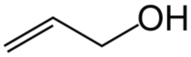
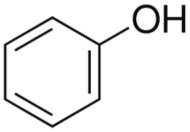
Hexamethylene triperoxide diamine HMTD is another explosive organic peroxide that is widely used and easily made. It can be prepared from hydrogen peroxide, hexamine (campfire starter fuel tablets) and citric acid. Similar to TATP it is unstable and is shock, heat and friction sensitive. It has three peroxide functional groups and also has two “amine” groups in it. The amine functional group is a group that contains the element nitrogen.

Alcohols

Alcohols are derivatives of hydrocarbons in which an –OH group has replaced a hydrogen atom. Although all alcohols have one or more hydroxyl (–OH) functional groups, they do not behave like bases such as NaOH and KOH. NaOH and KOH are ionic compounds that contain OH^- ions. Alcohols are covalent molecules; the –OH group in an alcohol molecule is attached to a carbon atom by a covalent bond.

In the alcohol functional group, a carbon is single-bonded to an OH group (the OH group, by itself, is referred to as a hydroxyl). Molecules of alcohols contain one or more hydroxyl groups (OH groups) substituted for hydrogen atoms along the carbon chain. The Alcohol functional group is a “polar functional group”. Molecules that have polar functional groups on them are also attracted to each other. The opposite poles align – opposites attract, and this increases the viscosity, increases the boiling point, flash point, etc., of the substance. Short chain alcohols will form a miscible system with water, just like the carbonyls. They mix with water (swimmers).

Examples of Alcohols

Common Name *IUPAC Name* Synonyms	DOT Hazard Class	Condensed Formula	Structural Formula
methanol *methanol* methyl alcohol wood alcohol	Flammable Liquid	CH_3OH	
ethanol *ethanol* alcohol grain alcohol ethyl alcohol	Flammable Liquid	C_2H_5OH	
isopropyl alcohol *propan-2-ol* IPA propanol propyl alcohol rubbing alcohol	Flammable Liquid	C_3H_7OH	
allyl alcohol *prop-2-en-1-ol*	Poison Inhalation Hazard, Flammable Liquid	C_2H_3 CH_2OH	
phenol *phenol* carbolic acid hydroxybenzene phenylic acid	Poison	C_6H_5OH	

Alcohols are named starting with the carbon group, then adding “alcohol”. The official nomenclature system uses the suffix “ol”, the letters “ol” in the middle of the name, or the prefix “hydroxyl” for compounds that contain an alcohol functional group.

The small chain alcohols are flammable and when burning they exhibit a barely visible blue base in the flame and no smoke. A methanol flame (CH_3OH with 1 carbon) is almost invisible and has an all-blue flame. Ethanol C_2H_5OH with 2 carbons burns with yellow edges around a blue base. Isopropyl alcohol C_3H_7OH with 3 carbons has a lot of yellow in the flame over a smaller blue base. Alcohols are also known for their toxicity and may be a skin absorption hazard. Methanol CH_3OH is very toxic. Ethanol C_2H_5OH, or grain alcohol, is drinking alcohol. Ethanol depresses the central nervous system and damages the liver (cirrhosis).

Alcohols can oxidize in air to form organic acid compounds (RCOOH). They oxidize by changing first to an aldehyde (RCHO), then to an organic acid. The aldehydes will cause a person to feel bad after drinking too much alcohol. The organic acid destroys the liver. When methanol CH_3OH is oxidized, it changes to formaldehyde HCHO, then to formic acid HCOOH.

Phenol C_6H_5OH is an aromatic alcohol. Phenol acts differently than straight chain alcohols. The hydrogen in an alcohol (hydroxyl) group can ionize away from the oxygen easily whenever the alcohol group is attached to a benzene ring, hence phenol's acidic character. Another name for phenol is carbolic acid. Phenol sublimes readily and has an antiseptic odor. It is quite toxic and was once used by the Nazis to kill prisoners in the concentration camps. Since the hydroxyl group acts so differently when it is attached to a benzene ring, there is actually a whole class of compounds called "phenols".

Trinitrophenol is a well-known phenol derivative, also known of as picric acid. It is a high explosive that can become friction and shock sensitive. We will take another look at Picric acid when we consider the Nitro functional group.

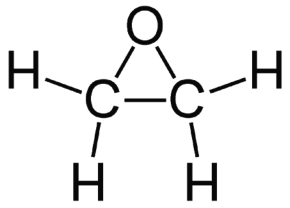
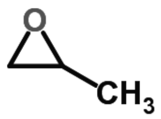
Epoxides

Epoxides are cyclic ethers with a triangle structure with oxygen at the apex. The oxygen atom is not only connected to two carbon atoms, but the two carbon atoms also have a covalent bond between them. They tend to be more reactive than ethers. They are produced on a large scale for many applications. In general, low molecular weight epoxides are colorless and nonpolar, and often volatile.

Ethylene oxide [CH_2OCH_2 or $(CH_2)_2O$] is the simplest epoxide and the most economically important. It is used as an industrial sterilant, a petroleum demulsifier, a rocket propellant and to make many other chemicals such as ethylene glycol (antifreeze). It is an extremely flammable, water soluble, reactive gas. It does not need oxygen to burn and can burn in an inert atmosphere. It is a severe irritant as well as a toxic and carcinogenic compound.

Propylene oxide CH_3CHCH_2O is a highly volatile, flammable, reactive liquid. It is used as a starting material for polyurethane plastics.

Examples of Epoxides

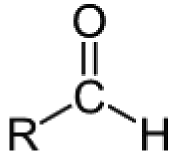
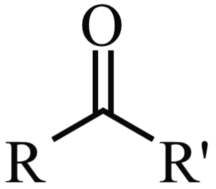
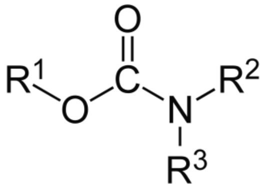
Functional Group	General Description	Condensed Formula	Structural Formula
Ethylene oxide	Poison Gas Flammable Gas	CH_2OCH_2 or $(CH_2)_2O$	
Propylene oxide	Flammable Liquid	CH_3CHCH_2O	

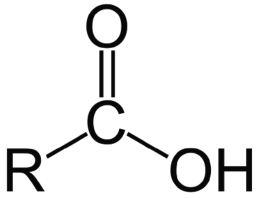
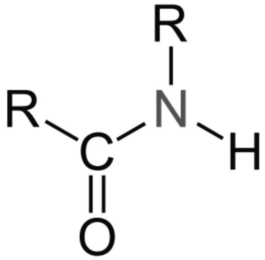
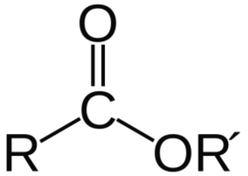
Carbonyls

There are six hydrocarbon derivatives which are referred to as carbonyls: ketones, aldehydes, carbamates and carboxylic acid derivatives (esters and amides). They contain a carbon-oxygen double bond (C=O) within the structure. These carbon-oxygen double bonds (pi bonds) have a greater stability then the pi bonds (double bonds) that can exist between two carbon atoms. Carbonyl compounds of low molecular weight (small # of carbons in their structure) are soluble in water. The table below displays a structural overview of the carbonyls and an indication of how to recognize a carbonyl when looking at a molecular formula. Each of these carbonyls will be addressed in more detail on the following pages.

Carbonyls	
Aldehydes	Carboxylic Acid Derivatives
Ketones	Esters
Carbamates	Amides

Structure of Carbonyls

Functional Group	General Description	Condensed Formula	Structural Formula
Aldehydes	Compounds RC(=O)H , in which a carbonyl group is bonded to one hydrogen atom and to one saturated hydrocarbon group.	R-CHO	
Ketone	Ketones are simple organic compounds that contain a carbonyl group (a carbon-oxygen double bond) that can be bonded to a variety of carbon-containing substituents.	R-CO-R	
Carbamates	Salts or esters of carbamic acid, (NH_2COOH).	R_2NCOOR	

Carboxylic Acid Derivatives	Oxoacids having the structure RC(=O)OH.	R-COOH	
Amides	An organic compound containing the group —C(O)NH_2 derived from ammonia by replacement of an atom of hydrogen with another element (such as a metal).	$RCONR_2$	
Esters	A Carboxylic Acid Derivative derived from an oxoacid.	R-COO-R or R-CO_2-R	

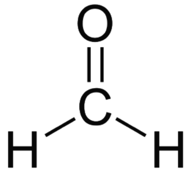
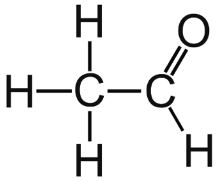
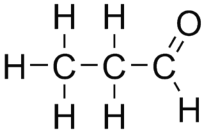
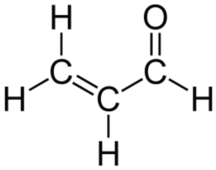
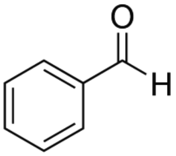
Aldehydes

Aldehydes are similar to ketones. An aldehyde is a carbonyl compound where the carbonyl carbon is bonded to two hydrogen atoms or to a hydrogen atom and a carbon atom. The CHO group in an aldehyde is called the aldehyde group. The formula of an aldehyde always appears with "CHO" on the end.

Formaldehyde (HCHO), the simplest aldehyde, has one carbon atom. It is a gas that readily dissolves in water to form a solution called formalin which is commonly used as a preservative. Formaldehyde is also a flammable gas with a wide flammable range and is quite toxic – it is a known carcinogen.

After formaldehyde, the next largest aldehyde is acetaldehyde (CH_3CHO), which has two carbons. Acetaldehyde is a flammable liquid. It has slow oxidation potential and can add oxygen into its chemical makeup to form an explosive peroxide. It will oxidize first into an organic acid – acetic acid, which then can continue to add oxygen to form peroxyacetic acid. It can polymerize when exposed to air and heat, acids, or bases with the potential for a fire or explosion. It polymerizes violently when mixed with concentrated sulfuric acid.

Examples of Aldehydes

Common Name *IUPAC Name* Synonyms	DOT Hazard Class	Condensed Formula	Structural Formula
formaldehyde *formaldehyde* methanal	Flammable Liquid	H_2CO	
acetaldehyde *ethanal* acetic aldehyde ethyl aldehyde	Flammable Liquid	CH_3CHO	
propionaldehyde *propanal* propaldehyde methylacetaldehyde	Flammable Liquid	CH_3CH_2CHO	
acrolein *propenal* acrylaldehyde ethylene aldehyde acrylic aldehyde	Poison	C_2H_3CHO	
benzaldehyde *phenylmethanal* benzoic aldehyde almond extract	Miscellaneous Dangerous Substance	C_6H_5CHO	

Acetaldehyde has a pungent, fruity odor. It exhibits a yellow flame with a blue base when burning. It is used to manufacture perfumes, dyes, plastics, synthetic rubber and is also used in silvering mirrors. It is a synthetic flavoring ingredient used to give orange, apple or butter flavors and is also used as a fruit and fish preservative. Acetaldehyde is a by-product of yeast production and occurs naturally in bread, wine and other yeast fermented products. Acetaldehyde CH_3CHO is a suspected carcinogen. When ingested or inhaled, acetaldehyde can irritate the eye, nose, and throat. It can cause central nervous system depression and delayed pulmonary edema.

Acrolein C_2H_3CHO is another aldehyde. The aldehyde functional group is attached to two carbon atoms that have a double bond between them. Acrolein is a slightly yellow liquid with a disagreeable odor. It is highly flammable and very reactive. Acute exposure to acrolein will cause severe eye and respiratory tract irritation. It easily polymerizes due to the unstable carbon-carbon (C=C) double bond and is used to make acrylic plastics, polyester resins and polyurethane. Acrolein is water soluble.

Benzaldehyde (almond oil) sinks in water and forms a layer on the bottom. This occurs because the intermolecular attraction between the poles of the "polar" aldehyde functional group cause the molecules of benzaldehyde to get closer together, thus increasing the liquid's density.

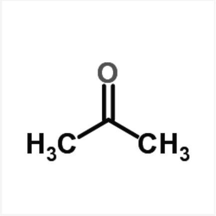
Ketones

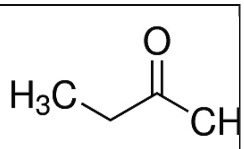
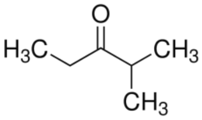
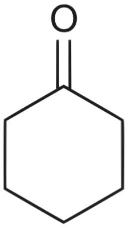
A ketone is a carbonyl compound where a carbonyl carbon is bonded to two carbon atoms. The official nomenclature system uses the suffix "one" or the letters "on" in the middle of a name for compounds that contain a ketone functional group. Anytime you see a name ending in "one," the chemical is most likely a ketone of some kind.

Ketones can be recognized by "CO" in the middle of the formula (R-CO-R). They contain a double bond between carbon and oxygen. The IUPAC system of nomenclature assigns a characteristic suffix of -one to ketones. A ketone carbonyl function may be located anywhere within a chain or ring, and its position is usually given by a location number.

Chain numbering normally starts from the end nearest the carbonyl group. Very simple ketones, such as propanone and phenylethanone do not require a locator number, since there is only one possible site for a ketone carbonyl function. The common names for ketones are formed by naming both alkyl groups attached to the carbonyl then adding the suffix -ketone. The attached alkyl groups are arranged in the name alphabetically.

Examples of Ketones

Common Name *IUPAC Name* Synonyms	DOT Hazard Class	Condensed Formula	Structural Formula
Acetone *2- propanone* dimethyl ketone	Flammable Liquid	CH_3COCH_3 or $(CH_3)_2CO$	

methyl ethyl ketone *2-butanone* MEK methyl propanone	Flammable Liquid	$CH_3C(O)CH_2CH_3$	
ethyl isopropyl ketone *2-methylpentan-3-one* 2-methyl-3-pentanone	Flammable Liquid	$C_2H_5COC_3H_7$	
cyclohexanone cyclohexyl ketone pimelic ketone	Flammable Liquid	$C_5H_{10}O$	

The small, straight-chain ketones; acetone and MEK, are flammable and water soluble. Acetone is miscible and the slightly larger MEK has about a 25% water solubility. They exhibit a yellow flame with a blue base when burning and they burn very clean (no smoke), due to the fact that they already have some oxygen content as part of their makeup. Acetone is used to remove nail polish, as a paint solvent and can be found in a variety of foods; fruits, beverages and baked goods. MEK is a solvent used in a wide variety of applications.

As the compounds having ketone functional groups get larger, a trend becomes apparent: the larger the hydrocarbon functional groups are the more the compound acts like a hydrocarbon and less like a ketone. Ethyl isopropyl ketone and cyclohexanone float on water. They are water soluble to a slight extent but to the naked eye they appear to float on water. The Ketone functional group is considered a "polar" functional group. The covalent bonds between the carbon and the oxygen are considered "polar covalent" bonds. The sharing between the oxygen and the carbon is not equal. Oxygen is more electronegative than carbon and draws the electron cloud closer. This imparts a negative pole to the oxygen atom and a positive pole to the carbon atom. Water is a polar solvent, and we have all heard the phrase: "like dissolves like". The Ketone functional group, because of its polarity, wants to dissolve into the polar solvent, water. As such, all compounds that contain the ketone functional group may exhibit some degree of water solubility.

Carbamates

A carbamate is an organic compound that is a derivative of carbamic acid (NH2COOH). Carbamate group are functional groups that are inter-related structurally and often are interconverted chemically. Carbamate esters are also called urethanes.

The carbamate functional group can be thought of as an amine attached to an ester. The formula may be recognized by R_2NCOOR. Many carbamates are pesticides. They are very toxic, generally nonflammable and soluble in water. They have in large part replaced the organochlorine insecticides (DDT) because they are more biodegradable. They are lower in dermal toxicity than most of the common organophosphate pesticides in use today. However, as pesticides, they still present a toxicity hazard and many decompose to form iso-cyanates when heated.

The carbamate 1-napthyl methylcarbamate, also known as carbaryl, was the insecticide that was being manufactured in Bhopal, India on Dec 2nd, 1984. A tank holding methyl isocyanate MIC, a chemical intermediate in the synthesis of carbaryl, over-pressurized and vented in the middle of the night spewing the gas into the night air. Over 2,250 people died from exposure to the gas in the middle of the night and sources say upwards of 11,000 may have died as a direct result of inhaling the gas. It was the largest industrial accident in history. Carbaryl is still a widely used carbamate pesticide. It is a colorless crystalline solid that is only sparingly soluble in water.

Examples of Carbamates

Name	Common/Trade Name	Structural Formula
1-napthyl-N-methyl carbamate	Carbaryl, Sevin	$C_{10}H_7OCONHCH_3$
S-methyl-N-(methylcarbamoyl-oxy) thioacetimidate	Methomyl (Lannate®)	$CH_3C(SCH_3)NOC(O)NHCH_3$
o-isopropoxyphenyl-N-methyl carbamate	Propoxur	$CH_3NHCOOC_6H_4OCH(CH_2)_3$

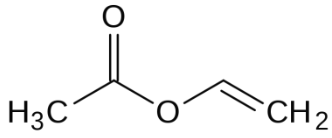
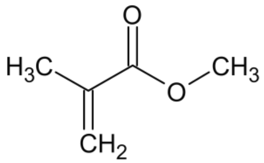
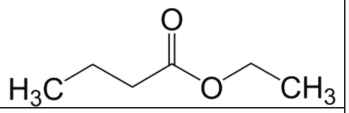
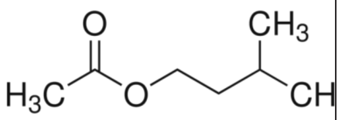
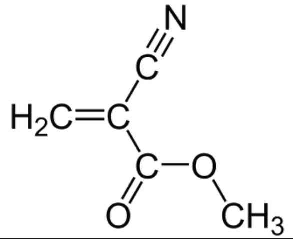
Carboxylic Acid Derivatives

There are two such derivatives that are of concern to hazmat responders: esters and amides.

Esters

Esters are organic compounds containing a carbonyl group with an attached oxygen atom that is bonded to a carbon substituent. Esters can be recognized by “RCOOR” or “CO2” in the middle of the formula. Although the ester functional group has a polar carbonyl, it contains no hydrogen atoms suitable for hydrogen bonding. Therefore esters have low boiling points relative to most molecules of similar size. Esters are known for their distinctive odors and are commonly used for food aroma and fragrances.

Examples of Esters

Functional Group	DOT Hazard Class	Condensed Formula	Structural Formula
Vinyl acetate	Flammable Liquid	$CH_3CO_2C_2H_3$	
Methyl acrylate	Flammable Liquid	$C_2H_3CO_2CH_3$	
Ethyl butyrate	Flammable Liquid	$CH_3CH_2CH_2COOCH_2CH_3$	
Isoamyl acetate	Flammable Liquid	$CH_3COOCH_2CH_2CH(CH_3)_2$	
Cyanoacrylate	none	$CH_3COOC(CH_2)CN$	

Vinyl acetate can polymerize because it has an unsaturated (pi) bond. Vinyl acetate is a flammable liquid with a flashpoint of 17°F. Methyl acrylate is a flammable liquid, flashpoint of 27°F. Methyl acrylate is also known to polymerize. They are both used to produce plastics.

The ester, ethyl butyrate, is a flammable liquid with a flashpoint of 78°F. This ester is used to make a large number of flavors and fragrance including peach, cherry, pineapple, apricot, mango, guava, plum and bubblegum.

Isoamyl acetate $CH_3COOCH_2CH_2CH(CH_3)_2$ is also known of as banana oil. Its official IUPAC name is 2-methyl-butyl acetate. Isoamyl acetate is a flammable liquid with a flashpoint of 77°F. It is only slightly soluble in water.

Cyanoacrylate $CH_3COOC(CH_2)CN$ is an ester that you are probably familiar with in the form of Superglue™. In addition to the ester functional group it has a double bond and has another functional group which we will consider later in this chapter – called the nitrile group, a carbon atom triple bonded to a nitrogen atom.

Amides

Amides contain a ketone connected to an amine. They can be recognized by $RCONR_2$ in the formula.

Acetamide CH_3CONH_2 is deliquescent (absorbs water out of the air), clear crystalline solid. The solid melts at 178°F. It is used as a plasticizer, an additive that helps keep plastics flexible and fluid.

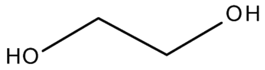
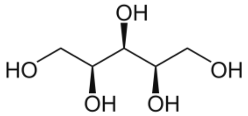
Acrylamide ($C_2H_3CONH_2$) is used in the plastics industry. It can readily polymerize due to the double bond between two carbons. It is a water soluble, white crystalline solid. It is used to make polyacrylamides which are used as thickening agents for wastewater treatment and in the manufacture of soft contact lenses. Acrylamide is a neurotoxin and possible carcinogen. Acrylamide was recently in the news after it was found to exist in starchy fried foods such as french fries.

Lysergic acid diethyl*amide*, LSD is a well-known amide known for the hallucinations it produces. Many other drugs contain the amide functional group. Penicillin and the local anesthetic lidocaine are both amides. DEET, *N*,*N*-Diethyl-*meta*-toluamide is an amide used as mosquito repellant.

Other Hydrocarbon Derivatives that contain the element Oxygen

The next set of hydrocarbon derivatives we will examine also contain only carbon, hydrogen, and oxygen, but do not contain a double bond between carbon and oxygen.

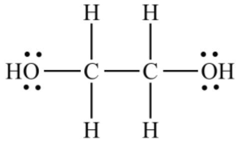
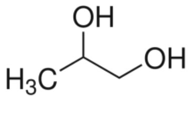
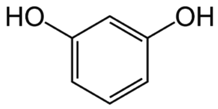
A Structural Overview of Other Hydrocarbon Derivatives that contain Oxygen

Type of Functional Group	Structural Formula	Recognize by this in the formula
Glycol		$(-OH)_2$
Polyol		$(-OH)_{3\text{or more}}$

Glycols

Glycols have two alcohol (hydroxyl) functional groups. Since the alcohol functional group is a *polar* functional group – glycols are twice as *polar* when compared to a similar size alcohol. They will be almost twice as water soluble and twice as viscous. The inter-molecular attraction between the individual molecules of a glycol compound will make it less flammable, give it a lower boiling point and lower flash point than a similar size alcohol.

Examples of Glycols

Common Name *IUPAC Name* Synonyms	DOT Hazard Class	Condensed Formula	Structural Formula
ethylene glycol *ethan-1,2-diol* ethylene alcohol MEG	n/a	$C_2H_4(OH)_2$	
propylene glycol *propane-1,2-diol* PG methyl ethyl glycol ethyl alcohol	n/a	$C_3H_6(OH)_2$	
butylene glycol *butane-1,3-diol*	n/a	$C_4H_8(OH)_2$	Not available
resorcinol *benzene-1,3-diol*	Poison	$C_6H_4(OH)_2$	

The small chain glycols are soluble in water, viscous, nonvolatile, and odorless. They are combustible liquids and may present a toxicity hazard if inhaled, absorbed through the skin or ingested.

Ethylene glycol $C_2H_4(OH)_2$, the simplest glycol, is a clear, colorless, syrupy, sweet tasting liquid. It is used primarily as an additive to lower the freezing point of water in various applications. An example is the antifreeze solution we use in our car radiators or in jet fuel deicing. Ethylene glycol is toxic. When ingested, ethylene glycol is metabolized to glycolic acid which is, in turn, oxidized to oxalic acid causing acute kidney failure. Ingestion of sufficient amounts can be fatal if untreated.

Propylene glycol $C_3H_6(OH)_2$ has one more carbon than ethylene glycol. Propylene glycol is much less toxic than ethylene glycol. It is widely used as a sweetener in cake frostings, toothpaste and as a solvent for food colors, flavors and mouthwash. Many brands of automotive antifreeze solutions have replaced the toxic ethylene glycol with propylene glycol.

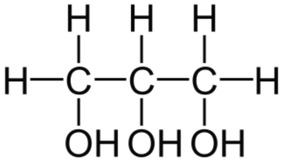
Butylene glycol is even less toxic and is widely used as a humectant (keeps foodstuffs, cigarettes, your skin – moist). Glycols are also called diols. Resorcinol is an aromatic diol. It is used as an ointment for the treatment of skin diseases, as an antiseptic and as a treatment for acne.

Polyols

When a hydrocarbon derivative has 3 or more hydroxyl groups it is called a polyalcohol or polyol. Sugars, cellulose, glycerin and inositol are polyalcohols. By convention, polyols do not refer to compounds that contain other functional groups.

Glycerol, or glycerin, has three –OH groups. It is a by-product in the manufacture of soap. Glycerin is used to make dynamite, pharmaceuticals, and cosmetics and is used as a lubricant and a softener. Glycerin is a combustible liquid with a high viscosity, low volatility and no odor. It sinks in water initially because of its high density. With three alcohol groups, glycerin is very polar and completely soluble, miscible in water.

The Polyol Glycerin

Common Name *Official Name* Synonyms	DOT Hazard Class	Condensed Structural Formula	Structural Formula
Glycerin *propane-1,2,3-triol* glycerine glycerol	n/a	$C_3H_5(OH)_3$	

Organic Acids

An organic acid is an organic compound with acidic properties. The most common organic acids are the carboxylic acids, whose acidity is associated with their carboxyl group –COOH. Sulfonic acids, containing the group –SO2OH, are relatively stronger acids. Alcohols, with –OH, can act as acids but they are usually very weak. The relative stability of the conjugate base of the acid determines its acidity. Other groups can also confer acidity, usually weakly: the thiol group –SH, the enol group, and the phenol group. In biological systems, organic compounds containing these groups are generally referred to as organic acids.

We discussed some members of the organic acid family, Carboxylic Acid Derivatives, earlier in this chapter. (They are the most common organic acids.) There are, though, a variety of other organic acids that hazmat responders will encounter.

Organic acids are organic compounds that are acidic. Organic acids are substances in which carbon and hydrogen are always present but which may also contain the elements of oxygen, nitrogen, sulfur, and phosphorus. The organic acid functional group has a carbonyl (carbon atom double bonded to an oxygen atom) with an –OH attached. Organic acids are generally named by starting with the hydrocarbon group, then adding "-ic acid" or "-oic acid." Organic Acids are just as the name implies: corrosives that can also burn. Most of the liquid organic acids have powerful distinct odors.

Odors of Organic Acids

Acid	Reported Odor
Acetic Acid (ethanoic acid) CH_3COOH	Vinegar
Propanoic Acid CH_3CH_2COOH	Pungent, swiss cheese
Butyric Acid (butanoic acid) C_3H_7COOH	Vomit, rancid butter
Valeric Acid (pentanoic acid) C_4H_9COOH	Barnyard animals, goats
Caproic Acid (hexanoic acid) $C_5H_{11}COOH$	Barnyard animals, body odor
Lactic Acid $CH_3CH(OH)COOH$	No odor

Organic acids are combustible hydrocarbons. The small straight chain organic acids exhibit a yellow flame with a blue base when burning and produce “clean” smoke. Many of the organic acids we are familiar with are combustible solids, white powders that may or may not have an odor and which will have some degree of water solubility. Tartaric acid, oxalic acid, citric acid and benzoic acid are all solid organic acids which we ingest on a regular basis as a part of our foodstuffs. Salicylic acid is a starting material for acetylsalicylic acid (aspirin). Aspirin has two functional groups in it; an organic acid group and an ester group (which we will discuss next).

Citric acid has three organic acid groups in it. It also has an alcohol group which we will discuss later in this chapter. Citric acid is considered a weak acid when compared to the inorganic acids. A 5% solution of citric acid will have a pH of about 2.

HCOOH is formic acid, also called methanoic acid. Formic acid is a low to moderately toxic but highly caustic compound. Many people are allergic to it. This is the same substance that fire ants inject when they bite and bees inject when they sting. Formic acid is used as a bactericide in livestock feed and beekeepers use it to protect the bees against tracheal mites.

Acetic acid (ethanoic acid or vinegar) is another organic acid. The formula is CH_3COOH. At concentrations >80% acid by weight, it is referred to as *glacial acetic acid* and may present as a semi-solid when it is just a little below room temperature. Household vinegar is 5% acetic acid in water. Acetic acid is a combustible liquid or semi-solid with a very pungent odor. It is corrosive to the skin and is completely miscible in water.

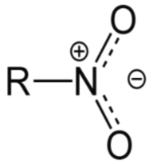
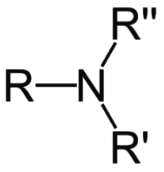
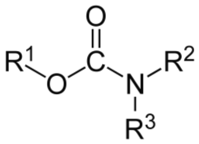
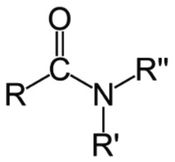
The organic acid functional group is also called the carboxyl group. The covalent bond that is between the oxygen and the hydrogen (see arrow) is a very weak bond. In water the hydrogen atom can dissociate from the compound through ionization: $CH_3COOH \rightarrow CH_3COO^- + H^+$. The dissociation of ($H^+$) gives the organic acids their acidic nature. In the example shown of acetic acid, the negative ion CH_3COO^- is called the acetate ion. It can bond with a metal and form the salt of an organic acid – in this example it would be called sodium acetate – the sodium salt of acetic acid CH_3COONa. Salt and Vinegar flavored potato chips use sodium acetate as the flavor additive. Sodium acetate is also the substance used in chemical hot packs.

Benzoic acid is an aromatic organic acid and sodium benzoate is the sodium salt of benzoic acid. Both of these compounds are used in a wide variety of soft drinks and processed foods as a bactericide/fungicide to inhibit mold growth. Sodium benzoate mixed with potassium chlorate is used in fireworks as whistle mix. Benzoic acid is a white solid which is almost insoluble in water and burns with a sooty flame.

Hydrocarbon Derivatives that contain Nitrogen

Some of these groups contain oxygen as well, but the presence of the element nitrogen changes their physical and chemical properties. One thing they all have in common is that when they burn they will produce oxides of nitrogen, such as nitrogen dioxide gas, and/or hydrogen cyanide gas as products of combustion. The table below is not a complete list of hydrocarbon derivatives that contain nitrogen. Others include the isocyanates, urethanes, ureas, azides, azos, and hydrazines.

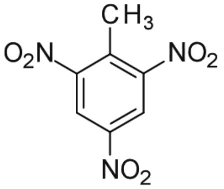
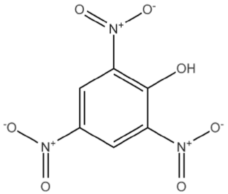
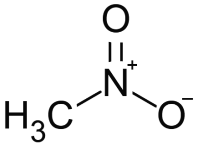
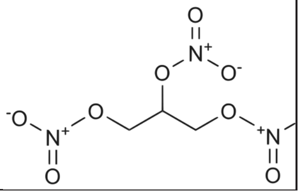
Overview of the Hydrocarbon Derivatives that contain Nitrogen

Functional Group	Structure	Recognize in a Formula by
Nitro		RNO_2
Amine		R_3N
Nitrile	$R-C\equiv N$	RCN
Carbamate		R_2NCOOR
Amide		$RCONR_2$

Nitro Compounds

Nitro compounds are known for their explosive characteristics. The formula contains a nitro group (-NO_2). Greek prefixes are used to denote the number of nitro groups.

Examples of Nitro Compounds

Name	Condensed Formula	Structural Formula
Trinitrotoluene (TNT)	$C_6H_2CH_3(NO_2)_3$	
Picric acid (2,4,6-trinitrophenol)	$C_6H_2OH(NO_2)_3$	
Nitromethane	CH_3NO_2	
Nitroglycerin	$C_3H_5(NO_3)_3$	

Trinitrotoluene (TNT) is a stable high explosive that can be melted at 176°F without explosive decomposition. It is insensitive to shock and friction making it one of the safest and most widely used military and industrial explosives. It is not even sensitive to blasting caps when cast in pure form and requires a booster explosive to detonate. It is a pale yellow, water insoluble, neutral solid. It is often mixed with other explosive compounds such as ammonium nitrate, aluminum powder and RDX.

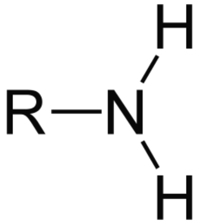
Trinitrophenol $C_6H_2OH(NO_2)_3$ (picric acid) is a bright yellow solid. Earlier in this chapter we looked at the aromatic alcohol phenol and saw how the hydrogen of the alcohol group has an acidic character. It tends to dissociate from the rest of the phenol compound, forming a hydrogen ion, an acid. Trinitrophenol has the same tendency, hence the synonym "picric acid." If a metal atom such as lead or potassium takes the place of the dissociated hydrogen atom, a picric acid salt is formed, called a picrate. Metal picrates such as copper picrate and lead picrate can be extremely shock and friction sensitive. As such, trinitrophenol is always stored in plastic containers, always measured, mixed, etc. with plastic tools and kept wetted for safe storage.

Nitromethane CH_3NO_2 is a clear highly flammable liquid that is commonly used as a racing fuel additive. It burns clean with a distinctive ghostly grey-white flame. It sinks in water and will form a layer on the bottom. It has a flashpoint of 95°F and a lower explosive limit of 7.3% by volume in air. When mixed in with ammonium nitrate it creates a powerful explosive called ANNM. This mixture was used in the Oklahoma City Bombing by Timothy McVeigh in 1995. Vapors may cause irritation to the respiratory tract. Nitromethane is a weak narcotic and exposure to higher concentrations may cause nausea, vomiting, diarrhea, and headaches.

Nitroglycerin $C_3H_5(NO_3)_3$ is an oily, yellow liquid that floats on water. It is made from glycerin the polyalcohol we looked at earlier in this chapter. It is a shock sensitive contact explosive compound that is mixed in with diatomaceous earth to make dynamite. Nitroglycerin is also called a nitrate ester. If you take a look at the structure here on the right you will see that the nitro group is bonded to an oxygen, not to a carbon. Nitroglycerin freezes at 55°F. It is used medicinally as a vasodilator to treat angina.

Most nitro compounds present either a dangerous fire risk or an explosion hazard. Many will explode when shocked or heated. They also pose a toxicity hazard when inhaled, ingested or absorbed through the skin. Nitro compounds vary in solubility. TNT is insoluble. Nitrobenzene is slightly soluble. Nitromethane sinks in water and forms a layer on the bottom. Nitroglycerine floats on water. Picric acid is soluble in water.

Amines



Amines are compounds and functional groups that contain a basic nitrogen atom with a lone pair. Amines are formally derivatives of ammonia, wherein one or more hydrogen atoms have been replaced by a substituent such as an alkyl or aryl group (these may respectively be called alkylamines and arylamines; amines in which both types of substituent are attached to one nitrogen atom may be called alkylarylamines). Important amines include amino acids, biogenic amines, trimethylamine, and aniline. Inorganic derivatives of ammonia are also called amines, such as chloramine ($NClH_2$).

The substituent -NH_2 is called an amino group

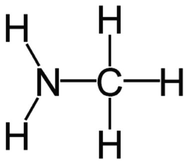
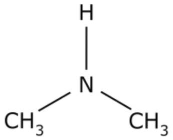
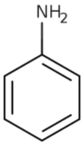
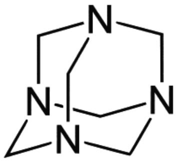
Amines are organic compounds derived from ammonia. One or more hydrogen atoms have been replaced by alkyl or aryl groups.

The word "amine" is derived from ammonia, and the class of compounds known as amines therefore are commonly named as substituted ammonias. An amine can have one, two, or three alkyl (or aryl) substituents bonded to the nitrogen atom.

Amines are organic derivatives of ammonia. Amines are the organic bases. The amine functional group is a polar functional group and is the reason many amines dissolve in water and raise the pH. The formula may contain RNH2, R2NH, or R3N.

An organic compound with multiple amino groups is called a diamine, triamine, tetraamine and so forth. Compounds formally derived from ammonia by replacing one, two or three hydrogen atoms by hydrocarbyl groups. Amines are named in several ways. Typically, the compound is given the prefix "amino" or the suffix: "amine".The simple small chain amines are typically called by common names wherein the carbon groups are named first, followed by the suffix "amine" as in dimethylethylamine.

Examples of Amines

Common Name *IUPAC Name* Synonyms	DOT Hazard Class	Condensed Formula	Structure
methylamine *aminomethane* monomethylamine MMA	Flammable Gas	CH_3NH_2	
dimethylamine *methylaminomethane* N-methylmethanamine DMA	Flammable Gas	$(CH_3)_2NH_2$	
aniline *aminobenzene* phenylamine	Poison	$C_6H_5NH_2$	
hexamine hexamethylenetetramine		$C_6H_{12}N_4$	

Methylamine, dimethylamine and trimethylamine are heavier than air, water soluble, flammable, fishy smelling corrosive gases. They are often shipped as solutions in water. They are used to synthesize other larger organic compounds that contain nitrogen such as carbamates and amides.

Many amines have distinctive odors, often fishy or putrid. They are gases at room temperature or are easily vaporized liquids.

Chronic exposure to amines may cause kidney or liver damage, while an acute exposure could cause a caustic burn. Fortunately, the foul odor (such as ammonia, rotten flesh, or fish oil) gives amines adequate warning properties to minimize the chances of overexposure. Cadaverine, $NH_2(CH_2)_5NH_2$, is a poisonous, viscous liquid found in rotting flesh. It has two amine groups and is partly responsible for the odor of urine and bad breath.

Amines exhibit a yellow flame when burning. Combustion products could include nitrogen oxides and hydrogen cyanide gases. Amines are soluble in water.

One example of an amine is phenylamine or aniline C6H5NH2. It's an aromatic amine. (Aromatic amines have the nitrogen atom connected to an aromatic ring.) It is mainly used for the production of a precursor to rigid polyurethane plastics. It is combustible, and very toxic via inhalation, ingestion and absorption through the skin. Aniline is an oily yellow brown viscous liquid. Aniline poisoning produces a cyanotic, blue skin appearance.

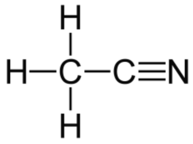
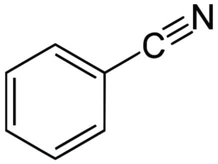
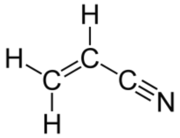
Nitriles (Organic Cyanide)

$$R-C\equiv N$$

Nitriles are organic compounds containing a cyanide functional group —CN bound to an alkyl group. The nitrile group consists of a carbon triple bonded to a nitrogen to form a cyanide group (-CN). The nitriles are also called organo-cyanides. In general, nitriles are named with by adding the suffix nitrile to the alkane chain. Substituents are named using numbers related to the carbon chain. For example, a five-carbon chain that has a nitrile group would be pentane nitrile. Nitriles are colorless solids or liquids with distinctive odors.

Nitriles are found in many useful compounds, including methyl cyanoacrylate, used in super glue. A nitrile rubber (a nitrile-containing polymer) is used in laboratory and medical gloves to prevent adverse effects of latex allergies. Nitrile rubber is also widely used as automotive and other seals since it is resistant to fuels and oils. In addition, the nitrile functional group is found in over 30 pharmaceuticals including Anastrozole a medication used to treat breast cancer.

Examples of Nitriles

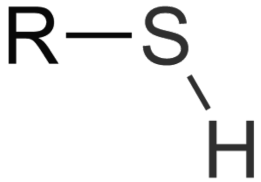
Common Name *IUPAC Name* Synonyms	DOT Hazard Class	Condensed Formula	Structural Formula
acetonitrile *acetonitrile* methyl cyanide cyanomethane ethyl nitrile	Flammable Liquid	CH_3CN	
benzonitrile *benzonitrile* cyanobenzene phenylcyanide	Poison	C_6H_5CN	
acrylonitrile *2-propenenitrile* vinyl cyanide cyanoethane cyanoethylene	Flammable Liquid	CH_2CHCN	

Acetonitrile is also used as a solvent. It is a clear, flammable polar solvent that is miscible with water. Several industrial fatalities have occurred as a result of acute overexposure to acetonitrile. The toxicity of acetonitrile derives from the fact that it is metabolized to hydrogen cyanide by the body and, as such, the symptoms of exposure are similar to cyanide poisoning. The treatment for acetonitrile poisoning is similar to that for hydrogen cyanide poisoning using the same cyanide antidotes such as sodium thiosulfate. Nitriles can be identified in the field by burning a small amount and looking for hydrogen cyanide gas in the products of combustion. When acetonitrile burns the flame has a yellow tip with a distinct pink-purple base.

Benzonitrile $C_6H_5CN$is used as a chemical intermediate and solvent in the pharmaceutical and dyestuffs industries. It is very toxic and burns with an orange sooty flame. Skin exposure to benzonitrile can cause extensive reddening and blister formation. Symptoms of acute exposure are fatigue, excessive sweating, thirst, anxiety, tachycardia, & hyperventilation. It has a sweet almond odor similar to benzaldehyde (almond extract).

Acrylonitrile CH_2CHCN is a common monomer used in the production of acrylic plastics and acrylic fibers used in clothing and carpets. It consists of a vinyl group linked to a nitrile. It can undergo explosive runaway polymerization and has caused numerous industrial scale accidents. Acrylonitrile has been used as a fumigant for food processing equipment, flour milling and for stored tobacco.

Hydrocarbon Derivatives Containing Sulfur, Phosphorus or a Halogen

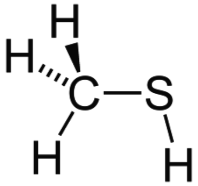
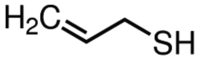
Thiols and Thiol Ethers	

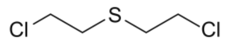
Thiols contain an -SH group, similar in structure to the alcohols that contained an –OH group. Many thiols are characterized by strong and repulsive “skunk-like” odors. Skunk spray contains the thiol “crotyl mercaptan”. Thiols are used as warning agents in fuel gas lines and other chemical intermediates. Thiols are also often called “mercaptans.” The term “mercaptan” literally means “mercury seizing.” Sulfur has an affinity for mercury and binds to it, and as such thiols form insoluble compounds with mercury. A thiol is a compound that is highly reactive with mercury. When mercury is present it creates a very strong chemical bond to the thiol group. Thiols are used in mercury remediation.

Methanethiol is a colorless, flammable gas with a moderate solubility in water. It is a product of the digestion/metabolism of asparagus and is responsible for the odor urine emits after eating asparagus. In high concentrations it is a neurotoxin.

There are many organosulfur compounds in garlic extract that have shown anticancer properties. Allyl mercaptan is one of them. It is a clear, insoluble flammable liquid with a flashpoint of 64.4°F.

Examples of Thiols and Thiol Ethers

Common Name *IUPAC Name* Synonyms	DOT Hazard Class	Condensed Formula	Structural Formula
methyl mercaptan *methanethiol*	Flammable gas	CH_3SH	
allyl mercaptan 1-propenethiol	Flammable liquid	CH_2CHCH_2SH	

mustard agent *dichlorodiethyl sulfide* sulfur mustard	Toxic	$C_4H_8Cl_2S$	

Thiol ethers are also called sulfides. In this case they are organic sulfides.

A thiol ether, organic sulfide that has some notoriety is the chemical warfare agent - mustard agent. It is not a gas but an oily liquid that sinks in water.

Alkyl Halides

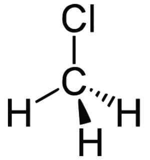
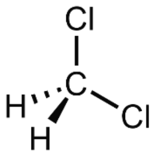
Alkyl halides are halogenated organics or halogenated hydrocarbons. They are also called haloalkanes or halogenoalkanes. An alkyl halide or haloalkane is a compound that has one or more halogen atoms bonded to asaturated carbon.

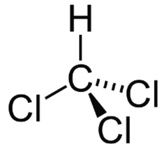
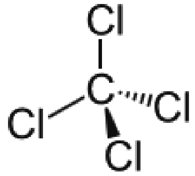
They are derived from alkanes and contain one or more halogens (fluorine, chlorine, bromine, or iodine). There are not many structures with iodine in them, but they are nevertheless included in this group.

When naming of haloalkanes the halogen is a prefix to the alkane. For example, ethane with bromine becomes bromoethane, methane with four chlorine groups becomes tetrachloromethane. Many of these compounds have already an established trivial name, which is endorsed by the IUPAC nomenclature, for example chloroform (trichloromethane) and methylene chloride (dichloromethane).

The flammability of alkyl halides shows wide variation. Some of the alkyl halides are flammable, but many do not burn. In fact, some make very effective extinguishing agents. The Halon extinguishing agents are all halogenated hydrocarbons (alkyl halides). The primary hazard of the alkyl halides is that they are toxic. Alkyl halides are insoluble in water. They are sinkers.

Examples of Alkyl Halides

Common Name *IUPAC Name* Synonyms	DOT Hazard Class	Condensed Formula	Structural Formula
methyl chloride *chloromethane* R 40 Freon	Flammable gas	CH_3Cl	
methylene chloride *dicloromethane* R 30 Freon	Toxic Substance	CH_2Cl_2	

chloroform *trichloromethane* R 40 Freon	Toxic Substance	$CHCl_3$	
carbon tetrachloride *tetrachloromethane* Freon 10 Halon 1040	Toxic Substance	CCl_4	

Methyl chloride CH_3Cl is a flammable gas that was once used as a refrigerant gas; it is now used as a chemical intermediate in organic synthesis. Dichloromethane (methylene chloride) CH_2Cl_2 is a common solvent you will find on the shelves at hardware stores as a paint stripper/thinner. It is also used as a degreaser and as an extraction solvent to decaffeinate coffee. Chloroform $CHCl_3$ was once used for general anesthesia. Inhalation of chloroform vapors depresses the central nervous system. Chloroform is now used as a solvent in the production of dyes, pharmaceuticals and pesticides. Carbon Tetrachloride is the last member of the chloromethane group of halogenated hydrocarbons. It was once used as a dry cleaning solvent, a pesticide and a fire extinguishing agent. When it is subjected to high heat it can produce phosgene $COCl_2$ as a product of combustion and, as such, its use as an extinguishing agent was stopped. It is a hepatotoxin.

Vinyl chloride C_2H_3Cl is a monomer used to produce PVC polyvinyl chloride plastics. It has a double bond. Vinyl chloride (VCM) is a flammable gas with a flammable range of 3.6-33%. The double bond can undergo slow oxidation and upon contact with air VCM can form peroxides which could then initiate exothermic polymerization. It is extremely toxic and is a known carcinogen which causes angiosarcoma of the liver. It even has a disease named after it, “vinyl chloride disease” which refers to necrosis and gangrene of the finger tips.

Alkyl halides were once very common finding many uses in our homes and in industry. Most of them have been phased out due to environmental or health concerns. Tetraflouroethane $C_2H_2F_4$ finds use as a propellant in aerosol cans. Perchlorethylene (tetrachloroethane) $C_2H_2Cl_4$ is a dry cleaning solvent. TCE trichloroethylene C_2HCl_3 has been used as a degreaser and an anesthetic. DDT was once a widely used chlorinated pesticide. Methyl bromide CH_3Br is a nonflammable gas used as a fumigant to keep pests away from tomatoes, strawberries and wood products.

The isomers 1,1-dichloroethane and 1,2-dichloroethane differ by the placement of one chlorine atom. The effect this has on their chemical properties is dramatic. 1,1-dichloroethane is used as a Halon fire extinguishing agent and 1,2-dichloroethane is a highly flammable solvent with a flashpoint of 55.4°F.

Organophosphates

An organophosphate is an organic compound that contains phosphorus double bonded either to sulfur or an oxygen atom in the structure. They are derivatives of phosphoric acid H_3PO_4, and they are often called phosphoric acid esters. They are relatively large organic compounds with high molecular weights. Organophosphates are used as low-cost insecticides and can be highly toxic.

Malathion is a yellowish liquid with a slight solubility in water. It is an insecticide that attacks the insect's nervous system.

Examples of Organophosphates

Name	Common name	Condensed Formula
O,O,diethyl p-nitrophenyl thiophosphate	Parathion	$C_{10}H_{14}NO_5PS$
[(Dimethoxyphosphinothioyl)thio] butanedioic acid diethylester	Malathion	$C_{10}H_{19}O_6PS_2$
Chlorpyrifos	Dursban	$C_9H_{11}O_3PS$

The Chemical Warfare Agents – sarin, soman, tabun and VX are all organophosphates. They create SLUDGEM symptoms (mnemonic for symptoms of nerve agent poisoning- Salivation, Lacrimation, Urination, Defecation, Gastrointestinal upset, Emesis, Miosis). They are acetylcholinesterase inhibitors and are toxic at extremely low doses as they attack the nervous system. One organophosphate that has been used as a chemical weapon in a terrorist incident is Sarin. It is a clear liquid which is miscible in water. It is about eight times less volatile than water and so it evaporates slowly.

Summary

A hydrocarbon compound in which another non-metal, other than hydrogen, or group of non-metals such as oxygen, nitrogen, sulfur, phosphorous, chlorine or fluorine is bonded to this backbone, to the carbon skeleton is called a *hydrocarbon derivative*. These groupings of other elements, such as the Nitro group, are called *functional groups.* Functional groups affect the physical and chemical behavior of the hydrocarbons they are attached to.

We presented about a dozen different functional groups in this chapter. To some extent, they all change the physical and chemical properties of the hydrocarbon skeleton they are bonded to. There is no rule that says there cannot be more than one functional group in a compound. A carbon skeleton can have several different functional groups attached to it; all of them affect the physical and chemical properties of the resultant compound in some way.

A large percentage of the hazardous materials that responders encounter are hydrocarbon derivatives. These hydrocarbon derivatives are categorized by their structure and composition. Understanding these various categories can assist response personnel in predicting the behavior and hazards of the chemicals they encounter.

Chapter Review

1. The formula of an aldehyde always appears with ___________ on the end.
   - A. OH
   - B. NO2
   - C. CHO
   - D. CH

2. What do the hydrocarbon derivatives Amine, Carbamate and Nitro have in common?
   - A. They are saturated.
   - B. Each contains pi bonds.
   - C. All contain sulfur.
   - D. They all contain nitrogen.

3. Which hydrocarbon derivatives have an –OH group that has replaced a hydrogen atom?
   - A. Ketones
   - B. Alcohols
   - C. Amines
   - D. Peroxides

4. Which hydrocarbon derivatives contain an -SH group?
   - A. Epoxides
   - B. Esters
   - C. Amines
   - D. Thiols

5. Organic compounds that consist of carbon and at least one other element that is not hydrogen are called ___________________________.
   - A. Hydrocarbon Derivatives
   - B. Isomeric Branches
   - C. Organic Peroxides
   - D. Heterogeneous Mixtures

6. Complete the following table to indicate the general hazard(s) of a given hydrocarbon derivative.

Substance	Flammable	Toxic	Reactive
Glycols			
Alkyl halides			
Ethers			
Aldehydes			
Nitro Compounds			
Organic acids			
Carbamates			

7. Identify the hydrocarbon derivative and/or substance that matches the description listed below.

Description	Derivative/Substance
Strong and repulsive odor.	
Extremely flammable, burns very clean and is a suspected carcinogen.	
Extremely flammable, water soluble, reactive gas.	
Extremely toxic and a known carcinogen.	
Shock and friction sensitive.	
Extremely unstable.	
Combustible liquid or semi-solid with a very pungent odor.	

Chapter 7: Physical and Chemical Properties of Hazardous Materials

There are four questions that responders need to ask in the initial stages of a hazmat incident about the material(s) involved. They are:

- What will this material do?
- Will it do something bad *right now*?
- How can it hurt me?
- How can I protect myself?

The physical and chemical properties of the materials will largely answer each of these questions. In this chapter we will focus on the first two questions.

The properties help us predict how the material will behave and recognize the hazards it presents. It's essential for hazmat Technicians to understand what these terms mean and what information they give us. In addition, we need to keep in mind that physical and chemical properties are often related to each other. Many of these properties are directly or inversely proportional to one another. Understanding what these terms mean and how they are related will make it possible to quickly assess the hazards we face.

Physical Properties

Physical properties of matter are those characteristics that do not involve a change in chemical identity. Physical properties can be observed or measured without changing the composition of matter. They are used to observe and describe matter. (See Appendix A for a complete list of physical properties and their definitions.)

Chemical Properties

Chemical properties describe a characteristic or behavior of a substance that may be observed when it undergoes a chemical change or reaction that changes the chemical composition or identity. They are properties that are seen either during or following a reaction. (See Appendix B for a complete list of chemical properties and their definitions.)

Chemical Terms

There are a variety of chemical terms that are related to the chemical and physical properties of a given substance. These terms can help to assess the risk involved in a release. (See Appendix C for a complete list of chemical terms and their definitions.)

What will this material do?

How a material will behave affects a variety of aspects of hazmat response. The behavior of a given material determines what DOT hazard class it belongs to, what protective equipment responders need and what tactics responders can use to mitigate an incident. The following properties will help you to evaluate how a material will behave when released: boiling point, flammable range, flash point, freezing/melting point, solubility, specific gravity, vapor density and vapor pressure.

Boiling Point

Boiling point is the temperature at which the vapor pressure of the liquid equals atmospheric pressure. The boiling point of water is 212°F (at sea level). Gasoline reaches its boiling point much sooner: 100°F.

Liquids may give off vapors from the surface of the liquid at any temperature (called "evaporation"). When heat is added the volume of vapor given off will increase. When the temperature of the liquid reaches the boiling point for that liquid the vapor pressure of the liquid becomes sufficient to overcome atmospheric pressure. Bubbles of vapor will form inside the liquid and rise to the surface. At this point the liquid changes from its liquid state to its vapor state.

Boiling point is determined by several chemical factors: polarity, molecular weight and branching of isomers. For example, highly polar materials have high boiling points, while smaller compounds and those that are branched have lower boiling points. The table below shows the relationship between molecular size and boiling point.

The Effects of Molecule Size on Boiling Point

Name	**Formula**	**Boiling Point (^{o}F)**
Methane	CH_4	-260
Ethane	C_2H_6	-128
Propane	C_3H_8	-44
Butane	C_4H_{10}	32
n-Pentane	C_5H_{12}	97
n-Hexane	C_6H_{14}	156
n-Heptane	C_7H_{16}	208
n-Octane	C_8H_{18}	259
n-Nonane	C_9H_{20}	304
n-Decane	$C_{10}H_{22}$	345

Flammable Properties

Most fatalities in hazmat incidents are caused by fire and explosion. There are several properties that will help responders evaluate the risk of flammability from a hazardous material. They include flash point, flammable range and ignition temperature.

Flash Point and Fire Point

Flash point is the minimum temperature at which a liquid produces enough vapor to form an ignitable mixture in air near the surface of the liquid. It is related to boiling point. A material with a lower boiling point will produce more vapors than a material with a higher boiling point. In general, a low flash point would indicate a higher flammability hazard.

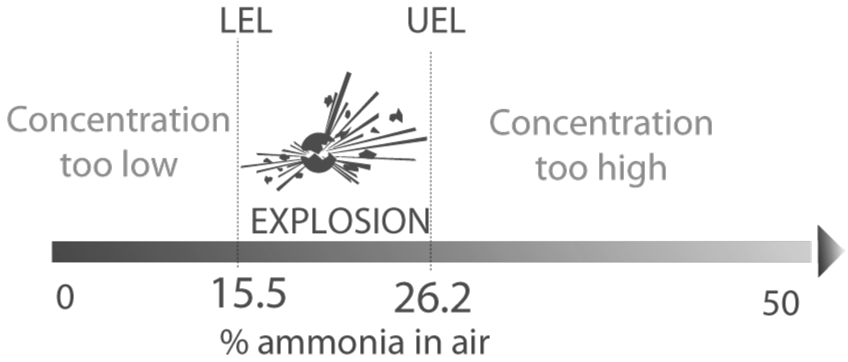
Fire point is a similar concept. It is the temperature at which enough vapors are now given off to support *continuous* burning. It is generally just a little above the flash point. (Note: the term "fire point" is not used as commonly as flash point.)

Flash point and fire point specifically apply to the liquids. US DOT uses flash point to determine if a material is flammable or combustible. DOT classifies a liquid with a flash point of not more than 60 °C (140 °F) as flammable. A liquid with a flash point above 60 °C (140 °F) and below 93 °C (200 °F) is classified as combustible. (§173.120)

Flammable Range

Flammable range (sometimes called explosive range or flammable limits) is the concentration range in which a flammable substance can produce a fire or explosion when an ignition source (e.g. spark or open flame) is present. The concentration is generally expressed as percent of vapor in air. Below the lower explosive limit (LEL), the vapors are too "lean" to burn, whereas above the upper explosive limit (UEL), the vapors are too "rich" to burn. (Figure 10.3) Three functional groups have wide flammable ranges: alcohols, ethers, and aldehydes. Most hydrocarbons have fairly narrow flammable ranges.

Figure 10.1: Flammable Range



Ignition Temperature

Ignition temperature is the temperature required to ignite the flammable vapors. Other terms that are often used are pilot ignition and autoignition. Pilot ignition specifically requires an outside ignition source, whereas with autoignition, the liquid is heated to a point where it's hot enough to ignite the vapors without an outside ignition source. Liquids with higher molecular weights have lower ignition temperatures.

Gasoline vapors, for example, have an ignition temperature of 536°F (depending upon the grade). The vapors can be ignited by a pilot source such as a match or a spark. However, the boiling temperature of gasoline is only about 100°F. It will evaporate rather than ignite when the temperature of the liquid is raised above its boiling point.

Relationships Between Various Physical and Chemical Properties

Many physical and chemical properties are directly or inversely proportional to one another. Understanding this concept will make it easier for response personnel to predict the behavior and hazards of the chemicals they encounter. The table below shows the effect of molecular size on physical and chemical properties.

Effect of Molecule Size on Physical and Chemical Properties

Property	Smaller Compounds (Low Molecular Weight)	Larger Compounds (High Molecular Weight)
Boiling point	Lower	Higher
Flash point	Lower	Higher
Heat output	Lower	Higher
Ignition temperature	Higher	Lower
Vapor content	Higher	Lower
Vapor pressure	Higher	Lower

Pentane (C_5H_{12}) and decane ($C_{10}H_{22}$) illustrate these relationships. Molecules are particles that are in constant motion, though the motion at the molecular level is so small that we cannot see it. The smaller the molecules, the faster they move. The larger they are, the slower they move.

The molecules of pentane move faster than those of decane because they are smaller. This translates into a higher vapor pressure as these molecules in motion exert more force on the sides of the container and more effort to break the surface of the liquid. The boiling point of pentane is lower than that of decane because it takes less heat to reach the point at which vapor pressure equals atmospheric pressure. Because pentane is producing vapor at a faster rate, there is more vapor residing above the surface of the liquid. In other words, the vapor content is higher. A smaller molecule also has less surface area than a larger molecule. Less surface area means that there is less attraction between the molecules, and thus a faster evaporation rate.

Smaller molecules produce *more* vapor therefore, the flash point is *lower*. It takes *less* heat to raise the temperature of the liquid to the point where it produces sufficient vapor to form an ignitable mixture in air. However, it takes *more* heat energy to actually ignite those vapors because they contain less hydrogen (fuel) than the vapors produced by a larger molecule.

Larger molecules, by comparison, produce *less* vapor. The flash point is *higher*; it takes *more heat* to raise the temperature of the liquid to the point where it produces sufficient vapor to form an ignitable mixture in air. However, when the ignitable mixture is produced, the vapors are closer to their ignition temperature. It takes *less heat energy* to cause ignition. The flash point and ignition temperature are closer together in relationship to one another. Because these larger molecules contain more hydrogen (fuel) they also have a *higher heat output* than smaller molecules.

Table 10.3 also illustrates the relationship between flash point and ignition temperature. Once again, the flash point is determined by the size of the molecule. Ignition temperature, on the other hand, is heavily influenced by the hydrogen content. The more hydrogen content, the lower the ignition temperature.

Many common petroleum products, such as gasoline, are mixtures. Mixtures do not have specific molecular weights, and thus don't have specific vapor pressures, flash points, or flammable limits. The values published for these mixtures merely approximate these parameters and therefore may show some variability.

Comparing Flash Point and Ignition Temperature

	Methane - CH_4	**Pentane - C_5H_{12}**	**Decane - $C_{10}H_{22}$**
Molecule Size	Smaller	Medium	Larger
Vapor Pressure	150 psi	8 psi	0.2 psi
Flash Point	NA (gas)	-40°F	+115°F
Hydrogen Content	4	12	22
Ignition Temperature	1200°F	588°F	410°F

Since molecular size is related to physical state it's also possible to predict the relative amount of vapor production based on physical state. This chapter has focused primarily on liquids. But solids have ignition temperatures too. For example, the vapors of paraffin wax, another hydrocarbon compound, will burn when heated sufficiently. Solids produce less vapors than liquids do because they're larger molecules. Of course, the smallest molecules are already gases; they have the highest degree of vapor production.

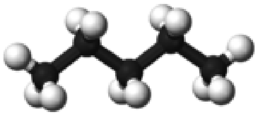
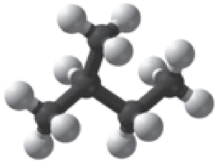
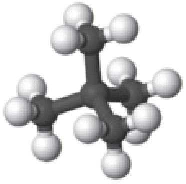
Polarity is also an important factor in determining the fire hazard. Compounds with OH^- in them are similar in structure to water (HOH). They are polar compounds. Polar compounds (e.g., alcohols) always have a higher boiling point and flash point than nonpolar compounds (e.g., hydrocarbons) of similar molecular weight.

The Effects of Isomers Upon Boiling Point and Flash Point

Long, flat isomers have large surface areas; they resemble the shape of a board. These molecules are mutually attracted. It therefore requires *more* energy to separate the molecules in order to vaporize the fluid. Because these molecules are more strongly attracted to one another and it takes more energy to separate them, the boiling point and flash point of the chemical are both higher.

Branched molecules have less surface area; they resemble the shape of a ball. These molecules have less attraction to one another. It therefore requires *less* energy to separate the molecules in order to vaporize the fluid. Because these molecules have less attraction to one another and it takes less energy to separate them, the boiling point and flash point of the chemical are both lower for branched molecules.

Figure 10.2: The Effects of Isomers on Boiling Point and Flash Point

Common name	*n*-pentane	isopentane	neopentane
Molecular form			
Boiling point (°C)	36.0	27.7	9.5

Other Properties Affecting Behavior

Freezing/Melting Point

Freezing point is the temperature at which a liquid changes to the solid state at normal atmospheric pressure. (Some sources may refer to this as the crystallization point.) Alternatively, a melting point is the temperature at which a solid becomes a liquid at normal atmospheric pressure. (Some sources may refer to this as the liquefaction point. The freezing point of a substance is usually, but not necessarily, the same as its melting point.)

Specific Gravity

Specific gravity is the ratio of the weight of a substance to the weight of an equal volume of fresh water. Water weighs approximately 8.35 pounds per gallon. The specific gravity of water is 1 ($8.35 \div 8.35 = 1$). In general, substances with a specific gravity less than 1 will float in water while substances with a specific gravity greater than 1 will sink in water.

The specific gravity of a substance will partially determine whether it floats, sinks, or suspends in water. A substance that has a lower specific gravity than water (less than 1) will initially rise to the top in water. Gasoline, for example has a specific gravity of 0.7. Gasoline is non-polar so it will not dissolve and will form a layer (will float) on top of the water. Methyl ethyl ketone (MEK) has a specific gravity of 0.81. It will initially rise to the top. It has a water solubility of 25%. Below this concentration it will dissolve, above this concentration two phases will exist and the MEK will appear to float on water even though some of it has dissolved.

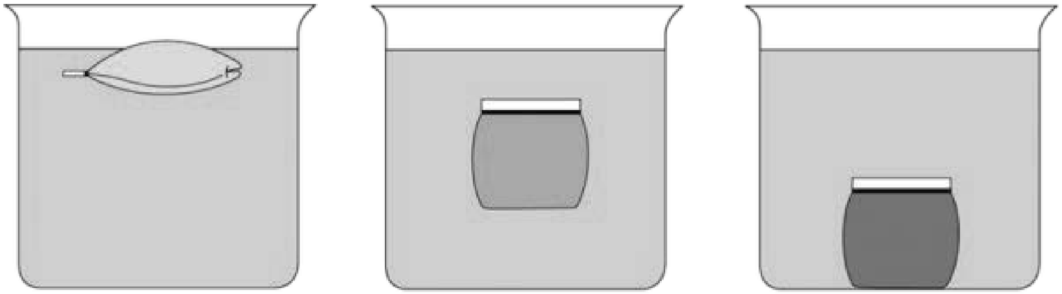
A substance that has a higher specific gravity than water (greater than 1) will initially sink in water. For example, trichloroethane (TCA) has a specific gravity of 1.4. Trichloroethane is non-polar so it will not dissolve and will form a layer underneath the water. Glycerin has a specific gravity of 1.3 and will also sink in water. Glycerin is very polar and so it will, with some mixing, dissolve completely in water. Without the mixing the glycerin would sit for a very long time on the bottom of the water, very slowly dissolving.

Insoluble, finely ground, non-polar solids will form a *suspension* in water. Insoluble, non-polar liquids can also form a suspension is water when they are mixed (agitated). When *immiscible* hydrocarbons with a specific gravity very close to 1, are mixed (agitated) in water, the suspension they form is called an *emulsion*. Emulsions in water often appear milky white. Many pesticides are mixed with a carrier solvent which is a very light petroleum hydrocarbon. These light petroleum hydrocarbons form milky white emulsions when mixed with water. Eventually, if allowed to settle the two liquids will separate.

Specific gravity is used as a means of testing the concentration of corrosive solutions. The more concentrated the solution, the heavier it is. By comparing the weight of a solution with water, it’s possible to indirectly determine the concentration of the solution. The common lead-acid battery tester uses this principle; a charged battery contains a concentration of sulfuric acid (H_2SO_4) of ~ 35%. Concentrated sulfuric acid is 98%, so if the battery tester shows a full charge you would know you had at least 35%. In a fully discharged car battery the acid concentration is probably less than 5%. This device can easily be used for field spills of H_2SO_4.

To understand how a substance will behave in water, several physical properties: polarity, solubility, concentration, degree of mixing, specific gravity and water reactivity must be taken into account.

Illustration of Specific Gravity



Less Than 1 Specific Gravity: 1 Greater Than 1

Vapor Density

When either a hazardous gas or the vapor of a hazardous liquid is released, we need to determine where that gas or vapor is located. This is significant because the location of the gas or vapor has a lot to do with its hazards. Heavy gases, for example, are usually the most dangerous because they stay low to the ground where both people and, in the case of flammable gases/vapors, where ignition sources are most often located.

Gases may rise, sink, or be neutrally buoyant, depending on their vapor densities. *Vapor density* is the weight of the vapor as compared to an equal volume of air. The vapor density of air has a value of 1. Gases with a low vapor density (less than 1) are *lighter* than air and will usually rise, whereas gases with a high vapor density (greater than 1) are *heavier* than air and will usually sink. Gases with vapor densities near 1 will float in air.

Vapor density is determined by dividing the molecular weight of the gas by 29 - the average "molecular weight" for air. If we took 100 pieces of air – roughly 79 of them would be nitrogen molecules each weighing 28amu and 21 of them would be oxygen molecules each weighing 32amu. The average weight of air them is (79 x 28) + (21 x 32) ÷ 100 = 29.

All vapors of hydrocarbon flammable liquids are heavier than air. Gasoline, for example, has a vapor density of 3.9. Anytime we encounter a flammable liquid spill we should expect that the vapors will be close to the ground and that they may accumulate in low-lying areas. Most *gases* are also heavier than air, with the exception of gases sometimes identified by the acronym HA HA MINCE.

Lighter than Air Gases (HA HA MINCE Gases)

H	**H**elium (He)
A	**A**cetylene (C_2H_2)
H	**H**ydrogen (H_2)
A	**A**mmonia (NH_3)
M	**M**ethane (CH_4)
I	**I**lluminating gas (Ne)
N	**N**atural gas (mixture, ~85% CH_4)
C	**C**arbon monoxide (CO)
E	**E**thylene (C_2H_4)

Vapor Pressure/Volatility

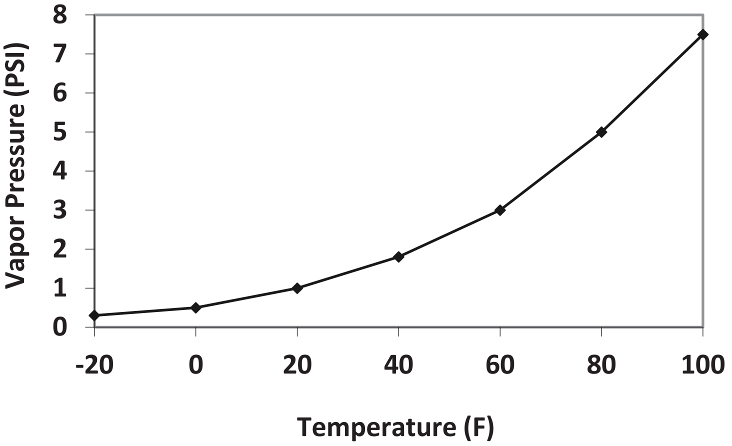
Vaporization is the tendency of molecules to escape from the surface of a liquid. Therefore, vapor pressure is the pressure exerted by a material against the walls of a container or the atmosphere. Volatility is the tendency of a solid or liquid material to pass into the vapor state at a given temperature.

Vapor pressure and volatility are related to boiling point. The higher the boiling point, the lower the vapor pressure and volatility. Boiling point, vapor pressure and volatility are related, in part, to molecular size; large, heavy compounds have low vapor pressures.

Vapor pressure is what's called a "temperature-dependent variable" which means it varies with ambient temperature. As the temperature of the material increases the vapor pressure increases. This can have a significant impact on a response. It's not unusual for the vapor pressure of a substance to double from nighttime to daytime. This means the pressure in a cylinder containing that substance will double and the amount of vapor given off from a pool of the substance will double.

The graph below shows how the vapor pressure of acetone increases as the temperature of the product increases.

Vapor Pressure of Acetone



Vapor pressure can be expressed in a variety of ways. The most common units of measure for pressure are:

Units of Measure for Pressure

Unit of Measure	Abbreviation
Pounds per square inch	PSI
Millimeters of Mercury	mmHg
torr	Torr
Pascal	Pa
millibars	mbar
Atmosphere	ATM
Inches of Mercury	inHg

These units are all measuring the same thing – air pressure. Various hazmat reference sources will use one or more of these units. The units of measure that they use will vary. In general, 15 psi = 1ATM = 760 mmHg = 30 inHg = 1 bar (at sea level).

Solubility

Solubility is the maximum quantity of a substance (called the solute) that may be dissolved in another (called the solvent). It can be thought of as the ability of a substance to mix with water. It is measured in terms of the maximum amount of solute dissolved in a solvent at equilibrium, commonly expressed as a concentration (grams of solute per liter of solvent). In hazmat reference material this is typically expressed as a per cent of volume.

Knowing the solubility of a substance can help you decide on mitigation and/or decontamination strategies. For example, the solubility of anhydrous ammonia is approximately 34% and the solubility of chlorine is 0.7%. If you sprayed water on an ammonia leak the gas will easily dissolve in the water and you can prevent the gas from moving downwind. This tactic would not be as effective on a chlorine release since chlorine gas is much less soluble in water.

The solubility of a substance depends on the physical and chemical properties of the solute and solvent as well as on temperature, pressure and the pH of the solution. The extent of the solubility of a substance in a specific solvent is measured as the saturation capacity. That is the maximum concentration of solute(s) that a solvent can contain under specified conditions. At that point, adding more solute does not increase the concentration of the solution. The solvent will begin to precipitate the excess amount of solute. For example, if you add sugar to a glass of iced tea the sugar will dissolve in the tea. Once the tea is saturated with sugar if you add more sugar it won't dissolve and will fall to the bottom of the glass.

Solubility and Polarity

Water solubility is directly determined by the polarity of a substance. Polar compounds, such as low molecular weight alcohols are water-soluble, while non-polar compounds, for example, xylene, are insoluble. Water is a polar solvent and since like-dissolves-like; polar substances are water-soluble. Polar solvents will dissolve other polar solvents (e.g., alcohol and water). A molecule is polar if it has polar covalent bonds and/or non-bonding pairs of negatively charged electrons positioned in its structure so that they act like the poles of a magnet. Polar covalent bonds are covalent bonds where the electrons between the atoms are not shared equally.

Nitrogen and oxygen atoms are highly electronegative; they attract electrons and hold them tightly. They do not share electrons equally with less electronegative atoms. When a nitrogen or oxygen atom is bonded to a hydrogen atom, the more electronegative atom will display a negative pole. This occurs because the negatively charged electrons are pulled closer to it. In this instance, the hydrogen atom would become the positive pole. Some of the functional groups we learned about that contain nitrogen or oxygen are polar. The presence of one of these polar functional groups on a hydrocarbon skeleton introduces a polar site on the molecule. We can divide the functional groups into three categories of polarity: super polar, polar, and nonpolar.

The Three Categories of Polarity

Super Polar		**Polar**		**Nonpolar**	
Alcohols	R-OH	Ketones	R-CO-R	Alkyl halides	R-X
Glycols	R-(OH)_2	Aldehydes	R-CHO	Ethers	R-O-R
Glycerols	R-(OH)_3	Organic acids	R-COOH	Organic peroxides	R-O-O-R
Organic acids	R-COOH	Esters	R-COO-R	Hydrocarbons	C_xH_y
		Amines	R-NH_2	Nitros	R-NO_2

Polar solvents have sites that can be characterized as having positive and negative poles. These poles are attracted to the negative and positive poles of the other nearby polar molecules in the sample. This creates a "network effect" where all of the molecules within the liquid are electrically attracted to all other molecules. It therefore requires more energy to break this network, to separate the molecules, and to vaporize the fluid. Consequently, polar solvents have lower vapor pressures, higher boiling points, and higher flash points when compared to similar sized nonpolar molecules. Compare water (H_2O) with a boiling point of 100°C and methane (CH_4) with a boiling point of -100°C.

Many Ionic compounds are water-soluble solids. The Metal Oxides are an exception. Most of them, excepting the alkali and alkali earth metal oxides are insoluble.

The Effect of Polarity on Physical and Chemical Properties

Property	**Saturated & Unsaturated Hydrocarbons (Nonpolar Compounds)**	**Alcohols (Polar Compounds)**
Boiling point	Lower	Higher
Flash point	Lower	Higher
Vapor content	Higher	Lower
Vapor pressure	Higher	Lower

Normal and Standard Temperature and Pressure (NTP and STP)

The properties of gases will vary with temperature and pressure. It would be impossible to compare experimental measurements without controlling for those variables. To allow comparisons to be made between different sets of data the International Union of Pure and Applied Chemistry (IUPAC) and the National Institute of Standards and Technology (NIST) have set standard conditions for temperature and pressure. These standards are called Standard Temperature and Pressure (STP) or Normal Temperature and Pressure (NTP).

IUPAC defines STP as a temperature of 273.15K (0C, 32F) and an absolute pressure of exactly 10^5Pa (100 kPa, 1 bar).

NIST uses a temperature of 20C (293.15K, 68F) and an absolute pressure of 1 atm (14.696 psi, 101.325 kPa). This standard is also called normal temperature and pressure (NTP).

Standard temperature and pressure is also employed in reporting gas volumes.

At normal temperatures, a combustible liquid is below its flash point. At these temperatures, a combustible liquid is quite safe because it does not generate an ignitable mixture of vapors. Under extra hot conditions, however, a combustible liquid may reach its flash point. Now the combustible liquid is much easier to ignite because of its low ignition temperature.

Summary

Understanding the various physical and chemical properties of hazardous materials can help response personnel predict how they will behave and the hazards they present. As a Hazardous Materials Technician your job may be to gather and interpret data such as specific gravity, vapor pressure and solubility. With this information you may be asked to predict behavior and outcomes. This chapter reviewed the various different properties and how they are related to one another.

Appendix A Physical Properties

Physical Property	**Definition and Examples**
Boiling point	The temperature at which the vapor pressure of the liquid equals atmospheric pressure. At this point, a liquid will transform from the liquid state into the gaseous state. Common units: ^oF, ^oC, K.
Color	The color of light reflected by the substance. A change in color usually indicates a chemical change. Color may be caused typically by an Organic Dye or may indicate that the substance is a Transition Metal Salt such as a Copper compound (blue) or a Cobalt compound (pink).
Concentration	The amount of material within a solution or mixture. Usually expressed by percentage of volume or weight. Common units: volume (mg/cm^3, % v/v), mass (% w/w), molarity (mole), parts per million, billion (ppm, ppb).
Critical temperature/pressure	The temperature above which a gas can't be liquefied. Critical pressure is the pressure required to liquefy a gas when at its critical temperature. Common units: ^oC, K/Pa.
Decomposition Temperature	The temperature at which a substance chemically decomposes.
Density	Ratio of mass (weight) to volume of a material, usually in grams per cubic centimeter or pounds per gallon. The density of water is 1g/cc at 4°C (39°F).
Expansion ratio	The volume of a gas when vaporized as compared to its original volume as a liquid. Liquid Oxygen has an Expansion Ratio of 862:1 and Liquid N_2 has an expansion ration of 697:1.
Freezing point	The temperature at which a material changes from a liquid to a solid state upon cooling.
Heat of Solution	The heat evolved (exothermic) or absorbed (endothermic) when a substance is dissolved in a solvent such as water. For example, chemical ice packs absorb heat: Ammonium nitrate (NH_4NO_3) + Water (H_2O) → heat absorption (gets colder). When the compound Calcium Chloride ($CaCl_2$) dissolves in water it produces a lot of heat. Heats of Solution are used as aids in identification of unknown materials.

Physical Property	**Definition and Examples**
Hydrophilic	The capacity of a molecular entity or of a substituent to interact with polar solvents, in particular with water, or with other polar groups. A substance that attracts and retains water ("water loving").
Hydrophobic	The association of non-polar groups or molecules in an aqueous environment which arises from the tendency of water to exclude non-polar molecules. A substance that repels water ("water fearing").
Melting point	The temperature at which a material changes from a solid to a liquid state upon heating. Common units: ^oF, ^oC.
Miscibility	The ability of two or more liquids to form a homogenous solution or to mix in all proportions without separation of two phases; for example water and acetone. Substances are considered *immiscible* if in any proportion, they do not form a solution; for example oil and water.
Specific gravity	The ratio of the density of a substance to the density of water. Water has a specific gravity of 1 by definition. A liquid with a specific gravity greater than 1 (>1) will sink in water. A liquid with a specific gravity less than 1 (<1) will float on water. Mercury has a specific gravity of 13.56.
Vapor density	The weight of a volume of vapor or gas compared to the weight of a like volume of air. Air has a vapor density of 1 by definition. Vapors or gases with vapor densities greater than 1 (>1) are heavier than air. Gases with densities less than 1 (<1) are lighter than air. The vapor density of propane is 1.5
Vapor pressure	The force exerted by the vapors of a liquid against the atmosphere or the sides of a container. The vapor pressure and the amount of vapors released into the air are determined by the temperature of the liquid and size of the molecule. Common units: psia, atm, torr, bar, mm Hg.
Viscosity	A measure of a liquid's ability to flow. Viscous liquids do not flow well. Common units: poise, centipoise. Glycerin has a viscosity of 1500 centipoise, as compared to water that has a viscosity of 0.89 centipoise. Viscosity is an important observation in field identification of unknown liquids. For a liquid that floats on water a determination of viscosity will indicate the size (carbon #) of the compound.

Physical Property	Definition and Examples
Water solubility	The ability of a substance to mix with water. Polar compounds, such as low molecular weight alcohols are water-soluble, while non-polar compounds, for example, xylene, are insoluble.

Appendix B Chemical Properties

Chemical Property	**Definition and Examples**
Air Reactivity	The reactivity of chemical compounds with some constituent of air. Most often, reactions occur with atmospheric oxygen (O_2) or water vapor (H_2O), although reactions with the other constituents of air such as carbon monoxide (CO), carbon dioxide (CO_2), and nitrogen (N_2) are also possible.
Corrosivity (pH)	The ability of a substance to cause corrosion (the destruction of metals and biological tissue). Common units 0-14 pH.
Electronegativity	Electronegativity is a chemical property that describes the ability of an atom or a functional group to attract electrons towards itself.
Fire point	The temperature at which a liquid gives off enough vapors to support continuous burning of an ignitable fuel mixture in air. Common units: ^oF, ^oC.
Flammable range (flammable limits)	The proportion of flammable vapors or gases in air that is between the upper and lower flammable limits. Expressed in per cent (%) by Volume in air. The *lower explosive (flammable) limit (LEL)* is the minimum concentration of flammable vapors or gases in air that will support combustion. The *upper explosive (flammable) limit (UEL)* is the maximum concentration of flammable vapors or gases in air that will support combustion.
Flash point	The minimum temperature at which a liquid gives off enough vapors to form an ignitable mixture in air in a test apparatus such as a Pensky-Martens Closed Cup. Toluene has a flashpoint of 4 ^oC (40 ^oF). Common units: ^oF, ^oC.
Heat output	The amount of heat released in a combustion reaction. Usually expressed in calories, Joules or British thermal units (BTU).
Ignition (autoignition) temperature	The minimum temperature required for flammable vapors to ignite without a continuing outside source of ignition. With autoignition, the liquid is heated to a point where the temperature is sufficient to ignite the vapors without an outside ignition source.
Instability	The tendency for a material to undergo chemical change (often violent) under normal conditions.

Chemical Property	**Definition and Examples**
Oxidation Potential	A measure of a substance's ability to oxidize other substances. These are materials that are electronegative and which take electrons from other substances.
Relative Density	The ratio of the density (mass of a unit volume) of a substance to the density of a given reference material. The most common reference materials are water (specific gravity) and air (vapor density).
Strength	The degree to which a corrosive ionizes or dissociates in water. Those that ionize the greatest number of hydrogen ions are the strongest acids ($pH < 2$), while those that dissociate the greatest number of hydroxide ions are the strongest bases ($pH > 12.5$).
Toxicity	The health effect of substances on living beings as measured by dose/response.
Water Reactivity	Substances that spontaneously undergo an often violent chemical reaction with water. Water reactive substances will often give off flammable and/or toxic gases when exposed to water.

Appendix C Chemical Terms

Chemical Term	Definition and Examples
Aerosol	A suspension of liquid droplets in air (or another gas).
Air reactive	Chemicals that exhibit moderate to extremely rapid reaction rates in the presence of air.
Auto refrigeration	A process where an unintentional and/or uncontrolled phase change of a hydrocarbon from a liquid state to a vapor occurs, resulting in a very rapid chilling (refrigeration) of the liquid. Auto-refrigeration is a phenomenon common to liquefied compressed gases.
Catalyst	A substance that increases the rate of a chemical reaction without itself undergoing any permanent chemical change. It enables a chemical reaction to proceed at a usually faster rate or under different conditions (as at a lower temperature) than otherwise possible.
Disassociation	A general process in which molecules (or ionic compounds such as salts, or complexes) separate or split into smaller particles such as atoms, ions or radicals, usually in a reversible manner. For instance, when an acid dissolves in water, a covalent bond between an electronegative atom and a hydrogen atom is broken which gives a proton (H^+) and a negative ion.
Inhibitor	A substance that interferes with a chemical reaction. Often used in monomers such as styrene to inhibit unwanted polymerization.
Molecular Weight	Molecular weight**,** also called molecular mass, mass of a molecule. It is calculated by summing the atomic weights of the atoms making up the substance's molecular formula. For example, the molecular weight of Butane (C_4H_{10}) is 58 (rounded off). Four carbon atoms = 48. Ten hydrogen atoms = 10.
Odor Threshold	The lowest concentration of an odor compound that is perceivable by the human sense of smell. Odor thresholds cannot be accurately predicted and can vary greatly from one individual to another.
Oxidization Potential	A measure of the tendency of a chemical species to acquire electrons and thereby be reduced. Reduction potential is measured in volts (V), or millivolts (mV). Each species has its own intrinsic reduction potential; the more positive the potential, the greater the species' affinity for electrons and tendency to be reduced. A common measurement for water quality.

Chemical Term	Definition and Examples
Partition Coefficient	The ratio of concentrations of a compound in a mixture of two immiscible phases at equilibrium. This ratio is therefore a measure of the difference in solubility of the compound in these two phases. The partition-coefficient generally refers to the concentration ratio of un-ionized species of compound whereas the distribution-coefficient refers to the concentration ratio of all species of the compound (ionized plus un-ionized).
Persistence	The ability of a chemical substance to remain in an environment in an unchanged form. The longer a chemical persists, the higher the potential for human or environmental exposure to it. The individual environmental media for which a chemical's persistence is usually measured or estimated are air, water, soil, and sediment.
Pyrophoric	A material that can spontaneously ignite in air.
Reactivity	The tendency of a chemical to undergo chemical reactions at normal ambient temperatures and humidity.
Solution	A homogenous mixture that is created when one substance dissolves another substance.
Solvent	The substance that dissolves another substance.
Sublimation	Sublimation is the transition from the solid phase to the gas phase without passing through an intermediate liquid phase. A common example is dry ice (solid carbon dioxide). At room temperature and pressure, it sublimates into carbon dioxide vapor.
Volatility (evaporation rate)	A measure of the tendency of a liquid to vaporize. Highly volatile liquids produce a lot of vapor.

Chapter Review

1. In general, the size of a molecule of a given substance will determine several of its physical properties. Complete the sentences below.

   If you compare the properties of a smaller molecule with the properties of a larger molecule then…

   The vapor pressure of the smaller molecule will be: ____________________

   The flash point of the smaller molecule will be: ____________________

   The ignition temperature of the smaller molecule will be: ____________________

   The boiling point of the smaller molecule will be: ____________________

2. The following sentences describe a specific property. Fill in the blank with the appropriate word(s).

   Vapor density is the weight of the vapor as compared to an equal volume of: ____________________

   Ignition temperature is the temperature required to (blank) the flammable vapors. ____________________

   Vaporization is the tendency of molecules to escape from the surface of a: ____________________

   Vapor pressure and volatility are related to: ____________________

3. Complete the following table to indicate the general characteristics of physical and chemical properties.

Characteristic	Chemical	Physical
Involves a change in chemical identify.		
Describes a behavior.		
Can be measured.		
Seen during a reaction.		
Involves a change in chemical composition.		

4. If the specific gravity of a substance is greater than 1 then the substance will _________________ in water.
   - A. Stay suspended
   - B. Float
   - C. Hover
   - D. Sink

5. Which of the following gases is *lighter* than air?
   - A. Chlorine
   - B. Methane
   - C. Ethylene oxide
   - D. Diborane

6. Various units are used to measure air pressure (at sea level). In general, ____ psi = 1ATM = ____ mmHg = ____ inHg = ____ bar. (Fill in the blanks.)

7. What property identifies the temperature at which a liquid changes to the solid state at normal atmospheric pressure.
   - A. Boiling point
   - B. Critical temperature
   - C. Melting point
   - D. Ignition point

Chapter 8: Explosives – Hazard Class 1

This section covers DOT Hazard Class 1 – Explosives. This chapter will help responders to recognize common explosives and identify their basic chemical characteristics. Although incidents involving explosives are relatively rare they can be catastrophic. They make up less than 1% of the hazardous materials shipped in the USA yet they are responsible for some of the greatest loss of life in hazmat incidents. In 1945, two ships loaded with ammonium nitrate (a fertilizer) destroyed the entire town of Texas City, Texas, and killed 581 people including all but one member of the fire department. (Although DOT classifies ammonium nitrate as an Oxidizer if it’s heated it can become unstable and explode.) In 1988, a truck loaded with ammonium nitrate fuel oil (ANFO), a Hazard Class 1 commodity, exploded in Kansas City, MO. The explosion claimed the lives of six firefighters.

A hazmat team may respond to an incident involving “explosives” of the homemade variety. With the advent of easily obtained recipes on the internet for making everything from TATP to smoke bombs, mixing your own black powder, making guncotton, etc., it is more likely we will respond to an incident in someone’s backyard or basement than an incident involving a placarded shipment of a DOT regulated explosive device.

Explosive products have existed for centuries. Their development was driven by the need to balance explosive properties and safe handling.

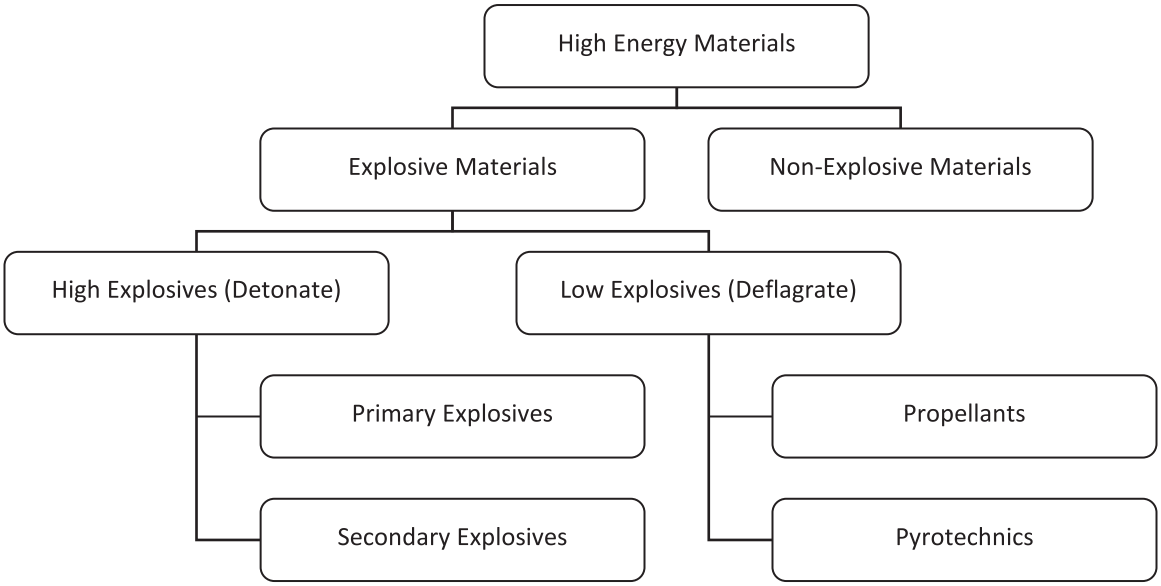
The first known explosive widely used was black powder, a mixture of potassium nitrate, sulfur, and charcoal, which the Chinese were using by the 9th century A.D. In 1846, the German-Swiss chemist Christian F. Schönbein synthesized one of the first explosives when he accidently nitrated cellulose with a mixture of nitric and sulfuric acids. In 1859, the Swedish inventor, Alfred Nobel, mixed nitroglycerine with diatomaceous earth to form dynamite. Prior to this explosives were often highly unstable and unsafe to handle. (In fact, Nobel’s brother was killed while trying to develop safer explosives.) Dynamite quickly became the most widely used explosive and remains in use to this day. A few years later a German chemist, Julius Wilbrand, discovered trinitrotoluene (TNT) a material originally used as a dye. In 1891 another German chemist, Carl Häussermann, discovered the explosive properties of TNT. It was stable and difficult to detonate. It was widely used in various types of military ordnance. Between World War I and World War II more insensitive yet powerful explosives were developed. These include RDX and PETN, both still commonly used in a variety of applications.

High Energy Materials

High energy materials fall into two broad categories – Explosives and Non-Explosive materials. This chapter will focus on explosives.

High energy materials are commonly broken down as shown below.

High Energy Materials



Terminology

Explosive: Any substance or article, including a device, that is designed to function by explosion (an extremely rapid release of gas and heat) or that, by chemical reaction within itself, is able to function in a similar manner even if not designed to function by explosion. Explosives in DOT Class I are divided into six divisions. Each division will have a number designation. These six divisions are listed in Table 8.2.

Detonation: The sudden and violent release of mechanical, chemical or nuclear energy. A detonation is a rapid, self-propagating *supersonic decomposition* propagating through an explosive by shock compression. It produces a high pressure and temperature shock wave that moves at greater than 1000 meters/sec (faster than the speed of sound).

Deflagration: From the Latin word “flagrare” meaning “to burn,” is a very rapid, subsonic combustion propagating through an explosive by thermal conductivity producing a rapid expansion of gas (not a pressure wave). This is typically a very rapid auto-combustion from the surface inward.

Brisance: The shattering or crushing capacity of an explosive determined mainly by its detonation pressure. TNT is used as a standard in the measurement of brisance. Brisance is of practical importance for determining the effectiveness of an explosive.

High Explosive: An explosive (such as TNT) that detonates. The reaction is so rapid as to be practically instantaneous. The explosive combusts nearly instantaneously producing a violent, shattering effect. Detonation involves a reaction propagating through the material, usually in the form of a shock wave, at speeds greater than that of sound. High explosives often require an activation device such as a blasting cap to initiate their detonation.

Low Explosive: An explosive that deflagrates rather than detonates. They are usually relatively slow-burning and often set off by heat or friction. Usually composed of a combustible material and an oxidizer. They can detonate if they are confined in a container and the detonation is initiated by a shock from another detonation. Black powder, smokeless powder, and cordite are examples of low explosives.

Primary Explosive: An explosive (as mercury fulminate or lead azide) that is sensitive to friction, blows or shock. A very sensitive explosive compound used as the first material in an explosive train that is initiated by the appropriate application of flame, friction, heat, impact, or spark. Also referred to as a primary high explosive. These materials are often used in small quantities in detonators to initiate the explosive chain for main charges of less sensitive secondary explosives. Some common primary explosives are mercuric fulminate, lead azide, and lead styphanate (lead trinitroresorcinate).

Secondary Explosive: A high explosive that is less sensitive to mechanical shock and heat than a primary explosive. Also referred to as secondary high explosive. They are often readily detonated by the shock from a primary explosive. Examples of secondary high explosives are dynamite, nitroglycerin, TNT, RDX (Cyclonite, Royal Demolition Explosive), and PETN (Pentearythrilol tetranitrate). They are used in larger quantities in an explosive train being initiated by a small quantity of a primary explosive.

Tertiary Explosive: Explosives that are insensitive to shock and cannot be reliably detonated by practical quantities of primary explosive, and instead require an intermediate explosive booster of secondary explosive. The main, and least sensitive, charge of an explosive or propellant system.

Blasting agents: This term denotes relatively low-sensitive explosives, usually based on ammonium nitrate, and do not contain any high explosives such as nitroglycerin or TNT. The most commonly used blasting agent is ammonium nitrate and fuel oil (diesel fuel). This formulation, termed ANFO, needs a primary explosive, like a blasting cap, to start the explosion. It is not considered a high explosive but can detonate if heated.

Chemical explosion: An explosion which occurs because of one of these three types of chemical reactions: rapid oxidation-reduction, decomposition, or runaway polymerization.

Rapid Oxidation-Reduction: A self sustaining exothermic reaction that involves the transfer of electrons from a fuel reducing agent) to an oxidizer (oxidizing agent) producing heat and light

Decomposition: A self-sustaining exothermic reaction whereby a chemical compound is reduced to its component substances. Organic peroxides, for example, decompose when exposed to heat and/or pressure.

Runaway Polymerization: Polymerization reactions occur when large numbers of simple small molecules called monomers, combine to form one huge compound — the polymer. This type of reaction usually takes place in an industrial setting under very controlled conditions. At the scene of a spill the controlled conditions no longer exist and an uncontrolled polymerization or “runaway” polymerization can occur. If it occurs inside a tank the tank may rupture violently. Heat, contamination or loss of inhibitors can cause an unwanted reaction to start. These reactions produce large amounts of heat and gas. In addition, the resulting products of the reaction will have a much larger volume than the original volume of the reactants.

Inhibitors are compounds that are added to monomers to slow or stop an undesirable chemical reaction. Inhibitors have limited shelf lives and become ineffective over time.

Explosions are not confined to closed systems. If the propagation rate of the gaseous products from the initiation site exceeds the velocity of sound, detonation may also occur in an open system. For example, 1 gram of nitroglycerine is completely transformed into carbon dioxide, nitrogen, oxygen and water in microseconds. Such high explosives undergo instantaneous reactions that release enormous energy which can rapidly heat the ambient temperature to 2000^{o}C – 3000^{o}C. The result is a tremendous increase in pressure, producing shock waves that cause an explosion's shattering power. The rate of detonation for high explosives can exceed 5000 meters (over 15,000 feet) per second. The explosive characteristics thus depend on two factors; how much energy is released and how fast the energy release occurs.

Chemistry of Explosives

An "explosion" is the result of an exothermic chemical reaction (or change in physical state) that happens rapidly and generates large amounts of heat and gas that exert a high pressure on its surroundings. It has two components: shock effect and the gas expansion effect. The proportion of each varies with the chemical makeup of the material.

An "explosive" is an energetic material that can explode by initiation by friction, impact, shock, spark, flame or heat.

Many explosives have two common molecular characteristics; they contain both an oxidizer component (sometimes called an explosophore) and a reducing agent (often carbon and hydrogen). When the oxidizer separates and combines with the fuel (reducing agent) the resulting reaction liberates energy. Most explosive compounds contain oxygen and release energy from a combustion process. There are, though, explosive compounds that don't contain oxygen. Lead azide doesn't contain oxygen but decomposes and explodes due to the unstable bonds between nitrogen and the metal component.

A single molecule of an explosive can have two of three sides of the fire triangle (oxidizer and reducing agent) already in its makeup. Other types of explosives may consist of an intimate mixture of a fuel and an oxidizer. Some explosives simply have a reactive site on the compound that can undergo a decomposition reaction producing voluminous amounts of gas. The molecular composition of explosives is what makes them so reactive. An explosion can occur when the one remaining side of the fire triangle is completed by the introduction of light, heat, shock, friction, impact, catalyst or pressure waves. Any of these initiators can provide enough energy to start the oxidizing and reducing parts of an explosive to react with each other, or to start the decomposition reaction. An explosion occurs when an unstable compound or mixture undergoes a reaction that produces a rapid and violent energy release. The reaction products (predominantly gases or fumes) cause high pressures, and if contained will result in the violent rupture of the container.

Explosophores

Explosophores are functional groups that give organic compounds explosive properties. In general, the bonds in these functional groups are unstable. The structure and composition of these molecules determines their explosive properties.

Examples of Explosophores

Name	Structure
Halogenated Nitrogen	$-R_nNX_m$
Chlorate & Perchlorate	$-OClO_2$ and $-OClO_3$
Nitrite, Nitro	$-NO_2$, $-ON{=}O$ and $-ONO_2$
Peroxide, Ozonide	$-O-O-$ and $-O_3-$
Fulminate	$-C{=}N-O-$
Acetylide	$-C{\equiv}C^- M^+$
Azo, Azide	$-N{=}N-$ and $-N^-{=}N^+{=}N^--$

Other substances have been characterized as explosophores outside of these classes. A functional group that is frequently considered as an explosophore is picrate, the salts or ethers of picric acid (2,4,6-trinitrophenol), which gains its explosive capability from the nitrate groups attached to it.

Many explosives have nitro-groups in their molecular structures. The nitro-groups provide a source of nitrogen, which reduces to the inert (highly-stable) nitrogen gas during the course of the reaction. Nitrogen has a higher energy level in its oxidized state within the nitro-group. The transition of nitrogen from a high energy state to a lower energy state produces heat. The nitro-groups also provide a source of oxygen with which the hydrocarbon parts of the molecule allowing combustion of the hydrocarbon without an external source of oxygen gas. Since combustion can happen as a result of an intramolecular rearrangement rather than an intermolecular reaction makes the combustion more likely and, therefore, faster.

Explosives developed in the twentieth century (e.g. RDX, HMX, and HNIW) make use of nitroamines. These compounds were far more powerful than other explosives of their time and capable of incredibly fast detonations. Nitroamines are a nitrogenous molecule with the nitro-groups on the nitrogen atoms.

DOT Hazard Class 1

DOT Divisions of Hazard Class 1: The Department of Transportation divides explosives into six divisions. Divisions 1.1 to 1.3 require placarding regardless of quantity. Divisions 1.4 to 1.6 require placarding when 1001 lbs. or more are carried.

U.S. DOT Divisions of Explosives (CFR 49)

Division	Definition
1.1	**Articles and substances having a mass explosion hazard.** A mass explosion is one that affects almost the entire load instantaneously. Examples include black powder, dynamite, and TNT.
1.2	**Articles and substances having a projection hazard, but not a mass explosion hazard**. Examples include pyrophoric articles, blank cartridges for firearms, detonating cord and some types of fireworks.
1.3	**Articles and substances having a fire hazard, a minor blast hazard, and/or a minor projection hazard, but not a mass explosion hazard.** Examples include liquid-fueled rocket motors and propellant explosives.
1.4	**Explosives that present a minor explosion hazard**. The explosive effects are largely confined to the package and no projection of fragments of appreciable size or range is to be expected. An external fire must not cause virtually instantaneous explosion of almost the entire contents of the package. Examples include line-throwing rockets, practice ammunition, and signal cartridges.
1.5	**Very insensitive substances having a mass explosion hazard.** This division is comprised of substances that have a mass explosion hazard but are so insensitive that there is very little probability of initiation or of transition from burning to detonation under normal conditions of transport. Examples include ammonium nitrate fertilizer-fuel oil mixture (blasting agents).
1.6	**Extremely insensitive articles which do not have a mass explosion hazard.** This division is comprised of articles that contain only extremely insensitive detonating substances and that demonstrate a negligible probability of accidental initiation or propagation.

Explosive Compounds

Azides, Fulminates and Acetylides

Azides, fulminates, and acetylides are highly explosive shock- and heat-sensitive metal salts. They differ from each other structurally, but they have similar detonating characteristics.

Azides are derivatives of hydrazoic acid, HN_3. Inorganic azides contain the azide anion attached to a metal by an ionic bond. Sodium azide is a moderately soluble clear solid used in automobile airbags. It undergoes a rapid decomposition reaction producing large volumes of nitrogen gas. Lead azide is a primary high explosive used in blasting caps and detonators.

Organic azides consist of a hydrocarbon radical attached to the azide functional group. Tetraazidomethane is a recently discovered clear, highly explosive liquid.

Fulminates are chemical compounds that include the fulminate ion. Fulminate ions are unstable so fulminate salts are friction-sensitive explosives. These compounds are powerful explosives and are highly sensitive to impact, friction and heat.

The best known is mercury(II) fulminate, which has been used as a primary explosive in detonators. Fulminates can be formed from metals, such as silver and mercury, dissolved in nitric acid and reacted with ethanol.

Acetylides are the metal derivatives of acetylene gas C_2H_2. Hydrogen attached to carbon atoms bearing a triple bond is acidic in nature and can be substituted by a metal ion to form an acetylide. Copper (I) acetylide, also called cuprous acetylide or copper carbide, is an amorphous red powder that is sensitive to shock and heat. It decomposes in water much like the calcium carbide. When it decomposes explosively it produces no gaseous products.

Nitro Compounds

Nitrated organics and inorganics constitute the largest class of chemical substances that are known for their explosive characteristics. Explosives that are used in bombs, actuating cartridges, boosters, bursters, torpedoes, igniter cords, rifle powder, blasting devices, propellants, signal flares, fireworks, and for many other military and commercial purposes contain primarily nitrated organics and inorganic substances in their compositions. Among the inorganic nitrates, ammonium nitrate and potassium nitrate are most common. Organic compounds containing nitro groups can be further divided into azo nitros, cyclic nitramines, nitramines, nitro benzenes, amino nitro benzenes, nitrate esters, nitrate triazoles, nitro phenyls, etc, the list goes on. The nitro hydrocarbon derivatives are perhaps one of the most studied class of organic compounds and are widely used.

Picric acid, trinitrophenol $C_6H_2OH(NO_2)_3$ is a poisonous, corrosive yellow solid. Its principle hazard is as an explosive, not as a corrosive. Picric acid is very similar chemically to TNT and was once used commonly in hand grenades. Picric acid, in quantities less than 25 pounds, is classified as a flammable solid when containing 10% or more water. However, when containing less than 10% water, or in quantities over 25 pounds regardless of water concentration, picric acid is classified as an explosive. Metallurgy labs use a reagent with ethanol, picric acid and hydrochloric acid called Viella's reagent or another reagent with just ethanol and picric acid called Picral to etch metals such as steel, cast iron and magnesium. If the waste etchant solution dries out after use it may have formed explosive picrate salts.

Nitroglycerine is a pale yellow oily liquid. In pure form, it is extremely shock-sensitive and will spontaneously detonate when heated to a temperature of 180°C or 35°F. Nitroglycerine detonates with a brisance which is roughly three times that of an equivalent quantity of gunpowder and proceeds 25 times faster. Although nitroglycerine is toxic, it is used at 10% nitro in alcohol as a medicine (classified as a flammable liquid). Old nitroglycerine hydrolyzes back into nitric acid and glycerol. The nitric acid, then acting as an oxidizer, makes aged nitroglycerine even more dangerous than freshly synthesized nitroglycerine. Dynamite, discovered by Alfred Nobel, is a composition of nitroglycerine and siliceous earth. Nitroglycerine, when absorbed into a porous material, is much safer to handle than the direct liquid. Dynamite is a high explosive, but can be transported without a danger of spontaneous decomposition. A detonating cap is used to explode it. A typical composition of dynamite is 75% nitroglycerine, 24.5% porous adsorbent (diatomaceous earth), and 0.5% sodium carbonate. Adsorbents such as wood pulp, sawdust, and other carbon based substances are used to make dynamite. Sodium carbonate or calcium carbonate is added to the composition to neutralize nitric acid, which forms by spontaneous decomposition.

Various forms of dynamites are manufactured, containing nitroglycerine concentrations usually between 20% - 60%. Certain types of dynamites have greater nitroglycerine content. Oxidizers such as sodium nitrate are also added. Gelatin dynamite consists of nitroglycerine gelatinized in nitrocellulose (1% by weight). Ammonia dynamite is composed of nitroglycerine and ammonium nitrate, a carbonaceous absorbent, sulfur, sodium carbonate, and moisture. The mixture is packed in cylindrical cartridges of varying size and made of waxed paper.

The addition of nitrocellulose or ammonium nitrate in dynamite produces additional brisance to the explosive. The detonation velocity ranges between 0.75 and 6.0 km/sec, depending on the type of dynamite and its composition.

RDX (Cyclotrimethylenetrinitramine or Cyclonite) is a fairly insensitive white crystalline solid of high density and melting point. RDX has the highest detonation pressure of any explosive in common use with a brisance greater than TNT. The detonation velocity is between 7 and 8 km/sec. It is soluble in acetone, but insoluble in water. In pure form, it is highly sensitive to shock, decomposing explosively. It is the principal constituent of plastic explosive compositions and artillery shells. It can explode under prolonged exposure to heat or fire.

Trinitrotoluene (TNT), when wet, is a yellow crystalline slurry or sludge that was once used as a high explosive in mining and in the military. In comparison to many other high explosives, it is relatively insensitive to heat, shock or friction. TNT may be found either dry or wet. The dry material is a high explosive. It's easily ignited and will burn vigorously. A violent detonation occurs almost instantaneously. The detonation velocity is between 5.1 and 6.9 km/sec. The wet material (classified as a flammable solid) can burn, though it may require some effort to ignite. It is insoluble in water. Toxic oxides of nitrogen are produced during combustion of this material.

Tetryl (or trinitrophenylmethylnitramine), a yellow crystalline solid, is a relatively sensitive high explosive. It will detonate at 500°F or 260°C and is very sensitive to shock, heat and friction. Detonation velocity is between 7.0 and 7.5 km/sec. Tetryl is used as an initiator for many less sensitive explosives. It is used as a booster in artillery ammunition.

PETN (pentaerythrite tetranitrate or pentaerythritol tetranitrate) is an insoluble white crystalline material that has moderate sensitivity. It is more sensitive to shock than TNT. The detonation velocity is 7.9 km/sec. It is insoluble in water and slightly soluble in alcohol. It may explode under exposure to intense heat or fire. It is a high explosive used as a detonation fuse (det cord or primacord) and as a booster in artillery ammunition. Detonating cord is a flexible line having an explosive core woven with a layer of fibers and coated in plastic. It is used to transfer a detonation from one point to another, both in military devices and in commercial blasting. PETN is used to make the plastic explosive called Semtex.

Summary

Explosives generally contain a fuel component and an oxidizer component bound into a compound/mixture or they have a functional group in their structure that easily undergoes a decomposition reaction to form gaseous products. These materials release vast amounts of energy in a very short period of time.

With the advent of the internet and the popularity of homemade explosives it is important for responders to recognize the conditions/clues that indicate an improvised explosives lab. The presence of concentrated nitric acid points to the potential for explosives manufacturing. A nitrating mixture consists of concentrated nitric and concentrated sulfuric acids mixed together. With this mixture of acids many nonhazardous organic compounds can be turned into explosives. An improvised explosives lab will have measures present for temperature control of the reactants. The presence of thermometers, ice baths and freezers is an indication of such an operation. Desensitizer and plasticizer compounds such as gum arabic, paraffin wax, chalk, diatomaceous earth, epoxies and putties may seem innocuous on the surface, but may indicate an explosives lab. Chemicals kept in a refrigerator or freezer are also indicators. Unlabeled explosive chemicals are identified in the field by subjecting very small amounts of them to thermal challenges.

Response to an incident involving explosives does not leave a lot of room for error. One mistake and we may not get a second chance. We may not be able to learn from the mistakes of others because their mistake is perhaps destroyed in the blast. It is important that we heed all recognition clues from the DOT placarding system, to nomenclature recognition clues, to those clues present at an improvised explosives lab.

Examples of Explosives

Chemical Name	UN #	Label
Ammonium Nitrate-Fuel Oil Mixtures	0331	Explosive 1.5d
Ammonium Nitrate, [> 0.2 Per Cent Combustible Substances]	0222	Explosive 1.1d
Ammonium Perchlorate, [High Explosive]	0402	Explosive 1.1d
Ammonium Picrate, [Dry]	0004	Explosive 1.1d
Barium Azide	0224	Explosive 1.1a, Poison
Black Powder	0028	Explosive 1.1d
Cyclotrimethylene Trinitramine, [Desensitized]	0483	Explosive 1.1d
Diazodinitrophenol	0074	Explosive 1.1a
2-Diazo-1-Naphthol-5-Sulfochloride	3043	Flammable Solid, Explosive
Dinitrophenol	0076	Explosive 1.1d, Poison
Dinitroresorcinol	0078	Explosive 1.1d
Dinitrosopentamethylene Tetramine	2972	Flammable Solid, Explosive
Dipicryl Sulphide	0401	Explosive 1.1d
Flash Powder	0094	Explosive 1.1g
Guanyl Nitrosaminoguanylidene Hydrazine	0113	Explosive 1.1a
Hexalite	0118	Explosive 1.1d
Hexanitrodiphenylamine	0079	Explosive 1.1d
Hexanitrostilbene	0392	Explosive 1.1d
Lead Azide	0129	Explosive 1.1a
Lead Mononitroresorcinate	0473	Explosive 1.1a
Lead Styphnate	0130	Explosive 1.1a
Manitol Hexanitrate	0133	Explosive 1.1d
Mercury Fulminate	0135	Explosive 1.1a
Nitrocellulose, [Dry]	0340	Explosive 1.1d
Nitrocellulose, [With Plasticizer]	0343	Explosive 1.3c
Nitroglycerin, Desensitized, [Liquid]	0143	Explosive 1.1d, Poison
Nitrosoguanidine	0473	Explosive 1.1a
Nitrostarch, [Dry]	0146	Explosive 1.1d
Nitrourea	0147	Explosive 1.1d
Octolite	0266	Explosive 1.1d

Pentaerythrite Tetranitrate With ≥ 7 % Wax	0411	Explosive 1.1d
Pentolite	0151	Explosive 1.1d
Powder, [Smokeless]	0160	Explosive 1.1c
Tetranitroaniline	0207	Explosive 1.1d
Trinitroaniline	0153	Explosive 1.1d
Trinitroanisole	0213	Explosive 1.1d
Trinitrobenzene	0214	Explosive 1.1d
Trinitrochlorobenzene	0155	Explosive 1.1d
Trinitrofluorenone	0387	Explosive 1.1d
Trinitrometacresol	0216	Explosive 1.1d
1,3,5-Trinitronaphthalene	0217	Explosive 1.1d
Trinitrophenetole	0218	Explosive 1.1d
Trinitrophenol, [Wet]	0154	Explosive 1.1d
Trinitrophenylmethylnitramine, [Tetryl]	0208	Explosive 1.1d
Trinitroresorcinol	0219	Explosive 1.1d
Trinitrotoluene (TNT)	0209	Explosive 1.1d
Tritonal	0390	Explosive 1.1d
Urea Nitrate	0220	Explosive 1.1d

Color Coding of Military Ordnance

MIL-STD-709D, *Ammunition Color Coding* is the Dept. of Defense (DOD) standard for color coding ammunition and ordnance. The following is a partial list of the color codes.

Type	Body Color	Marking Color
High Explosive (HE)	Olive Drab	Yellow
Incendiary	Light Red	Black
Armor Piercing	Black	White
Practice	Light Blue	White
Screening, Marking, Smoke	Light Green	Black*
Chemical (riot control agents)	Gray	Dark Red
Chemical (toxic agents)	Gray	Dark Green

*If the ordnance contains white phosphorous the marking color will be light red.

Chapter Review

1. Check the correct box for each Hazard Class 1 Division.

Division	Mass Explosion Hazard	Not a Mass Explosion Hazard
1.1		
1.2		
1.3		
1.4		
1.5		
1.6		

2. List three shock-sensitive explosives.

____

____

____

3. What type of compounds constitute the largest class of chemical substances that are known for their explosive characteristics?
   - A. Nitro compounds
   - B. Sulfinated mixtures
   - C. Halogenated compounds
   - D. Picrated groups

4. Which of the following is a component of ANFO?
   - A. Alkaline nitrite
   - B. Amyl nitrate
   - C. Ammonium nitrate
   - D. Arsenic naphthalene

5. Which of the following is an explosive that deflagrates rather than detonates?
    A. Secondary explosive
    B. Low explosive
    C. Organic explosive
    D. Tertiary explosive

6. Which of the following Division of Hazard Class 1 is comprised of substances that have a mass explosion hazard but are so insensitive that there is very little probability of initiation?
    A. 1.3
    B. 1.4
    C. 1.5
    D. 1.6

7. Who invented dynamite?
    A. Christian F. Schönbein
    B. Julius Wilbrand
    C. Linus Pauling
    D. Alfred Nobel

8. Fill in the blanks in the following statements:

An "explosion" is the result of a/an ________________ chemical reaction.

________________ ______ is a flexible line having an explosive core.

Hazard Class 1 has _________ divisions.

Ammonium nitrate and __________________ nitrate are most common inorganic nitrates.

Divisions 1.1 to 1.3 of Hazard Class 1 require _______________ regardless of quantity.

The most commonly used blasting agent is ammonium nitrate and _______________ oil.

Chapter 9: Gases – Hazard Class 2

Gases are the most diverse of the hazard classes. Other hazard classes are defined by their properties. The gases hazard class, on the other hand, describes only the physical state of its members and says little about the other properties of those gases.

Gases are broken into divisions as indicated in the table below. These divisions alone do not reflect all the hazards. Gases can be corrosive, pyrophoric, oxidizing, flammable, nonflammable, radioactive, or explosive.

Hazard Class 2 Divisions

Division	Description
2.1	Flammable Gas Any material which is a gas at 68°F or less and 14.7 psi of pressure which is ignitable when in a mixture of 13 percent or less by volume with air; or has a flammable range at with air of at least 12% regardless of the LEL
2.2	Non-Flammable Gas A compressed gas, liquefied gas, pressurized cryogenic gas, compressed gas in solution, asphyxiant gas or oxidizing gas. A non-flammable, nonpoisonous compressed gas means any material which exerts in the packaging an absolute pressure of 40.6 psia or > at 68°F, and does not meet the definition of Division 2.1 or 2.3.
2.3	Poison Gas Any material which is a gas at 68°F or less and 14.7 psi of pressure which is known to be so toxic to humans as to pose a hazard to health during transportation, or in the absence of adequate data on human toxicity, is presumed to be toxic to humans because when tested on laboratory animals it has an LC_{50} value of not more than 5000 ml/m3.
2.4	Corrosive gas (Canada only)

Divisions of Common Gases

Gas	Division	Comments
Acetylene	2.1	Widely used as a welding gas. It is one of the hottest burning gases and it has a wide flammable range (2.5-100%). Unstable in its pure form. Usually shipped and stored in solution.
Anhydrous Ammonia	2.2 & 2.3	Used in a variety of applications including cleaning products, fertilizers, a precursor to nitrogen-containing compounds and as a refrigerant. (Note: not classified as a flammable gas because the LEL is too high and the flammable range is too narrow for it to fall into Division 2.1. It has nothing to do with lobbying by the cold storage industry since the DOT regulations don't apply to them.)
Arsine	2.3 & 2.1	Used in the synthesis of semiconducting materials. Highly flammable and toxic.
Butane	2.1	Butane and its isomers are highly flammable, colorless and easily liquefied. A component of LPG. Added to gasoline to increase the octane. A feedstock for the manufacture of ethylene and butadiene.
Carbon Dioxide	2.2	A naturally occurring gas with varied commercial uses including in the production of carbonated beverages. Can be toxic at high concentrations.
Carbon Monoxide	2.3 & 2.1	Commonly known for its toxicity but is also flammable (flammable range: 12.5–74.2%). An industrial gas with many applications in bulk chemicals manufacturing. Kills more people than any other hazardous material (an average of 430 people per year according to CDC).

Chlorine	2.3	Extremely reactive and a strong oxidizer. Used in WWI as the first gaseous chemical weapon. One of the most widely made and shipped elements. About 15,000 chlorine-containing compounds are used commercially.
Diborane	2.1 & 2.3	A highly unstable and pyrophoric gas. Used as a catalyst for hydrocarbon polymerization and in the production of semiconductors. Extremely toxic and flammable (flammable range: 0.8-88%).
Dimethylamine	2.1	A precursor to several industrially significant compounds. Flammable and mildly toxic. At an incident in 1983 a large leak caused CPC suite facepieces to craze and melt. NFPA promulgated standards for facepieces after this incident.
Ethylene Oxide	2.3 & 2.1	Highly reactive gas used for making many consumer products as well as non-consumer chemicals and intermediates. Carcinogenic, mutagenic, irritating and extremely flammable. Used in hospitals and the medical equipment industry as a sterilant. Commonly referred to as “ETO”.
Fluorine	2.3	Extremely reactive. Powerful oxidizer. Dangerous to use. (Several 19th-century scientists experimenting with fluorine were killed before it was isolated.) Used in the preparation of uranium hexafluoride, a key component in the manufacture of nuclear fuel rods.
Hydrogen Chloride	2.3	Used to produce hydrochloric acid. Used in the semiconductor industry to etch semiconductor crystals and to purify silicon. (Canada classifies it as a Corrosive gas.)

Hydrogen Sulfide	2.3 & 2.1	Toxic, corrosive and flammable. Used as a precursor to make elemental sulfur. Pronounced rotten egg odor but quickly deadens the sense of smell. Results from the breakdown of organic matter in the absence of oxygen.
Liquefied Petroleum Gas (LPG)	2.1	Composed mainly of propane and butane. Used as fuel in heating appliances, cooking equipment and vehicles. Also widely used as an aerosol propellant.
Methyl Mercaptan	2.3 & 2.1	A colorless gas with a distinctive putrid smell. Due to its extremely strong and repulsive smell it's used as an odorant in natural gas. According to the National Library of Medicine: "It is also one of the main chemicals responsible for bad breath and flatulence."
Nitrous Oxide	2.2	Used as an anesthetic. Called "laughing gas" due to due to the euphoric effects upon inhaling it. Also is used as an oxidizer in rocket propellants, and in motor racing
Phosgene	2.3	Widely used in industry as a reagent and in synthesizing pharmaceuticals. Used in WWI as a chemical weapon. Odor threshold is 4 times as high as the TLV.
Phosphine	2.3 & 2.1	Toxic, flammable (although it's used as an intermediate in the synthesis of flame retardants for cotton fabrics) and corrosive. Used as a fumigant in pest control.
Propane	2.1	A component of LPG along with butane, propylene, butadiene, butylene, isobutylene. It's a by-product of oil refining and natural gas processing. Shipped and stored as both a compressed and liquefied gas.

Sulfur Dioxide	2.3	Primarily produced for sulfuric acid manufacture. It's also used to preserve various types of fruits. In municipal wastewater treatment, sulfur dioxide is used to treat chlorinated wastewater prior to release to remove excess chlorine compounds.
Vinyl Chloride	2.1	Used to produce poly vinyl chloride (PVC). Flammable and toxic (is hepatotoxic and carcinogenic). Usually stored as a liquid.

Recognizing Gases

In the previous chapters we have learned about many types of compounds/elements that are gases: Diatomic Elements, Halogens, Noble Gases, C1 to C4 Hydrocarbons, Alkenes & Alkynes, Halogenated Hydrocarbons, Aldehydes, Ethers, Epoxides, Amines, Thiols, Inorganic Non-Salts, and the Binary Acids.

Gases are fluids, meaning they can flow from one place to another. Technically, gases are fluids with vapor pressures higher than 40 psia (pounds per square inch absolute) at 68°F or 20°C. The molecules in a gas are very far apart and are in constant random motion colliding with each other and, if contained, with the walls of the container. The gas molecules are moving at an average speed equal to the speed of sound, about 1100 feet/sec.

Most gases are invisible. They are difficult to observe directly with our senses, and so instead we observe them with four physical properties: volume, temperature, pressure and number of particles. Gases are measured and monitored using these four physical properties.

Although many gases have a pronounced and easily recognizable odor there are several that cause olfactory fatigue (also known as odor fatigue or olfactory adaptation). Olfactory fatigue is the temporary, normal inability to distinguish the odor of a particular compound after a prolonged exposure to that airborne compound. Hydrogen Sulfide and Phosphine can both quickly cause olfactory fatigue.

Measuring Gases

Gases are usually measured in terms of volume (cubic feet or liters) at standard temperature and pressure (STP). STP: temperature of 0°C (32°F) and pressure of 1 atm (atmosphere) or 14.7 psia (pounds per square inch absolute). Since the volume of a gas depends on the temperature and pressure of the gas, properties are measured at STP to allow comparison of one gas to another.

The temperature of a gas is essentially a measure of the energy in molecular motion (kinetic energy). As the temperature of a gas increases, the molecular motion increases - molecules move faster. The number of collisions between gas molecules and the sides of a container increases also and thus the pressure increases. The pressure of a gas is a measure of the force of the collisions between the gas molecules and the sides of a container. As pressure increases, the number and force of the collisions between gas molecules and the sides of a container also increases. Gases always expand to fill the container they occupy, and the pressure of a gas is always uniform within the container. Gases outside of a container always assume the ambient (atmospheric) pressure.

Gas Laws

Gases behave in predictable ways based on four variables; temperature, pressure, volume and # of particles. Gas behavior can be summarized by several laws that can help responders understand how a gas will behave at an incident.

Gas Laws

Amontons' Law	For a given quantity (number of molecules) and volume of a gas, the pressure is proportional to the temperature.
Avogadro's Law	Any like volumes of any gases at a given temperature and pressure will contain the same number of gas molecules.
Boyle's Law	For a given quantity of gas at a constant temperature, the volume of the gas is inversely proportional to the pressure. As pressure increases, the volume of the gas decreases.
Charles' Law	For a given quantity of gas at a constant pressure the volume increases as the temperature increases. Conversely, when the temperature decreases so does the volume.
The Ideal Gas Law	For a given temperature and volume, the pressure of a gas is proportional to the quantity of the gas (number of gas molecules). As the number of gas molecules increases, so does the pressure.

The Effects of the Gas Laws

Pressure vessels have a fixed volume. The only variables are the temperature, pressure, and amount of gas in the container. Heating the surface of a gas cylinder will cause a transfer of heat from the cylinder to the gas through conduction and radiation. Heating the gas will cause the pressure in the cylinder to increase (Amontons' Law). Cooling the surface of a gas cylinder has the opposite effect.

Gas that has escaped from a cylinder will increase in volume until the pressure of the gas equals atmospheric pressure (Boyle's Law). Boyle's law explains how the contents of a single gas cylinder, for example, can occupy large volumes of space.

An important effect of gases being compressed into or released from cylinders is temperature change due to the pressure changes (Amontons' Law). When gases are released from a cylinder that cylinder cools. This principle is called adiabatic decompression. You might have noticed this effect when quickly discharging an oxygen bottle or a CO2 extinguisher; the container became cool or cold. Conversely, when gases are compressed into a cylinder, the cylinder heats up. Filling a cylinder too quickly may cause so much heat that the cylinder could fail. This is called adiabatic compression. Adiabatic compression can create enough heat to ignite flammable vapors. Diesel engines operate under this principle. Diesel fuel vapor is ignited when compressed and heated to its ignition temperature within the cylinder of the engine.

When gas is added to a cylinder, more molecules of gas are occupying the same volume. This causes an increase in the pressure of the gas (Ideal Gas Law). Gas leaking from or let out of a cylinder causes the opposite effect; the pressure decreases.

Storage and Handling of Gases

Gases are typically stored and transported in one of three different conditions: compressed, liquefied, and cryogenic. All three methods have a single objective: to store and transport gases in the most efficient means possible. The most efficient means is the one that makes the product take up the least amount of space possible. The type of gas and its properties determine the method used.

There are two properties that govern how a gas can be stored and/or transported; critical temperature and critical pressure. Making a gas take up less space (i.e. to be liquefied) requires a combination of high pressure and low temperature. As we increase the temperature of a gas, liquefaction becomes more and more difficult because higher pressures are required to overcome the increased kinetic energy of the molecules. For every gas there is a temperature above which the gas can't be liquefied, regardless of pressure. This temperature is the critical temperature. Critical pressure is the pressure required to liquefy a gas that is at its critical temperature. As the temperature of a gas drops below its critical temperature, the pressure (compression) required to liquefy the gas also decreases.

Examples of Critical Temperatures and Pressures

Gas	Critical Temperature (°F)	Critical Pressure (psi)
Hydrogen	-400	188
Nitrogen	-233	492
Oxygen	-182	730
Water (reference)	705	3200
Ammonia	271	1639
Carbon Dioxide	88	1073

Compressed Gases

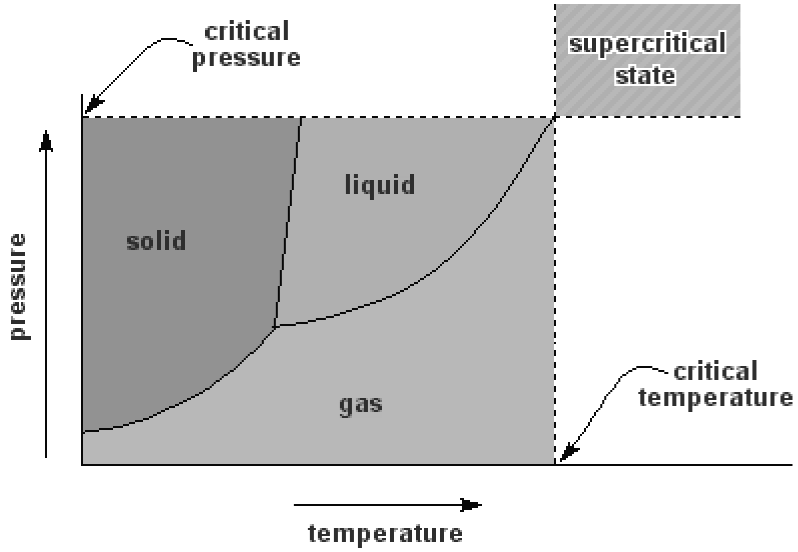
Compressed gases are typically those gases that are stored above their critical temperatures. Merely compressing a gas is the least efficient means of storing large volumes of gas, so most compressed gases are stored and transported in relatively small containers and quantities.

There are multiple hazards with compressed gases; can encompass the whole range of hazard classes. Since they are all under pressure they present a physical hazard due to the possibility of cylinder rupture. Their chemical hazards are varied. They may be flammable (e.g., methane and hydrogen), oxidizing (e.g., oxygen and the halogens), toxic (e.g., halogens), corrosive (e.g., acid gases and ammonia), or unstable (e.g., acetylene and ethylene oxide). The primary factor that makes compressed gases so hazardous is the difficulty in containing or controlling unconfined gases.

The potential for catastrophic container failure or a BLEVE (boiling liquid expanding vapor explosion) exists whenever there is flame impingement on a pressure vessel. Heat will increase the pressure of the gas and may compromise the structural integrity of the container.

Some gases may be liquefied by compression or cooling. Some gases require both compression and cooling to be liquefied.

Relationship Between Physical State, Temperature and Pressure



Liquefied compressed gases

Compressed Liquefied gases. There are three ways to liquefy a gas. Either the gas can be pressurized, or it can be cooled to below its boiling point, or a combination of both. Each method reduces the distance between gas molecules until the gas behaves like a liquid.

All gases will condense when cooled. Some, though, can become liquid. Liquefied compressed gases have some general hazards. As mentioned earlier, liquids are merely gases in their most concentrated form. A small amount of liquid vaporizes into a large volume of gas. When liquefied gases are released from a container as a liquid, the liquid has a tendency to flash boil (instantaneously vaporize). Room temperature is usually well above the boiling point of these liquids so any liquid released will flash boil.

Gases escaping from a pressure vessel, especially liquefied compressed gases, will expand in volume. This property is called the “expansion ratio” which is the ratio of a liquefied (or cryogenic) substance in liquid form compared to the volume of the same amount of substance in gaseous form. Expansion ratios can be extremely high. The expansion ratio of cryogenic liquids is even higher. Even relatively small amount of a liquefied gas can be asphyxiating when released from its container. Liquefied gases are also very cold. Skin contact can quickly result in a frostbite injury.

Cryogenic liquids

The difference between a liquefied gas and a cryogenic liquid is their temperature and pressure under storage. For DOT purposes a Cryogenic is a liquefied, refrigerated gas with a boiling point less than -130°F. Cryogenic liquids are produced through a process of compression and cooling. The expansion ratios of cryogenic liquids released into the air can be in excess of 560 to 1. Because cryogenic and liquefied gases can expand greatly in volume when released they can displace the oxygen in a confined space. When this occurs a release of a gas that is otherwise not hazardous can kill.

Cryogenic liquids may be flammable (e.g., hydrogen and LPG, liquefied petroleum gas), oxidizing (e.g., fluorine and oxygen), toxic, thermally damaging to tissues (extreme cold), or a combination of these.

Gases Commonly Shipped in a Cryogenic State

Gas	Boiling Point °F	Expansion Ratio
Methane (LNG) CH4	-257	600:1
Oxygen O_2	-291	862:1
Nitrogen N_2	-321	697-1
Hydrogen H_2	-423	840:1
Helium He	-452	754:1
Neon Ne	-415	1438:1
Argon Ar	-302	847:1
Fluorine F_2	-306	981:1

Heat Transfer and Cryogenic Liquids

Heat is transferred by conduction, convection and radiation. Any surface emits, reflects and absorbs radiation, including thermal radiation (heat). Cryogenic gases have to be stored or transported in containers built to prevent heat transfer from the cryogenic liquid to the containment system. We'll discuss these systems in more detail in later chapters.

Containers used to hold or transport cryogenic liquids incorporate some sort of passive thermal shielding using insulation, a reflective surface, a vacuum or some combination of the above. Containment systems will often use a multilayer insulation (MLI) system that is made up of an assembly of reflective films (usually aluminum or aluminized polyester film) separated by insulating interlayers (polyester, glass-fiber nets, or paper), operated under vacuum. The reflecting layers reduce heat transfer by radiation, the insulating interlayers reduce heat transfer by conduction between reflecting layers, and the high vacuum reduces convection and residual gas conduction.

Summary

Gases present a unique problem to responders because they possess so many different potential problems. They may be under a great deal of pressure. Some may cause instant tissue death by frostbite. They can expand their volumes many hundred times, and they can be toxic, flammable, oxidizing, asphyxiating, corrosive, radioactive or some combination of those.

Gases can be difficult (if not impossible) to detect. For the most part gases are invisible and many are odorless. There are five gases we can see with the naked eye and they all happen to be oxidizers: nitrogen dioxide (reddish brown), fluorine (light yellow), chlorine (yellow-green), bromine (red-orange) and iodine (purple). There are many gases that have very distinct odors and releases are often reported because someone smelled them. (Hydrogen sulfide has a rotten egg odor, phosgene smells like freshly mown grass, hydrogen cyanide like bitter almonds, arsine smells like garlic, dimethyl amine like dead fish and we all know the smell of ammonia.) Many, though, have no odor and may be impossible to detect with human senses.

Chapter Review

1. Which of the following gases is commonly shipped in a cryogenic state?
   - A. Diborane
   - B. Breathing air
   - C. Anhydrous ammonia
   - D. Helium

2. Fill in the DOT Hazard Class Division for each type of hazard listed.

Hazard	**Division**
Flammable	
Corrosive	
Toxic	
Non-Flammable	

3. Olfactory fatigue is the temporary, normal inability to distinguish the odor of a particular compound after a prolonged exposure to an airborne compound. Which of the following can cause olfactory fatigue?
   - A. Arsine
   - B. Vinyl Chloride
   - C. Hydrogen sulfide
   - D. Nitrous Oxide

4. Gases are usually measured in terms of volume (cubic feet or liters) at standard temperature and pressure (STP). Fill in the value for each property.

Property	**Value**
Temperature	
Pressure	

5. Gases escaping from a pressure vessel, especially liquefied compressed gases, will expand in volume. The term that measures this is:
   - A. Critical Temperature
   - B. Expansion Ratio
   - C. Adiabatic Decompression
   - D. Avogadro's Number

6. The temperature above which the gas can’t be liquefied, regardless of pressure is called the:
    - A. Critical Temperature
    - B. Standard Temperature
    - C. Proportional Temperature
    - D. Cryogenic Compression Temperature

7. Fill in the name of the gas law that applies to the description.

Description	**Law**
For a given quantity of gas at a constant pressure the volume increases as the temperature increases. Conversely, when the temperature decreases so does the volume.	______________________
Any like volumes of any gases at a given temperature and pressure will contain the same number of gas molecules.	______________________
For a given temperature and volume, the pressure of a gas is proportional to the quantity of the gas (number of gas molecules). As the number of gas molecules increases, so does the pressure.	______________________
For a given quantity of gas at a constant temperature, the volume of the gas is inversely proportional to the pressure. As pressure increases, the volume of the gas decreases.	______________________

8. According to the DOT, a gas is any material that exerts in the packaging an absolute pressure of _________ psia or greater at 68°F.
    - A. 20.9
    - B. 40.6
    - C. 14.7
    - D. 8.35

Chapter 10: Flammable and Combustible Liquids – Hazard Class 3

Flammable and combustible liquids are found nearly everywhere and are the most widely used hazardous material. According to the US DOT over 80% of the hazardous material shipped in the U.S. are in Hazard Class 3. 50% of all transportation-related hazmat incidents involve flammable or combustible liquids. They account for nearly all of the fatalities in transportation-related incidents. Hazmat responders can expect to regularly encounter this hazard class. Agency for Toxic Substances and Disease Registry (ATSDR) Hazardous Substances Emergency Events Surveillance (HSEES) system has found that around 20% of the incidents at fixed facilities involve flammable/combustible liquids.

DOT Hazard Class 3

Flammable and combustible liquids are in DOT Hazard Class 3. The U.S. Department of Transportation defines this class as follows:

49 CFR §173.120 Class 3—Definitions.

(a) *Flammable liquid.* For the purpose of this subchapter, a *flammable liquid* (Class 3) means a liquid having a flash point of not more than 60°C (140°F), or any material in a liquid phase with a flash point at or above 37.8°C (100°F) that is intentionally heated and offered for transportation or transported at or above its flash point in a bulk packaging, with the following exceptions:

(1) Any liquid meeting one of the definitions specified in §173.115.

(2) Any mixture having one or more components with a flash point of 60°C (140°F) or higher, that make up at least 99 percent of the total volume of the mixture, if the mixture is not offered for transportation or transported at or above its flash point.

(3) Any liquid with a flash point greater than 35°C (95°F) that does not sustain combustion according to ASTM D 4206 (IBR, see §171.7 of this subchapter) or the procedure in appendix H of this part.

(4) Any liquid with a flash point greater than 35°C (95°F) and with a fire point greater than 100 °C (212 °F) according to ISO 2592 (IBR, see §171.7 of this subchapter).

(5) Any liquid with a flash point greater than 35°C (95°F) which is in a water-miscible solution with a water content of more than 90 percent by mass.

(b) Combustible liquid. (1) For the purpose of this subchapter, a *combustible liquid* means any liquid that does not meet the definition of any other hazard class specified in this subchapter and has a flash point above 60°C (140°F) and below 93°C (200°F).

(2) A flammable liquid with a flash point at or above 38°C (100°F) that does not meet the definition of any other hazard class may be reclassed as a combustible liquid. This provision does not apply to transportation by vessel or aircraft, except where other means of transportation is impracticable. An elevated temperature material that meets the definition of a Class 3 material because it is intentionally heated and offered for transportation or transported at or above its flash point may not be reclassed as a combustible liquid.

(3) A combustible liquid that does not sustain combustion is not subject to the requirements of this subchapter as a combustible liquid. Either the test method specified in ASTM D 4206 or the procedure in appendix H of this part may be used to determine if a material sustains combustion when heated under test conditions and exposed to an external source of flame.

GHS Definitions

The Globally Harmonized System (GHS) has different definitions for flammable liquids.

- *Category 1:* Flash point < 23° C and initial boiling point ≤ 35° C
- *Category 2:* Flash point < 23° C and initial boiling point > 35° C
- *Category 3:* Flash point ≥ 23° C and initial boiling point ≤ 60° C
- *Category 4:* Flash point > 60° C and initial boiling point ≤ 93° C

NFPA Classifications

The National Fire Protection Association (NFPA) Code 30 “Flammable and Combustible Liquids Code” defines and classifies flammable liquids as follows:

- *Class IA:* Flash point below 73° F and boiling point below 100° F.
- *Class IB:* Flash point below 73° F and boiling point at or above 100° F.
- *Class IC:* Flash point at or above 73° F but below 100° F.

The National Fire Protection Association (NFPA) Code 30 “Flammable and Combustible Liquids Code” defines and classifies combustible liquids as follows:

- *Class II:* Flash point at or above 100° F and below 140° F.
- *Class III:* Flash point at or above 140° F.
- *Class IIIA:* Flash point at or above 140° F but below 200° F.
- *Class IIIB:* Flash point at or below 200° F.

Properties

Flammable liquids can have characteristics that overlap other hazard classes. Some are toxic (e.g., allyl alcohol, a hepatotoxin), some are corrosive (e.g., glacial acetic acid), while others are water-reactive (e.g., methyl dichlorosilane). Like any other hazard class, the class of flammable liquids includes materials that exhibit multiple hazards.

Flammable *liquids* themselves don’t burn. Liquids must first be volatilized or vaporized before combustion occurs. When a flammable liquid is ignited it’s not the liquid burning but rather the vapors being given off by the liquid.

Flammable liquids with wide flammable ranges are more dangerous than those with narrow flammable ranges. The wider the flammable range of the liquid, the higher the probability of vapors being present within the flammable limits. A flammable liquid such as acetaldehyde has a fairly wide flammable range 4-57% and as such is more dangerous than ethanol which has a flammable range of 3-19%.

Molecules of combustible liquids have a higher hydrogen content than molecules of flammable liquids. Since combustible liquids have larger molecules than flammable liquids they have higher boiling points, lower vapor pressures and are more viscous. A combustible liquid, though, will behave like a flammable liquid in high temperature conditions if the liquid is in aerosol form or in the presence of oxidizers. Combustible liquids have a higher heat output than flammable liquids when they burn.

Fires Involving Flammable/Combustible Liquids

The burn rates of flammable liquids vary greatly. The type of product and its properties will largely determine the basic burn rate. For example, crude oil, a mixture of light and heavy fractions, will often burn rapidly at first when the lighter fractions are burning. When the more volatile components burn off, the heavier fractions will then burn at a slower rate. Other flammable/combustible liquids such as diesel fuel are much more uniform in their chemical makeup so will behave in a more predictable manner.

Other variables that influence burn rate are:

- Size of the spill, the diameter and the depth of the liquid pool.
- The type of surface the product is spilled on.
- The ambient temperature.
- Whether the spill is continuous or limited in duration.

Oxidizers can change the behavior of flammable liquids. Oxidizers can combine with fuels (reducing agents) to produce accelerated burning. The presence of an oxidizer may also cause a flammable liquid to burn outside of its flammable range. Accelerated burning and explosions are always possibilities when fuels come in contact with oxidizers. This is especially true of hypergolic combustion, a reaction where two substances spontaneously ignite when they come into contact with each other. Substances that undergo hypergolic combustion are used as rocket propellants since they don’t need any source of ignition. Hypergolic propellants include nitrogen tetroxide (fuel) and nitric acid (oxidizer) and kerosene (fuel) and hydrazine (oxidizer).

Solubility of Flammable Liquids

Most hydrocarbons are nonpolar, meaning they do not mix with water. They include the alkanes (saturated), the alkenes (unsaturated), and the aromatic hydrocarbons. Another major group of nonpolar liquids are the halogenated hydrocarbons, however, most of them are not flammable.

Nonpolar liquids make an immiscible system with water. That means they either float on or sink in water, depending on their specific gravity. Crude oil, on the other hand, will often form an emulsion with water. The specific gravity of the emulsion would be nearly the same as the specific gravity of water.

Low molecular weight carbonyls (ketones, esters, aldehydes, and organic acids), alcohols, amines, amides, and nitriles will have some degree of water-solubility – they are polar. As the carbon chain length or the molecular weight of these compounds increases, the water solubility decreases. Ethyl alcohol (two carbons) is highly water soluble, whereas octanol (eight carbons) is only slightly soluble in water. Polar solvents are recognized by name or by formula.

Polar Solvents

Generic Formula	Liquids	Group
R-O-H	CH_3OH	alcohol
R-CHO	CH_3CHO	aldehyde
R-CO-R	CH_3COCH_3	ketone
R-COOH	CH_3COOH	organic acid
$R\text{-}NH_2$	$C_2H_5NH_2$	amine
R-CN	CH_3CN	nitrile

Some polar solvents make miscible systems with water. The vapor pressure of miscible systems is a percentage of the vapor pressure of each of the liquids proportional to the concentration of that liquid in the system.

Summary

Flammable and combustible liquids are the most common hazardous materials encountered, so it’s important to understand how their properties can affect their behavior, particularly how they behave in water.

Chapter Review

1. According to the US DOT, a flammable liquid is a liquid having a flash point of not more than ____________ .
   A. 110°F
   B. 120°F
   C. 130°F
   D. 140°F

2. Most hydrocarbons are ____________ , meaning they do not mix with water.
   A. Nonpolar
   B. Insoluble
   C. Unsaturated
   D. Straight chain

3. In a fire involving flammable liquids, what is actually burning?
   A. Smoke
   B. Residue
   C. Vapor
   D. Aromatics

4. According to the NFPA, a flammable liquid is a liquid having a flash point below:
   A. 100°F
   B. 120°F
   C. 140°F
   D. 160°F

5. What is a factor or condition that may make a combustible liquid behave like a flammable liquid?
   A. The ignition temperature is variable.
   B. The liquid is in aerosol form.
   C. The material is non-polar.
   D. It's a limited quantity.

Chapter 11: Flammable Solids – Hazard Class 4

A flammable solid is any solid material, other than an explosive, which is liable to cause fires through friction or through retained heat from manufacturing or processing or which can be ignited readily on exposure to water or air. Although less than 1% of transportation-related hazmat incidents involve flammable solids they burn so vigorously and persistently that they create a serious transportation and storage hazard.

In general, flammable solids are compounds that contain oxygen or nitro groups.

DOT Hazard Class 4

Flammable solids are in DOT Hazard Class 4. The U.S. Department of Transportation defines this class as follows:

49 CFR §173.124 Class 4, Divisions 4.1, 4.2 and 4.3—Definitions.

(a) *Division 4.1 (Flammable Solid).* For the purposes of this subchapter, *flammable solid* (Division 4.1) means any of the following four types of materials:

(1) Desensitized explosives…

(2)(i) Self-reactive materials that are thermally unstable and can undergo an exothermic decomposition even without participation of oxygen (air).

(*3*) It is an oxidizing substance in Division 5.1 containing less than 5.0% combustible organic substances…

(b) *Division 4.2 (Spontaneously Combustible Material).* For the purposes of this subchapter, *spontaneously combustible material* (Division 4.2) means—

(1) *A pyrophoric material.* A pyrophoric material is a liquid or solid that, even in small quantities and without an external ignition source, can ignite within five (5) minutes after coming in contact with air…

(2) *Self-heating material.* A self-heating material is a material that through a process where the gradual reaction of that substance with oxygen (in air) generates heat. If the rate of heat production exceeds the rate of heat loss, then the temperature of the substance will rise which, after an induction time, may lead to self-ignition and combustion.

(c) *Division 4.3 (Dangerous when wet material).* For the purposes of this chapter, *dangerous when wet material* (Division 4.3) means a material that, by contact with water, is liable to become spontaneously flammable or to give off flammable or toxic gas at a rate greater than 1 L per kilogram of the material, per hour…

Examples of Flammable Solids (DOT Hazard Class 4)

Division 4.1, Flammable Solid

- Black Powder
- Fusee
- Matches
- Sulfur

Division 4.2, Spontaneously Combustible

- Activated Carbon
- Copra
- Titanium Powder
- White Phosphorous
- Wet Cotton

Division 4.3, Dangerous When Wet

- Aluminum Carbide
- Calcium
- Lithium
- Sodium
- Zinc Phosphide

GHS Definitions

The Globally Harmonized System (GHS) has different definitions for flammable solids.

Flammable solid means a solid which is a readily combustible solid, or which may cause or contribute to fire through friction.

Readily combustible solids are powdered, granular, or pasty chemicals which are dangerous if they can be easily ignited by brief contact with an ignition source, such as a burning match, and if the flame spreads rapidly.

Note: Pyrophoric, self-heating or water-reactive chemicals are in separate GHS categories.

Properties

The primary hazard of flammable solids is that they ignite readily, burn intensely, and when burning are difficult (and sometimes impossible) to extinguish. Some are toxic or produce toxic combustion products.

Flammable metals

Most metals in their solid state are not flammable. When they are in the form of shavings, dusts, or powders, though, they can form explosive mixtures in air. The increased fuel surface exposure of these forms increases the amount of oxidation reaction for a given volume of the metal. Metals that are normally stable in air can become pyrophoric if finely divided.

Once ignited, flammable metals/elements burn very intensely and generate a great amount of heat. Temperatures can reach 2,500° C (4,530° F). Examples of flammable metals include: cerium, lutetium, silicon (powder), neodymium (in some forms), and aluminum (granules).

When metals burn, heat accelerates and supports the oxidation of the metal surface. The oxides and other gases produced when metals burn are all hazardous. They may be toxic, corrosive, or asphyxiating.

Pyrophoric

Substances that are pyrophoric have the potential to ignite spontaneously in air at room temperature. Many pyrophoric materials are also water-reactive (but not all water-reactive materials are pyrophoric).

Exposure to air or moisture can cause these materials to evolve heat, fire and/or corrosive byproducts by violent decomposition. These materials are typically packaged and stored under an inert atmosphere, under oil, or within a solvent.

Self-heating

A *self-heating chemical* is a solid or liquid chemical, other than a pyrophoric liquid or solid, which, by reaction with air and without energy supply, is liable to self-heat; this chemical differs from a pyrophoric liquid or solid in that it will ignite only when in large amounts (kilograms) and after long periods of time (hours or days). (GHS definition)

Self-heating of a substance or mixture is a process where the gradual reaction of that substance or mixture with oxygen (in air) generates heat. If the rate of heat production exceeds the rate of heat loss, then the temperature of the substance or mixture will rise which, after an induction time, may lead to self-ignition and combustion. (DOT definition)

There are a variety of oxidizable materials that when finely divided can self-heat including metal turnings, sawdust and activated charcoal. Some otherwise non-hazardous substances such as cotton can self-heat if stored or shipped in large quantities and if there is sufficient moisture.

Water-Reactive Materials

Water-reactive substances are materials that react vigorously (or even explosively) with water (including moisture in the air). Metals such as sodium, potassium and lithium fall into this category. When such substances contact water they emit spontaneously flammable gases or give off flammable gases in dangerous quantities. Calcium carbide is an example of a water-reactive material. When it combines with water it produces acetylene gas.

Summary

Responders rarely encounter flammable solids, however, when they do, they face dynamic and challenging events. Fires involving flammable solids can be catastrophic and nearly impossible to extinguish. It’s essential to understand the properties and potential hazards of these materials to be able to effectively respond to an incident involving these materials.

Chapter Review

1. What water-reactive material produces acetylene gas when it combines with water?
   A. Calcium sulfide
   B. Divinyl sulfide
   C. Sodium hydroxide
   D. Calcium carbide

2. Which Division of Hazard Class 4 includes Flammable Solids?
   A. 4.1
   B. 4.2
   C. 4.3
   D. 4.4

3. What type of substances have the potential to ignite spontaneously in air at room temperature?
   A. Readily combustible
   B. Self-heating
   C. Pyrophoric
   D. Hypergolic

4. Which of the following materials can self-heat?
   A. Molten sulfur
   B. Cotton
   C. Solid lithium
   D. Mercury

Chapter 12: Oxidizers and Organic Peroxides – Hazard Class 5

Oxidizing materials are liquids, gases or solids that readily give off oxygen or other oxidizing substances (e.g. bromine, chlorine, or fluorine) with little or no energy input. (Oxidizing agents remove electrons from another substance.) Oxidizing liquids and solids can be severe fire and explosion hazards. They are not necessarily combustible, but they can intensify combustion and increase the flammable range for chemicals so they ignite more readily. They can cause a material that normally doesn't burn freely to spontaneously ignite in air.

Organic peroxides are organic compounds having two oxygen atoms joined together (-O-O-). This chemical group is called a "peroxy" group. Organic peroxides can be severe fire and explosion hazards. They may also be toxic and corrosive. They are generally unstable.

Both can make an otherwise routine incident potentially catastrophic.

On 16 April 1947 the SS Grandcamp, loaded with a cargo of ammonium nitrate exploded in Texas City, TX. A fire in a cargo hold heated the ammonium nitrate to the point where it became unstable. At 9:12 AM the ship exploded. 500-600 people were killed and thousands were injured.

On April 17, 2013, a fire occurred at the West Fertilizer Company storage and distribution facility in West, TX. The facility stored a large quantity of ammonium nitrate .While emergency services personnel were responding to the fire the facility exploded. Fifteen people were killed and more than 160 were injured.

On 4 May 1988 a fire started at the Pacific Engineering and Production Company of Nevada (PEPCON) plant in Henderson, NV. The facility produced and stored ammonium perchlorate, an oxidizer used in solid propellant rocket boosters, including the Space Shuttle. The conflagration and subsequent explosions killed two people, injured 372 others.

DOT Hazard Class 5

Oxidizers and Organic Peroxides are in DOT Hazard Class 5. This Hazard Class has two Divisions. The U.S. Department of Transportation defines this class as follows:

49 CFR §173.127 Class 5, Division 5.1—Definition

(a) A material that may, generally by yielding oxygen, cause or enhance the combustion of other materials.

(1) A solid material is classed as a Division 5.1 material if, when tested in accordance with the UN Manual of Tests and Criteria (IBR, see §171.7 of this subchapter):

(2) A liquid material is classed as a Division 5.1 material if, when tested in accordance with the UN Manual of Tests and Criteria, it spontaneously ignites or its mean time for a pressure rise from 690 kPa to 2070 kPa gauge is less than the time of a 1:1 nitric acid (65 percent)/cellulose mixture.

49 CFR §173.128 Class 5, Division 5.2—Definition and Types

(a) *Definitions.* For the purposes of this subchapter, *organic peroxide (Division 5.2)* means any organic compound containing oxygen (O) in the bivalent -O-O- structure and which may be considered a derivative of hydrogen peroxide, where one or more of the hydrogen atoms have been replaced by organic radicals…

(b) *Generic types.* Division 5.2 organic peroxides are assigned to a generic system which consists of seven types. An organic peroxide identified by technical name in the Organic Peroxides Table in §173.225 is assigned to a generic type in accordance with that table. Organic peroxides not identified in the Organic Peroxides table are assigned to generic types under the procedures of paragraph (c) of this section.

(1) *Type A.* Organic peroxide type A is an organic peroxide which can detonate or deflagrate rapidly as packaged for transport. Transportation of type A organic peroxides is forbidden.

(2) *Type B.* Organic peroxide type B is an organic peroxide which, as packaged for transport, neither detonates nor deflagrates rapidly, but can undergo a thermal explosion.

(3) *Type C.* Organic peroxide type C is an organic peroxide which, as packaged for transport, neither detonates nor deflagrates rapidly and cannot undergo a thermal explosion.

(4) *Type D.* Organic peroxide type D is an organic peroxide which—

(i) Detonates only partially, but does not deflagrate rapidly and is not affected by heat when confined;

(ii) Does not detonate, deflagrates slowly, and shows no violent effect if heated when confined; or

(iii) Does not detonate or deflagrate, and shows a medium effect when heated under confinement.

(5) *Type E.* Organic peroxide type E is an organic peroxide which neither detonates nor deflagrates and shows low, or no, effect when heated under confinement.

(6) *Type F.* Organic peroxide type F is an organic peroxide which will not detonate in a cavitated state, does not deflagrate, shows only a low, or no, effect if heated when confined, and has low, or no, explosive power.

(7) *Type G.* Organic peroxide type G is an organic peroxide which will not detonate in a cavitated state, will not deflagrate at all, shows no effect when heated under confinement, and shows no explosive power. A type G organic peroxide is not subject to the requirements of this subchapter for organic peroxides of Division 5.2 provided that it is thermally stable (self-accelerating decomposition temperature is 50 °C (122 °F) or higher for a 50 kg (110 pounds) package). An organic peroxide meeting all characteristics of type G except thermal stability and requiring temperature control is classed as a type F, temperature control organic peroxide.

Examples of Oxidizers and Organic Peroxides (DOT Hazard Class 5)

Division 5.1, Oxidizers

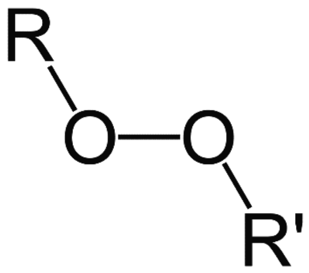
- Ammonium perchlorate
- Calcium Chlorate
- Calcium Hypochlorite
- Hydrogen Peroxide
- Nitrates
- Red Fuming Nitric Acid

Division 5.2, Organic Peroxides

- Benzoyl Peroxide
- Methyl Ethyl Ketone Peroxide
- Peracetic acid

Organic Peroxide Chemical Structure

Contains the peroxide functional group (ROOR')



GHS Definitions

The Globally Harmonized System (GHS) has different definitions for oxidizers.

Oxidizing Gas: A gas which may, generally by providing oxygen, cause or contribute to the combustion of other material more than air dies.

Oxidizing Liquids: A liquid which, while in itself not necessarily combustible, may, generally by yielding oxygen, cause, or contribute to, the combustion of other material.

Oxidizing Solids: A solid which, while in itself is not necessarily combustible, may, generally by yielding oxygen, cause, or contribute to, the combustion of other material.

NFPA Classifications

The National Fire Protection Association (NFPA) Code 430 "Code for the Storage of Liquid and Solid Oxidizers" has classified oxidizing materials according to their ability to cause spontaneous combustion and how much they can increase the burning rate.

- *Class 1:* Does not moderately increase the burning rate of combustible materials with which it comes into contact.
- *Class 2:* Causes a moderate increase in the burning rate of combustible materials with which it comes into contact.
- *Class 3:* Causes a severe increase in the burning rate of combustible materials with which it comes into contact.
- *Class 4:* Can undergo an explosive reaction due to contamination or exposure thermal or physical shock and that causes a severe increase in the burning rate of combustible materials with which it comes into contact.

NFPA 432 "Code for the Storage of Organic Peroxide Formulations" classifies organic peroxides as follows:

- Class I: Formulations that present a deflagration hazard through easily initiated, rapid explosive decomposition.
- Class II: Formulations that present a severe fire hazard. The decomposition is not as rapid, violent, or complete as that produced by Class I formulations.
- Class III: Formulations that are characterized by rapid burning and high heat liberation due to decomposition.
- Class IV: Formulations that present fire hazards that are easily controlled. Reactivity has little effect on fire intensity.
- Class V: Formulations that do not present severe fire hazards. Those that do burn, do so with less intensity than ordinary combustibles.

Properties

General

Energy content increases with active oxygen content; the higher the molecular weight of the organic groups, the lower the energy content and, usually, the lower the hazard. However, the active oxygen content, in which transition from a simple to a higher order decomposition can occur, varies considerably between organic peroxide types (structures) and individuals within the types. For example, benzoyl peroxide (98%) at 6.5% active oxygen undergoes transition when burning from low- to high-order decomposition with slight confinement. By comparison, cumyl hydroperoxide (85%) at 8.9% active oxygen is relatively unaffected by the confinement of a steel drum.

Oxidation and Reduction

Oxidation is defined as the loss of one or more electrons by an atom or the gain of oxygen during a reaction. A fuel is oxidized when its electrons are removed and taken by another material, called an oxidizing agent or oxidizer.

Reduction is defined as the gain of one or more electrons by an atom or the loss of oxygen. Oxidation and reduction always occur together. The reducing agent (the fuel) supplies or donates the electrons to the oxidizing agent. Chemical reactions that involve the transfer of electrons are called oxidation-reduction (or redox) reactions.

Oxidizing Agents

Halogens: Oxidizing agents must be able to accept electrons readily. The elemental halogens, fluorine, chlorine, bromine and iodine, are able to accept electrons. Halogens are highly reactive due to the high electronegativity of the atoms. (In fact, they are so reactive that they don't exist in nature in their elemental form.) Because the halogens have seven valence electrons in their outermost energy level, they can gain an electron by reacting with atoms of other elements to satisfy the octet rule. Fluorine is one of the most reactive elements, attacking otherwise-inert materials such as glass.

Oxygen gas: An electronegative element which is a good oxidizing agent. It is very slightly weaker than chlorine, but considerably stronger than bromine. (Because the atmosphere contains such a strong oxidant, few substances occur in reduced form at the earth's surface.) Oxygen gas can act as an oxidizer in both its pure form and in combination with other elements, such as air. Oxygen in the air can react with materials with slow oxidation potential (e.g., linseed oil) to produce combustion. Oxygen in the air can also react with ethers, aldehydes, and alcohols to produce unstable organic peroxides.

Elemental oxygen in both its gaseous and liquid states can react violently with hydrocarbon-based materials. Oxygen gas in contact with oil or grease can cause combustion or an explosion. Liquid oxygen in contact with asphalt can also result in a violent chemical reaction.

Oxyanions and oxyacids: In aqueous solution NO_3–, IO_3–, MnO_4–, $Cr_2O_7^{-2}$–, and a number of other oxyanions are strong oxidizing agents. Many oxyacids are very corrosive in addition to being oxidizers. Nitric acid (HNO_3) in concentrations above 40% is extremely corrosive and is an oxidizing oxyacid. (Nitric acid is commonly used to manufacture rocket propellants and explosives.) Perchloric acid ($HClO_4$) is another strong oxyacid. It has such strong oxidizing properties that it can readily react with combustible materials to cause ignition. Perchloric acid at 100% concentration is unstable and can detonate if it comes in contact with a cellulose-based material. Oxyacids can be sensitive to friction. Some, such as Peracetic acid can be toxic.

Metal peroxide salts: Most of the metal peroxide salts**,** which are strong oxidizers, are combinations of the peroxide functional group (-O-O-) and a Group 1 alkali metal or Group 2 alkaline earth metal. Many of these salts are also water-reactive.

Examples of Metal Peroxides

Name	Formula
Lithium Peroxide	Li_2O_2
Sodium Peroxide	Na_2O_2
Potassium Peroxide	K_2O_2
Calcium Peroxide	CaO_2

Inorganic peroxides: The most common inorganic peroxide is hydrogen peroxide (H_2O_2). In its concentrated form, it is highly corrosive, toxic, and sensitive (reactive) to contamination (especially organic matter). Concentrated hydrogen peroxide is a common industrial chemical.

Oxidizers

Oxidizers contain two or more covalently bonded oxygen atoms and/or halogen atoms. A variety of materials can be oxidizers. Examples include halogens, peroxide salts, oxysalts, oxyacids, organic peroxides, or organic peroxy acids.

Oxidizers, as a class, are reactive and support combustion through the release of oxygen, heat or both. The reactions can be violent and explosive. Contact between oxidizers and flammable or combustible materials can be extremely hazardous. Oxidizers are recognized by name or by formula. A general rule of thumb: if a compound name has a "hypo-" or "per-" prefix, an "-ate," "-ite" or "peroxide" ending, or "peroxy" as part of the name, treat it as an oxidizer.

Prefixes and Suffixes of the Names of Oxidizers

Prefixes/Suffixes	Meaning
-ate	A salt that contains a large number of oxygen atoms
-ite	A salt that contains a fewer number of oxygen atoms
Per-	A compound containing an element in its highest state of oxidation
Peroxy-	A compound containing the peroxide functional group (-O-O-) in its highest state of oxidation

Examples of Common Oxidizers

Ammonium nitrate

Ammonium nitrate is a nitrate salt. The chemical formula is NH_4NO_3, often simplified to $N_2H_4O_3$. It is a white crystal solid and is highly soluble in water. It is predominantly used in agriculture as a high-nitrogen fertilizer. Ammonium nitrate based fertilizers are usually a grayish white solid in the form of prills. It’s frequently added to other fertilizers to increase their nitrogen content.

Its other major use is as a component of explosive mixtures used in mining, quarrying, and civil construction. It is the major constituent of ammonium nitrate fuel oil (ANFO), a widely used industrial explosive. It accounts for 80% of explosives used in North America.

It’s relatively stable under most conditions and is inexpensive to manufacture. Ammonium nitrate is not, on its own, an explosive, but it readily forms explosive mixtures with varying properties when combined with primary explosives such as azides or with fuels such as aluminum powder and/or fuel oil.

DOT classifies ammonium nitrate as an oxidizer (5.1). Some formulations of ANFO are classified as explosives (1.1D).

Hydrogen peroxide

Hydrogen peroxide (H_2O_2) is a liquid slightly more viscous than water. The nature of the peroxide bond makes it unstable. It slowly decomposes exothermically in the presence of a base or a catalyst to oxygen and water. (At room temperature the rate of decomposition is very low.) It is the simplest of the peroxides and has strong oxidizing properties. It can cause spontaneous combustion when it comes in contact with organic material.

It is commonly used (in concentrations typically around 5%) to bleach human hair. It burns the skin upon contact in sufficient concentration. In lower concentrations (3%), it is used medically for cleaning wounds, removing dead tissue and to clean blood from cloth and equipment. Concentrated hydrogen peroxide has been used as a component of rocket fuels.

DOT classifies hydrogen peroxide as an oxidizer (5.1).

Ammonium permanganate

Ammonium permanganate is a crystal or powder with a rich violet-brown or dark purple metallic sheen. It is toxic by ingestion or inhalation of dust. Dry ammonium permanganate may explode on shock, friction or heating. Mixtures with acetic acid or acetic anhydride may explode if not kept cold. Explosions can occur when permanganates that have been treated with sulfuric acid come in contact with benzene, carbon disulfide, diethyl ether, ethyl alcohol, petroleum, or organic matter.

It is soluble in water and is a strong oxidizer. It is a moderately strong explosive, owing to the combination of oxidizer permanganate anion and reducing ammonium cation. Dry ammonium permanganate can detonate by heat, shock, or friction, and it may explode at temperatures above 140F (60C).

Ammonium permanganate decomposes explosively to manganese dioxide, nitrogen, and water. Ammonium permanganate decomposes slowly in storage even at normal temperatures. It emits toxic fumes when decomposed by heat.

DOT doesn't allow ammonium permanganate or its aqueous solutions to be transported.

Ammonium perchlorate

Ammonium perchlorate is a white, crystalline, solid or powder inorganic compound with the formula NH4ClO4. It is the salt of perchloric acid and ammonia. It's a powerful oxidizer is used in the manufacture of rocket propellants; explosives and pyrotechnics. It will burn if contaminated by combustible materials. It may explode under prolonged exposure to heat or fire such as in the PEPCON disaster.

Ammonium perchlorate is considered acutely toxic and can be harmful if swallowed, cause serious eye irritation, skin irritation, and may cause respiratory tract irritation if its dust is inhaled.

When powdered into particles smaller than 15 microns in diameter or if powdered into larger particles but thoroughly dried, ammonium perchlorate is classified as a division 1.1 explosive. Otherwise, DOT classifies it as an oxidizer (5.1).

Perchloric acid (>72.5%)

Perchloric acid ($HClO_4$) is a strong mineral acid. It is a clear liquid with no odor. Perchloric acid becomes a strong oxidizer when heated or at higher concentrations, at or above 73%. Organic, metallic and non-organic salts formed from oxidation are shock sensitive and pose a fire and explosion hazard.

Perchloric acid is destructive to human tissue as well as very reactive. Anhydrous perchloric acid (> 85% concentration) is very unstable and will usually explode when it comes in contact with organic materials.

DOT doesn't allow Perchloric acid (>72.5%) to be transported. Perchloric acid with more than 50 percent but not more than 72 percent acid, by mass is classified as an oxidizer (5.1).

Tetranitromethane

Tetranitromethane is a pale yellow liquid. It irritates skin and respiratory tract and is very toxic by inhalation. It's difficult to ignite but burns at a steady rate once ignited. Under prolonged exposure to fire or heat containers may rupture violently and rocket Tetranitromethane produces toxic oxides of nitrogen during combustion. Tetranitromethane is a dangerous substance of relatively limited practical use.

It has been investigated for use as an oxidizer in bipropellant rockets; however, its high freezing temperature makes it unsuitable. Highly purified tetranitromethane cannot be made to explode, but its sensitivity is increased dramatically by oxidizable contaminants, such as anti-freezing additives. This makes it effectively unusable as a propellant.[

In the laboratory it is used as a reagent for the detection of double bonds in organic compounds and as a nitrating reagent. It has also found use as an additive to diesel fuel to increase the cetane number.

DOT classifies Tetranitromethane as toxic (6.1) and an oxidizer (5.1).

Red Fuming nitric acid (>86%)

Red Fuming nitric acid is concentrated nitric acid that contains dissolved nitrogen dioxide. It isn’t combustible but increases the flammability of combustible materials. Nitric acid is a highly corrosive mineral acid. The pure compound is colorless, but older samples tend to acquire a yellow cast due to decomposition into oxides of nitrogen and water. Most commercially available nitric acid has a concentration of 68% in water. When the solution contains more than 86% HNO_3, it is referred to as fuming nitric acid. Nitric acid is commonly used as a strong oxidizing agent. It reacts violently with many non-metallic compounds. The reactions may be explosive.

DOT classifies nitric acid other than red fuming, with more than 70 percent nitric acid as a corrosive (8) and an oxidizer (5.1).

Calcium chlorate

Calcium chlorate is a white crystalline solid. It forms a very flammable mixture with combustible materials and this mixture may be explosive if the combustible material is finely divided. The mixture can be ignited by friction. Contact with strong sulfuric acid can cause fires or explosions. When mixed with ammonium salts, spontaneous decomposition and ignition may result. Prolonged exposure of the material to fire or heat can result in an explosion. It is used in photography, in pyrotechnics, and as an herbicide.

DOT classifies calcium chlorate as an oxidizer (5.1)

Organic Peroxides

Organic peroxides are useful in chemical synthesis due to their propensity to decompose. When they decompose they generate radicals that can initiate polymerization to create or modify polymers. Organic peroxides and mixtures containing organic peroxides are used as accelerators, activators, catalysts, cross-linking agents, curing agents, hardeners, initiators and promoters in the plastics and rubber industries. (However, these terms can also refer to materials that do not contain organic peroxides.)

When used for these purposes, the peroxide is highly diluted, so the heat generated by the exothermic decomposition is safely absorbed by the surrounding medium (e.g. polymer compound or emulsion). But when a peroxide is in a more pure form, the heat evolved by its decomposition may not dissipate as quickly as it is generated, which can result in increasing temperature, which further intensifies the rate of exothermic decomposition. This can create a dangerous situation known as a self-accelerating decomposition.

Organic peroxides contain the “peroxy” group which has a double oxygen component (with a relatively weak bond). The peroxy group is chemically unstable. It can easily decompose, giving off heat at a rate that increases as the temperature rises. Many organic peroxides give off flammable vapors when they decompose. These vapors can easily catch fire.

Most undiluted organic peroxides can catch fire easily and burn very rapidly and intensely. This is because they combine both fuel (carbon) and oxygen in the same compound. Some organic peroxides are dangerously reactive. They can decompose very rapidly or explosively if they are exposed to only slight heat, friction, mechanical shock or contamination with incompatible materials. This is especially problematic when organic peroxides are contaminated with other materials. Heat, mechanical shock, friction, shaking or contamination can initiate explosive decomposition of many organic peroxides.

Organic peroxides can form spontaneously. This can occur when materials such as ethyl ether, tetrahydrofuran (THF), p-dioxane become concentrated (e.g., by distillation). Exposure to light and heat can increase the rate of peroxide formation. Unsaturated monomers such as uninhibited styrene that can form a peroxide that can cause the styrene to polymerize exothermically. Under the proper conditions this can result in a violent explosion. Other examples of unsaturated monomeric compounds that can spontaneously form peroxides are acrylic acid, acrylonitrile, butadiene, methyl methacrylate, and vinyl chloride.

Reactivity

Organic peroxides are very sensitive to contamination (especially heavy-metal compounds, metal oxide salts, alkaline materials including amines, strong acids, and many varieties of dust and dirt). This can initiate rapid, uncontrolled decomposition of peroxides and possible fire or explosion. The consequences of accidental contamination from returning withdrawn material to the storage container can be disastrous. Once withdrawn, peroxides must never be returned to its storage container.

Autoxidation

Autoxidation is the spontaneous oxidation of a compound in air. It can occur in open air or in presence of oxygen (and sometimes UV radiation). The process forms peroxides and hydro peroxides which can be unstable and explosion-prone. A classic example of autoxidation is that of simple ethers like diethyl ether, whose peroxides can be dangerously explosive. In the presence of oxygen ethers slowly autoxidize to form hydroperoxides and dialkyl peroxides. If concentrated or heated these peroxides may explode.

Although ethers are commonly recognized as being subject to autoxidation, other organic compounds are capable of spontaneous autoxidation. Other common compounds such as acetals, certain allylic alkenes, chloro- and fluoroalkenes, aldehydes, amides, ureas, some alkylarenes, ketones, vinyl monomers, and some alcohols can undergo autoxidation to produce unstable and dangerous hydroperoxide and peroxides products.

Self-Accelerating Decomposition Temperature (SADT)

Organic peroxides may have what is known as a "self-accelerating decomposition temperature" (SADT). Temperature is the main factor in the rate of decomposition. A self-accelerating decomposition occurs when the rate of decomposition generates heat at a faster rate than it can be dissipated. The resulting reaction can be violent. If the container ruptures decomposition products can spread considerable distances. The heat generated by this decomposition may ignite flammable vapors.

SADT represents the lowest temperature in which a particular organic peroxide formulation in its commercial packaging will undergo self-accelerating decomposition (i.e. begin the chemical process that can lead to a violent explosion). The SADT value will vary with each organic peroxide formulation and the size and shape of its packaging. Responders should consult the Safety Data Sheet (SDS) for the material involved to determine the SADT. (For shipping purposes, the SADT is the lowest temperature at which self-accelerating decomposition occurs in the DOT shipping container when held at that temperature for a period of seven days. Storage requirements will generally be 10°F below the SADT.)

Another important property is the Maximum Safe Storage Temperature (MSST). This is the highest storage temperature above which a decomposition reaction and explosion may ensue.

In an incident involving organic peroxides, if the temperature of the product involved is at or near the SADT or MSST this is an extremely dangerous situation. Responders should expect a violent explosion and take action accordingly.

Peroxide-Forming Chemicals

These are often "time-sensitive" chemicals which are any chemicals or chemical products that develop additional hazards upon prolonged storage.

Time-sensitive chemicals may include substances known as "Peroxide Former" which are oxygenated organic compounds that react with atmospheric oxygen to form explosive peroxides. Examples are commonly found in university labs. They include: sodium amide, diethyl ether, dioxane, tetrahydrofuran, and benzyl alcohol.

Peroxide Formers may be characterized by having a mossy look around the cap. There may be a white film or residue around the neck, threads or cap of the container or there may be crystals in the liquid. For solid peroxide formers, there may be discoloration or the formation of a surface crust.

Note: Never, under any circumstances, touch or attempt to open a container of peroxide-forming liquid if there are whitish crystals around the cap and/or in the bottle. The friction of unscrewing the cap could detonate the bottle and cause severe injury.

Summary

Oxidizers

Oxidizers have a wide variety of uses. They are used to support combustion such as in various types of pyrotechnics, rocket fuels and explosives. Others, such as ammonium nitrate and calcium chlorate are used in agriculture as fertilizers or herbicides. Oxidizers such as chlorine dioxide and calcium hypochlorite are used as bleaching agents or to sanitize water. They are also used as precursors in the synthesis of other substances.

Organic Peroxides

The plastics and rubber industries are the heaviest users of organic peroxides. Organic peroxides and mixtures containing an organic peroxide are used as accelerators, activators, catalysts, cross-linking agents, curing agents, hardeners, initiators and promoters. Organic peroxides and mixtures containing an organic peroxide are often referred to by these terms. However, using terms like accelerator, activator, etc. to mean “organic peroxide” can be misleading since they can also refer to materials that do not contain organic peroxides. This can cause confusion and a serious accident could result if these substances were mixed with organic peroxides. They are also used as bleaching and disinfecting agents.

Prevalence

Although oxidizers and organic peroxides account for less than 5% of both transportation-related and fixed facility hazmat incidents they are capable of making a bad incident a lot worse. Under the right conditions and incident involved organic peroxides can be catastrophic. Anytime these substances are involved in and incident it should be cause for concern.

Chapter Review

1. What is the primary hazard of oxidizers?
    - A. They deplete oxygen in the atmosphere
    - B. They can interfere with reduction
    - C. They are above the line
    - D. They can intensify combustion

2. Oxidizers contain what chemical structure?
    - A. –OH
    - B. –COOH
    - C. -O-O-
    - D. H-O

3. Organic Peroxides are in which DOT Division?
    - A. 5.1
    - B. 5.2
    - C. 5.3
    - D. 5.4

4. Which of the following is an example of an oxidizer?
    - A. Calcium chlorate
    - B. Benzene
    - C. Hafnium powder
    - D. Trimethyl borate

5. Which Group on the Periodic Table tend to be oxidizers?
    - A. Noble gases
    - B. Halogens
    - C. Actinides
    - D. Metalloids

6. Which of the following suffixes would indicate a material that is a salt that contains a large number of oxygen atoms?
    - A. hyper
    - B. per
    - C. ite
    - D. ate

7. Organic peroxides tend to decompose ___________________________ .
   - A. Slowly
   - B. Evaporatively
   - C. Exothermically
   - D. Endothermically

8. Fill in the acronym for the property described.

Property/Behavior	Acronym
The rate of decomposition generates heat at a faster rate than it can be dissipated:	___________________________
The highest storage temperature above which a decomposition reaction and explosion may ensue:	___________________________

9. Many oxidizers and organic peroxides will fall into two or more DOT hazard classes. Fill in the hazard classes for the substance listed.

Substance	Hazard Classes
Red Fuming Nitric Acid	___________________________
Tetranitromethane	___________________________
Ammonium nitrate	___________________________
Ammonium perchlorate	___________________________
Nitric acid	___________________________

Chapter 13: Poisonous Materials and Infectious Substance – Hazard Class 6

Nearly every substance is toxic, but not all fall into Hazard Class 6. Materials in Hazard Class 6 are those that can kill you or make you sick in small quantities. DOT regulations have detailed and precise definitions for what they consider to be poisonous.

About 15% of the materials regulated by the U.S. Department of Transportation (DOT) are classified as Poisonous. However, only a relative handful of materials in this Hazard Class are involved in hazmat incidents. Many of these substances are only permitted to be transported in small containers and are not allowed to be transported by some modes of transportation.

DOT Hazard Class 6

This Hazard Class has two Divisions: Poisonous Materials (6.1) and Infectious Substance (Etiologic agent) (6.2). The U.S. Department of Transportation defines this class as follows:

49 CFR §173.132 Class 6, Division 6.1—Definitions

(a) For the purpose of this subchapter, *poisonous material* (Division 6.1) means a material, other than a gas, which is known to be so toxic to humans as to afford a hazard to health during transportation, or which, in the absence of adequate data on human toxicity:

(1) Is presumed to be toxic to humans because it falls within any one of the following categories when tested on laboratory animals (whenever possible, animal test data that has been reported in the chemical literature should be used):

(i) *Oral Toxicity.* A liquid or solid with an LD_{50} for acute oral toxicity of not more than 300 mg/kg.

(ii) *Dermal Toxicity.* A material with an LD_{50} for acute dermal toxicity of not more than 1000 mg/kg.

(iii) *Inhalation Toxicity.* (A) A dust or mist with an LC_{50} for acute toxicity on inhalation of not more than 4 mg/L; or

(B) A material with a saturated vapor concentration in air at 20 °C (68 °F) greater than or equal to one-fifth of the LC_{50} for acute toxicity on inhalation of vapors and with an LC_{50} for acute toxicity on inhalation of vapors of not more than 5000 mL/m^3; or

(2) Is an irritating material, with properties similar to tear gas, which causes extreme irritation, especially in confined spaces.

§173.132 Class 6, Division 6.2—Definitions and exceptions.

(a) *Definitions and classification criteria.* For the purposes of this subchapter, the following definitions and classification criteria apply to Division 6.2 materials.

(1) *Division 6.2 (Infectious substance)* means a material known or reasonably expected to contain a pathogen. A pathogen is a microorganism (including bacteria, viruses, rickettsiae, parasites, fungi) or other agent, such as a proteinaceous infectious particle (prion), that can cause disease in humans or animals.

(2) *Biological product* means a virus, therapeutic serum, toxin, antitoxin, vaccine, blood, blood component or derivative, allergenic product, or analogous product, or arsphenamine or derivative of arsphenamine (or any other trivalent arsenic compound) applicable to the prevention, treatment, or cure of a disease or condition of human beings or animals.

(3) *Culture* means an infectious substance containing a pathogen that is intentionally propagated. *Culture* does not include a human or animal patient specimen as defined in paragraph (a)(4) of this section.

(4) *Patient specimen* means human or animal material collected directly from humans or animals and transported for research, diagnosis, investigational activities, or disease treatment or prevention. *Patient specimen* includes excreta, secreta, blood and its components, tissue and tissue swabs, body parts, and specimens in transport media (*e.g.*, transwabs, culture media, and blood culture bottles).

(5) *Regulated medical waste or clinical waste or (bio) medical waste* means a waste or reusable material derived from the medical treatment of an animal or human, which includes diagnosis and immunization, or from biomedical research, which includes the production and testing of biological products. Regulated medical waste or clinical waste or (bio) medical waste containing a Category A infectious substance must be classed as an infectious substance, and assigned to UN2814 or UN2900, as appropriate.

(6) *Sharps* means any object contaminated with a pathogen or that may become contaminated with a pathogen through handling or during transportation and also capable of cutting or penetrating skin or a packaging material. *Sharps* includes needles, syringes, scalpels, broken glass, culture slides, culture dishes, broken capillary tubes, broken rigid plastic, and exposed ends of dental wires.

(7) *Toxin* means a Division 6.1 material from a plant, animal, or bacterial source. A *toxin* containing an infectious substance or a *toxin* contained in an infectious substance must be classed as Division 6.2, described as an infectious substance, and assigned to UN 2814 or UN 2900, as appropriate.

(8) *Used health care product* means a medical, diagnostic, or research device or piece of equipment, or a personal care product used by consumers, medical professionals, or pharmaceutical providers that does not meet the definition of a patient specimen, biological product, or regulated medical waste, is contaminated with potentially infectious body fluids or materials, and is not decontaminated or disinfected to remove or mitigate the infectious hazard prior to transportation.

(9) Dried blood spots or specimens for fecal occult blood detection placed on absorbent filter paper or other material.

(10) A Division 6.2 material, other than a Category A infectious substance, contained in a patient sample being transported for research, diagnosis, investigational activities, or disease treatment or prevention, or a biological product, when such materials are transported by a private or contract carrier in a motor vehicle used exclusively to transport such materials. Medical or clinical equipment and laboratory products may be transported aboard the same vehicle provided they are properly packaged and secured against exposure or contamination. If the human or animal sample or biological product meets the definition of regulated medical waste in paragraph (a)(5) of this section, it must be offered for transportation and transported in conformance with the appropriate requirements for regulated medical waste.

(11) A human or animal sample (including, but not limited to, secreta, excreta, blood and its components, tissue and tissue fluids, and body parts) being transported for routine testing not related to the diagnosis of an infectious disease, such as for drug/alcohol testing, cholesterol testing, blood glucose level testing, prostate specific antibody testing, testing to monitor kidney or liver function, or pregnancy testing, or for tests for diagnosis of non-infectious diseases, such as cancer biopsies, and for which there is a low probability the sample is infectious.

(12) Laundry and medical equipment and used health care products…

(13) Any waste or recyclable material, other than regulated medical waste, including—

(i) Household waste as defined in §171.8, when transported in accordance with applicable state, local, or tribal requirements.

(ii) Sanitary waste or sewage;

(iii) Sewage sludge or compost;

(iv) Animal waste generated in animal husbandry or food production; or

(v) Medical waste generated from households and transported in accordance with applicable state, local, or tribal requirements.

(14) Corpses, remains, and anatomical parts intended for interment, cremation, or medical research at a college, hospital, or laboratory.

(15) Forensic material transported on behalf of a U.S. Government, state, local or Indian tribal government agency…

(16) Agricultural products and food as defined in the Federal Food, Drug, and Cosmetics Act (21 U.S.C. 332 *et seq.*).

Examples of Poisonous Materials and Infectious Substance (Etiologic agent) (Hazard Class 6).

Division 6.1, Poisonous Materials

- Acrolein, stabilized
- Allyl alcohol
- Uranium hexafluoride
- Tear gas
- Strychnine
- Sodium fluoride

Division 6.2, Infectious Substances

- Medical Waste
- Biological substance, Category B
- Infectious substances

GHS Definitions

The Globally Harmonized System (GHS) classifies toxic materials as follows:

GHS Categories, Acute Toxicity

Exposure Route	**Category 1**	**Category 2**	**Category 3**	**Category 4**	**Category 5**
Oral (mg/kg of bodyweight)	≤ 5	> 5 ≤ 50	> 50 ≤ 300	> 300 ≤ 2000	> 2000 ≤ 5000
Dermal (mg/kg of bodyweight)	≤ 50	> 50 ≤ 200	> 200 ≤ 1000	> 1000 ≤ 2000	
Gases (ppm)	≤ 100	> 100 ≤ 500	> 500 ≤ 2500	> 2500 ≤ 5000	
Vapors (mg/l)	≤ 0.5	> 0.5 ≤ 2.0	> 2.0 ≤ 10	> 10 ≤ 20	
Dusts & Mists (mg/l)	≤ 0.05	> 0.05 ≤ 0.5	> 0.5 ≤ 1.0	> 1.0 ≤ 5	

Label Elements for Acute Toxicity

	Category 1	**Category 2**	**Category 3**	**Category 4**	**Category 5**
Symbol	Skull & Crossbones	Skull & Crossbones	Skull & Crossbones	Exclamation Mark	None
Signal Word	Danger	Danger	Danger	Warning	Warning
Hazard Statement					
Oral	Fatal if swallowed	Fatal if swallowed	Toxic if swallowed	Harmful if swallowed	May be harmful if swallowed
Dermal	Fatal in contact with skin	Fatal in contact with skin	Toxic in contact with skin	Harmful in contact with skin	May be harmful in contact with skin
Inhalation	Fatal if inhaled	Fatal if inhaled	Toxic if inhaled	Harmful if inhaled	May be harmful if inhaled

NFPA Classifications

The National Fire Protection Association (NFPA) Code 704 “Standard System for the Identification of the Hazards of Materials for Emergency Response” has classified toxic materials according to the probable severity of the effects of exposure to emergency response personnel.

- 4: Materials that, under emergency conditions, can be lethal.
- 3: Materials that, under emergency conditions, can cause serious or permanent injury.
- 2: Materials that, under emergency conditions, can cause temporary incapacitation or residual injury.
- 1: Materials that, under emergency conditions, can cause significant irritation.
- 0: Materials that, under emergency conditions, would offer no hazard beyond that of ordinary combustible materials.

Properties

General

Materials in DOT Hazard Class 6, Division 6.1 can be solids or liquids. (Toxic gases are included in Hazard Class 2.) They can be toxic by inhalation, ingestion and absorption. Materials in Division 6.2 can be solids, liquids, live pathogens (or their toxins), patient specimens, medical waste and used health care products. Their physical and chemical properties vary according to the physical state and physical makeup. Their properties can be broadly described as follows:

Terminology and Description of Poisons

Term	Definition
Carcinogen	A substance that causes cancer or promotes the formation of cancer.
Convulsant	A substance that induces convulsions and/or seizures.
“-icide”	Suffix meaning “to kill” (e.g., pesticide, insecticide, or herbicide).
Irritant	A substance that causes inflammation or other discomfort.
Mutagen	A substance that causes genetic mutation.
Poison	A toxin that is lethal at a given quantity.
Sensitizer	A substance that causes an allergic reaction after repeated exposures.
Teratogen	A substance that can disturb the development of an embryo or fetus.
Toxin	A poisonous substance produced within living cells or organisms.

Common Poison Groups

Alkyl halides. Also known as haloalkanes, are compounds in which one or more hydrogen atoms in an alkane have been replaced by halogen atoms (fluorine, chlorine, bromine or iodine). Alkyl halides fall into different classes depending on how the halogen atom is positioned on the chain of carbon atoms; there are some chemical differences between the various types. They are *usually* not flammable.

Aromatic hydrocarbons Six-sided ring structures. Some are naturally formed. These solvents tend to destabilize the membranes of the nervous system and disrupt their normal function. Some are also anesthetic.

Carbamates are compounds based upon esters of carbamic acid (NH_2COOH) which is only used in its numerous derivatives and salts (including aldicarb, carbaryl, formetamate, methomyl and propoxur), attached to an ammonia compound. Much like their organophosphate cousins, they inhibit cholinesterase. Carbamates are insecticides or herbicides, but are less dermally toxic and more environmentally friendly than the organophosphates. The insecticides are commonly mixed with hydrocarbon compounds for application, meaning they may also burn. The herbicides are commonly mixed with water for application purposes.

Cyanides have two distinctly different formulations. One, commonly referred to as “nitrile,” is an organo-cyanide covalently bonded to hydrocarbons to form pesticide liquids. The other, a solid, is ionically bonded to metals to form cyanide salts. These salts may then be mixed with water or acids to form solutions or gases of cyanide. Some of these materials are flammable and subject to polymerization.

Heavy metals are any of the metals having an atomic weight greater than sodium (22.9) or a specific gravity greater than 5.0, such as lead or mercury. Heavy metals are bioaccumulated in the body, causing damage to various organs such as the brain, kidneys, liver, and lungs.

Organophosphates are organic compounds containing phosphorous that are double bonded to sulfur or oxygen, such as the pyrophosphates, the esters of phosphynic and phosphonic acid, and the phosphoric esters of glycerol, glycol, and sorbitol. They are commonly used as pesticides. The pesticides are commonly mixed with hydrocarbon compounds for application purposes. These materials are cholinesterase inhibitors.

Summary

There are thousands of products classified as poisons and they are found everywhere. They are a diverse group consisting of a wide variety of substances. Responders should be alert for their presence.

Chapter Review

1. Which Division in Hazard Class 6 is *Infectious Substances*?
   - A. 6.1
   - B. 6.2
   - C. 6.3
   - D. 6.4

2. Which type of substance can cause inflammation or other discomfort?
   - A. Vexatiant
   - B. Mutagen
   - C. Sensitizer
   - D. Irritant

3. DOT Hazard Class 6, Division 6.1 can be in various physical states. Which physical state is *not* included in Hazard Class 6?
   - A. Solid
   - B. Liquid
   - C. Gas
   - D. Plasma

4. The Globally Harmonized System (GHS) classifies toxic materials into 5 categories. Which GHS symbol would indicate a substance is in Category 1?

A.

B.

C.

D.

5. What family of toxic substances will often bio accumulate?
   - A. Heavy metals
   - B. Carbamates
   - C. Organophosphates
   - D. Aromatic hydrocarbons

6. What NFPA 704 category would indicate that a substance can cause temporary incapacitation or residual injury?
   - A. 1
   - B. 2
   - C. 3
   - D. 4

Chapter 14: Radioactive Materials– Hazard Class 7

Most hazardous materials incidents have obvious hazards. For example, flammable liquid spills give off vapors that may either be burning or can easily be observed by smell or by combustible gas indicators. The effects of being exposed to burning flammable liquids (a skin burn) are obvious and immediate. Recognizing incidents involving radioactive materials can be a challenging task as it is impossible to detect radiation with human senses. We can't see, hear or smell radiation. It can only be detected with special instruments. Fortunately these instruments allow us to reliably detect and measure radiation.

Although recognizing incidents involving radioactive materials can be challenging there are standard protocols for assessing the hazards and protecting ourselves.

DOT Hazard Class 7

49 CFR §173.403 Subpart I—Class 7 (Radioactive) Materials — Definitions

Radioactive material means any material containing radionuclides where both the activity concentration and the total activity in the consignment exceed the values specified in the table in §173.436 or values derived according to the instructions in §173.433.

Properties

General

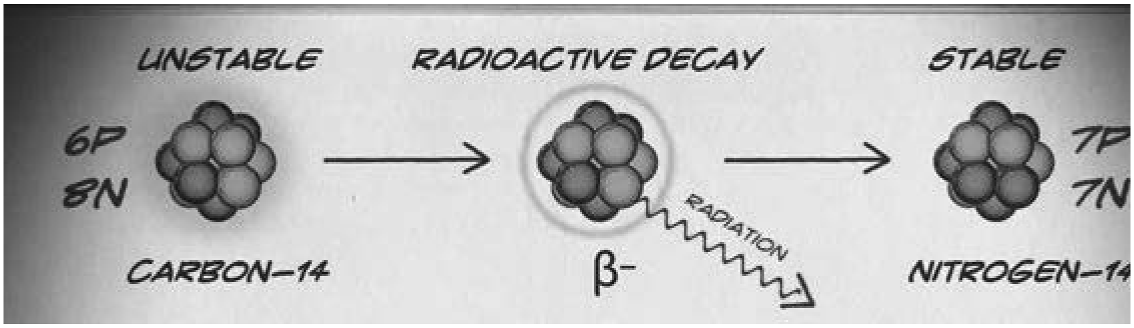
Radioactivity is the property of an unstable nuclide of undergoing spontaneous nuclear transformations with the emission of radiation from atomic nuclei. Radiation is electromagnetic waves (gamma radiation) as well as fast moving particles (alpha or beta particles) emitted during a nuclear process (i.e. radioactive decay, nuclear reaction or nuclear fission).

Radioactive Decay

Radioactive decay occurs when an atom has too many protons (or too few neutrons). As discussed in previous chapters, the nucleus of an atom consists of protons and neutrons. The protons have a positive charge and the neutrons have a neutral charge. In a stable atom the nuclear (i.e. attractive) force of the neutrons balances out the repulsive forces between the positively charged protons. If the attractive forces from the neutrons and the repulsive forces of the protons are imbalanced the nucleus of the atom then becomes unstable. The atom will eventually decay to reach a stable state.

Nuclear decay reactions always produce daughter nuclei that have a more favorable neutron-to- proton ratio and hence are more stable than the parent nucleus. Some radionuclides go through a series of transformations before they reach a stable state. For example, uranium-238 ultimately transforms into a stable atom of lead. But in the process, several types of radioactive atoms are generated. This is called a decay chain. When uranium-238 decays, it produces several isotopes of Thorium, Radium Radon and Bismuth.

Electromagnetic Spectrum



Half-Life

The length of time it takes for an atom to decay is measured in half-lives. Half-life is the length of time it takes for half of the radioactive atoms of a specific radionuclide to decay. A good rule of thumb is that, after seven half-lives, you will have less than one percent of the original amount of radiation.

Radioactive half-lives can range from milliseconds to hours, days, sometimes millions of years. In general, radionuclides used in nuclear medicine procedures have short half-lives. For example, technetium-99m, one of the most common medical isotopes used for imaging studies, has a half-life of 6 hours. After 24 hours, the radioactivity from the procedure will be reduced by more than 90%.The short half-life of technetium-99m helps keep the dose to the patient as low as possible.

Naturally occurring radioactive materials tend to have much longer half-lives. For example, uranium has an extremely long half-life. Naturally occurring uranium-238 present in the Earth's crust has a half-life of almost 4.5 billion years.

Behavior of Radioactive Materials

In previous chapters we discussed how atoms share or transfer electrons to form new compounds. In this type of reaction the atomic nuclei remain largely unaffected. When a compound (or element) is radioactive, though, the changes occur in the nucleus. In this case, the identity of the elements involved change.

The behavior of non-radioactive elements, compounds and substances is affected by changes in external forces such as temperature or atmospheric pressure or the presence of things such as catalysts or solvents. In the case of radioactive materials the rates of a nuclear reaction are generally unaffected by changes in temperature, pressure, or the presence of a catalyst.

Terminology of Radioactivity

Term	**Definition**
Nuclide	An atomic species in which the atoms all have the same atomic number and mass number.
Radionuclide	An unstable and therefore radioactive form of a nuclide.
Isotope	A chemical element, having the same number of protons in the nucleus, or the same atomic number, but having different numbers of neutrons in the nucleus, or different atomic weights.
Alpha Particle	Positively charged particles that consist of two protons and two neutrons bound together into a particle identical to a helium nucleus.
Beta Particle	A high-energy, high-speed electron or positron emitted in the radioactive decay of an atomic nucleus.
Gamma Radiation	An extremely high-frequency electromagnetic radiation consisting of high-energy photons.
Half Life	The time required for half the radioactive atoms in a specific radionuclide to decay.
Radioactive Decay	The change of one unstable nuclide into a stable nuclide by the release of radiation with a different proton number or nucleon number.
Radiation	Energy moving in the form of particles or waves. Familiar radiations are heat, light, radio waves, and microwaves. Ionizing radiation is a very high-energy form of electromagnetic radiation.
Fission	A radioactive decay process in which the nucleus of an atom splits into smaller parts (lighter nuclei).
Ionizing Radiation	The division of a nucleus into two or more parts with masses of equal order of magnitude, usually accompanied by the emission of neutrons, gamma radiation and, rarely, small charged nuclear fragments.

Types of Radiation

Radiation is a product of radioactive decay. It is important to distinguish between radioactive material and the radiation it gives off.

In general, there are two types of radiation, ionizing and non-ionizing. This chapter will focus on ionizing radiation.

The Nuclear Regulatory Commission (NRC) and the U. S. Department of Transportation (DOT) both regulate various aspects of the transportation and use of ionizing radiation. The Occupational Safety and Health Administration (OSHA) has regulations and policies designed to protect workers from non-ionizing radiation.

Non-ionizing Radiation

Non-ionizing radiation is a series of energy waves composed of oscillating electric and magnetic fields traveling at the speed of light. Non-ionizing radiation includes the spectrum of ultraviolet (UV), visible light, infrared (IR), microwave (MW), radio frequency (RF), and extremely low frequency (ELF). Lasers commonly operate in the UV, visible, and IR frequencies.

The dividing line between ionizing and non-ionizing radiation occurs in the ultraviolet part of the electromagnetic spectrum. Radiation in the ultraviolet band and at lower energies (to the left of ultraviolet) is called non-ionizing radiation, while at the higher energies to the right of the ultraviolet band is called ionizing radiation.

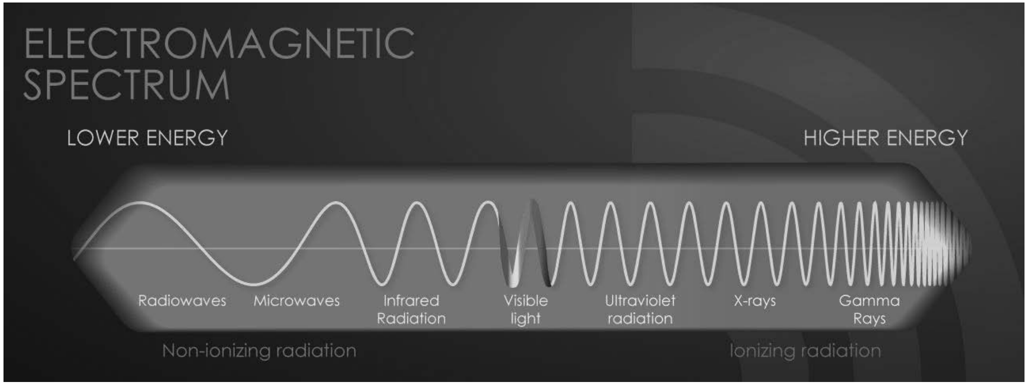
Non-ionizing radiation differs from ionizing radiation in the way it acts on materials like air, water, and living tissue. Unlike x-rays and other forms of ionizing radiation, non-ionizing radiation does not have enough energy to remove electrons from atoms and molecules.

Ionizing Radiation

Ionizing radiation occurs when an unstable atom decays. It is any radiation consisting of directly or indirectly ionizing particles or a mixture of both, or photons with energy higher than the energy of photons of ultraviolet light or a mixture of both such particles and photons.

It affects other matter by removing electrons from atoms and molecules of materials that include air, water, and living tissue. Ionizing radiation can travel unseen and pass through these materials. It is on the right side of the electromagnetic spectrum in the figure below.

Electromagnetic Spectrum



Ionizing radiation includes alpha particles, beta particles, gamma rays, x-rays, neutrons, high-speed electrons, high-speed protons, and other particles capable of producing ions. Compared to non-ionizing radiation, such as radio or microwaves, or visible, infrared, or ultraviolet light, ionizing radiation is considerably more energetic. When ionizing radiation passes through material such as air, water, or living tissue, it deposits enough energy to produce ions by breaking molecular bonds and displace (or remove) electrons from atoms or molecules. This electron displacement may lead to changes in living cells. Given this ability, ionizing radiation has a number of beneficial uses, including treating cancer or sterilizing medical equipment. However, ionizing radiation is potentially harmful if not used correctly, and high doses may result in severe skin or tissue damage.

Types of Ionizing Radiation

Alpha Particles

Alpha particles are energetic, positively charged particles consisting of two protons and two neutrons. Alpha particles are commonly emitted in the radioactive decay of the heaviest radioactive elements such as uranium-238, radium-226, and polonium-210. Even though they are highly energetic, the high mass of alpha particles means they move slowly through the air and only travel up to an inch in the air. They are easy to block, even with something as thin as a sheet of paper.

Alpha particles do not present an internal hazard to people because they can’t get through our outer layer of dead skin cells. However, they can cause adverse effects via other routes of entry. If alpha emitters are inhaled, ingested (swallowed), or absorbed into the blood stream though an open wound, sensitive living tissue can be exposed to alpha radiation.

Beta Particles

Beta particles are smaller particles that travel several feet in air. They are fast moving electrons emitted from the nucleus during radioactive decay. Humans are exposed to beta particles from man-made and natural radiation sources, such as tritium, carbon-14, and strontium-90.

Beta particles can be blocked effectively with a few inches of plastic, or even a layer of clothing. However, beta particles carry enough energy to cause burns on exposed skin and present an internal hazard if we breathe or eat beta-emitting radioactive material or if the radioactive material is introduced through an open wound.

Gamma Rays

Gamma rays are high-energy, short-wavelength, electromagnetic radiation emitted from the nucleus of an atom. Gamma radiation frequently accompanies emissions of alpha particles and beta particles, and always accompanies fission. They have neither a charge nor a mass and are very penetrating. Several feet of concrete or a few inches of lead may be required to stop gamma rays. One source of gamma rays in the environment is naturally-occurring potassium-40. Man-made sources include cobalt-60 and cesium-137.

Gamma rays are a radiation hazard for the entire body. While gamma rays can easily pass completely through the human body, a fraction will always be absorbed by body tissues. Gamma rays also can be an internal hazard if we breathe or eat gamma-emitting radioactive materials.

Neutrons

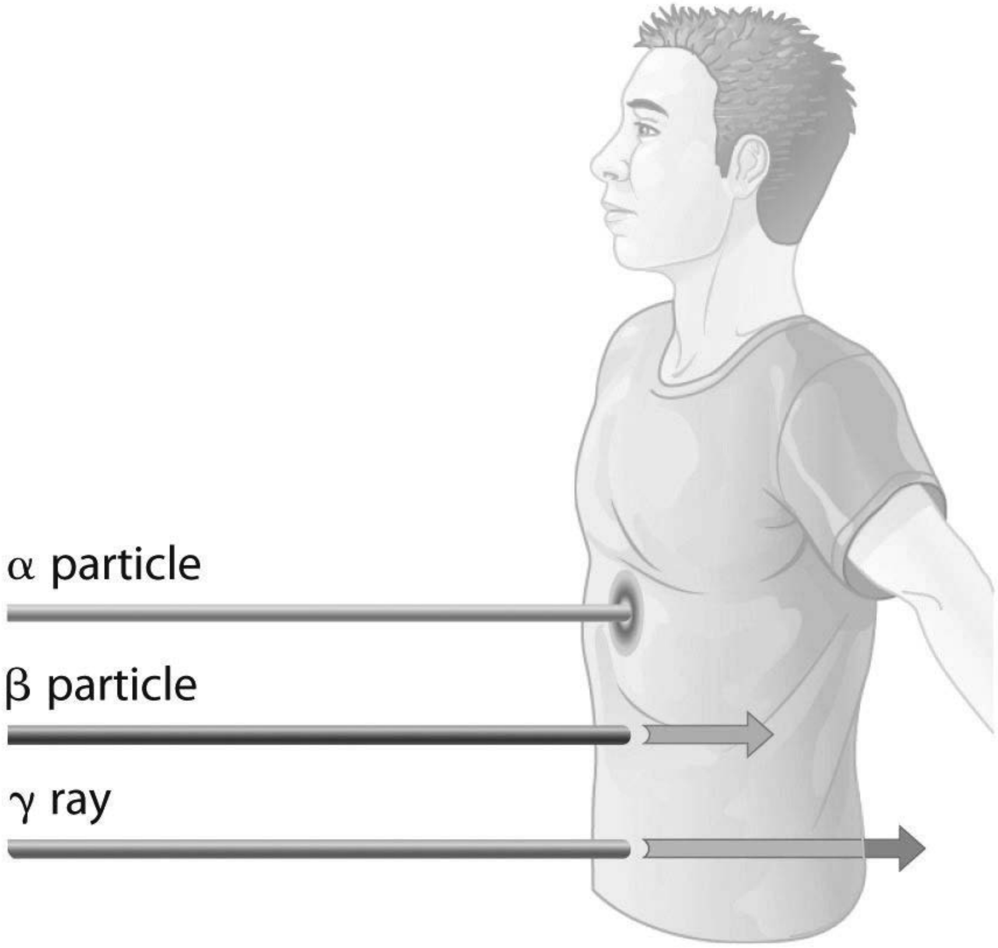
Neutrons are neutral particles with no electrical charge that can travel great distances in the air. Phenomena such as nuclear fission or nuclear fusion cause the release of free neutrons. They react with nuclei of other atoms to form new isotopes—which, in turn, may trigger further neutron radiation. Neutrons are more effective at damaging cells of the body than are other forms of ionizing radiation, such as x-rays or gamma rays. The best way to protect against neutron radiation is by providing shielding with thick, heavy materials such as lead, concrete, rock, or dirt. Free neutrons are unstable, decaying into a proton, an electron, plus an anti-electron-neutrino with a mean lifetime of 887 seconds (about 14 minutes, 47 seconds).

Symbols

There are standard symbols used to represent the different types of ionizing radiation. The symbols used are letters from the Greek alphabet. They are:

Type of Emission	Symbol
Alpha	α
Beta	β
Gamma	γ

Penetrating Power of Radiation



Human Health Effects of Radiation Exposure

Radiation exposure is one of the best-understood human health hazards. Scientists have been studying the effects of radiation on humans for over 100 years. A considerable body of information is available in the literature on the acute exposure, high-dose health effects of ionizing radiation.

Historical Record

These effects were noticed in the earliest days of research into radioactivity. Marie Curie, the discoverer of radium and polonium, fell victim to the effects of exposure to radiation. She developed cataracts at an early age and died of aplastic anemia in 1934 at the age of 66. Henri Becquerel, the first person to discover evidence of radioactivity, repeatedly suffered burns on his skin from handling radioactive materials. In 1917 a company started making watches with luminous dials. They hired young women (later called the "Radium Girls") to paint the dials with paint that contained radium. The women later began to suffer from anemia, bone fractures and necrosis of the jaw due to exposure to the radium.

The most complete data available to scientists are on the survivors of the atomic bomb explosions in Japan, on radiation industry workers such as the radium girls, and on people receiving large doses of medical radiation. These data demonstrate a higher incidence of cancer among exposed individuals and a greater probability of cancer as the level of exposure increases. In the absence of more direct information, the data also are used to estimate what the effects might be at lower exposures.

Mechanism of Injury

Biological effects are due to the ionization process that destroys the capacity for cell reproduction or division or causes cell mutation. When charged particles travel through tissue they damage tissue by stripping electrons from atoms and molecules, thus destroying their ability to function. This can cause cell damage or cell death. In some cases there may be no noticeable effect. In other cases, the cell may survive but become abnormal, either temporarily or permanently. Additionally, an abnormal cell may become malignant. Both large and small doses of radiation can cause cellular damage. The extent of the damage depends upon the total amount of energy absorbed, the amount of time you're exposed, dose rate of the exposure and the particular organs exposed.

Radiation can interact with DNA directly and cause damage by breaking bonds in the DNA or indirectly by breaking water molecules surrounding the DNA. When these water molecules are broken, they produce free radicals–unstable oxygen molecules that can damage cells and organs. By damaging the genetic material (DNA) contained in the body's cells, radiation can cause cancer. Damage to genetic material in reproductive cells can cause genetic mutations that can be passed on to future generations. Where there is a large amount of radiation exposure, sickness or even death can occur in hours or days due to cell death and organ failure.

Evidence of injury from low or moderate doses of radiation may not show up for months or even years. For example, the minimum time period between the radiation exposure and the appearance of leukemia (latency period) is 2 years. For solid tumors, the latency period is more than 5 years. It should be noted that all of the long-term health effects associated with exposure to radiation can also be caused by other factors. The types of effects and their probability of occurrence can depend on whether the exposure was chronic or acute.

Chronic Exposure

Chronic exposure is continuous or intermittent exposure to low doses of radiation over a long period of time. With chronic exposure, there is a delay between the exposure and the observed health effect. These effects can include cancer and other health outcomes such as benign tumors, cataracts, and potentially harmful genetic effects.

Acute Exposure

Acute exposure is exposure to a large, single dose of radiation, or a series of moderate doses received during a short period of time. Large acute doses can result from accidental or emergency exposures or from specific medical procedures (radiation therapy). For approved medical exposures, the benefit of the procedure may outweigh the risk from exposure.

In most cases, a large acute exposure to radiation causes both immediate and delayed effects. Delayed biological effects can include cataracts, temporary or permanent sterility, cancer, and harmful genetic effects. For humans and other mammals, acute exposure to the whole body, if large enough, can cause rapid development of radiation sickness, evidenced by gastrointestinal disorders, bacterial infections, hemorrhaging, anemia, loss of body fluids, and electrolyte imbalance. Extremely high dose of acute radiation exposure can result in death within a few hours, days, or weeks.

High doses of ionizing radiation can lead to various effects, such as skin burns, hair loss, birth defects, illness, cancer, and death. The following table summarizes the effects of acute exposure.

Acute Dose (Rad) Effect

Dose	Effect
0-25	No observable effect.
25-50	Minor temporary blood changes.
50-150	Possible nausea and vomiting.
150-300	Increased severity of above and diarrhea, malaise, loss of appetite. Some death. Increased severity of above and hemorrhaging, depilation.
300-500	Above symptoms appear sooner. Cognitive impairment. LD_{50} at 450-500 rads.
500-800	LD_{100} approx. 600 rads.
>800	Rapid incapacitation. Significant neurological symptoms. Very high mortality.

Source: Medical Management of Radiological Casualties, Second Edition, Armed Forces Radiobiology Research Institute. Bethesda, MD, April 2003 (DoD 2003) and OSHA recommendations.

In general, the higher the radiation dose, the sooner the effects will appear, and the higher the probability of death. In 1986 approximately 134 plant workers and firefighters battling the fire at the Chernobyl power plant received high radiation doses of 70,000 to 1,340,000 mrem (700 to 13,400 mSv) and suffered acute radiation sickness. Of those 134, 28 died from the radiation injuries that they sustained.

Cancer

Although radiation may cause cancer at high doses and high dose rates, public health data do not absolutely establish the occurrence of cancer following exposure to low doses and dose rates — below about 10,000 mrem (100 mSv). Studies of occupational workers who are chronically exposed to low levels of radiation above normal background have shown no adverse biological effects. Even so, the radiation protection community conservatively assumes that any amount of radiation may pose some risk for causing cancer and hereditary effect, and that the risk is higher for higher radiation exposures.

Increasing the radiation dose does not increase the severity of the cancer; instead it increases the chance of cancer induction. Increasing the size of the dose increases the probability of inducing a cancer with that carcinogen. Cancers that are, in fact, caused by radiation are completely indistinguishable from those that seem to occur spontaneously or are caused by other known or suspected carcinogens.

As with other toxins, “the dose makes the poison.” It is the radiation dose, or the amount of radiation a person is exposed to, that is the critical issue in determining health consequences. Based on current scientific evidence, any exposure to radiation can be harmful (e.g., can increase the risk of cancer); however, at very low exposures, the estimated increases in risk are very small. As with other hazardous materials, the effects of exposure are determined by the type of toxin (i.e. alpha, beta, gamma and/or neutron), duration of exposure, the route of entry and the concentration (i.e. level of radioactivity) of the toxin.

The effects of one type of radiation can be reproduced by any other type. A given total dose will cause more damage if received in a shorter time period. If doses are spread out over time, instead of being delivered all at once, their effects tend to be less severe.

Factors that Influence Health Effects

How fast the dose is received (dose rate). If a person receives a dose over an extended period of time, the impact on health won’t be as severe as if the same dose were received all at once.

Where the dose is received. If the dose is received by only a portion of the body, the impact on health won’t be as severe as if the dose were delivered to the entire body.

How sensitive the body is to radiation. A developing fetus is the most vulnerable to the effects of radiation. Infants, children, the elderly, pregnant women, and people with compromised immune systems are more vulnerable to health effects than healthy adults. (Some people within the same age group may have different sensitivity to radiation.)

The risk from radiation is higher for younger people is mainly because younger people have more cells that are dividing rapidly and tissues that are growing. Younger people have a longer lifespan ahead of them, giving cancers more time to develop.

Sources of Exposure

Any release of radioactive material is a potential source of radiation exposure. In addition to exposure from external sources, radiation exposure can occur internally from ingesting, inhaling, injecting, or absorbing radioactive materials. Both external and internal sources may irradiate the whole body or a portion of the body.

Background Radiation

Background radiation is the normal ionizing radiation present in the environment at a particular location. It can come from a variety of sources such as:

- *Radon gas.* Radon forms naturally when uranium, thorium, or radium, (radioactive metals) breaks down in rocks, soil and groundwater. Exposure comes primarily from breathing radon in air that comes through cracks and gaps in buildings and homes. It comes naturally from the earth.
- *Cosmic radiation.* It consists of high-energy charged particles, x-rays and gamma rays produced in space. Charged particles react with the earth's atmosphere to produce secondary radiation which reaches the earth. Cosmic radiation is produced by the stars, including our own sun. The amount of exposure will generally vary by altitude.
- *Terrestrial radiation.* Radioactive materials are all around us and can be naturally found in the earth.

According to National Council on Radiation Protection and Measurements (NCRP) Report No. 160, *Ionizing Radiation Exposure of the Population of the United States,* the average annual dose from background radiation is 300 millirem.

Natural Sources of Radiation

We receive low doses of radiation from our natural environment. Trace amounts of naturally occurring uranium and thorium are found in the earth. Traces of radioactive materials can be found in the body, mainly naturally occurring potassium-40. Potassium-40 is found in the food, soil, and water we ingest. Our bodies contain small amounts of radiation because the body metabolizes the non-radioactive and radioactive forms of potassium and other elements in the same way.

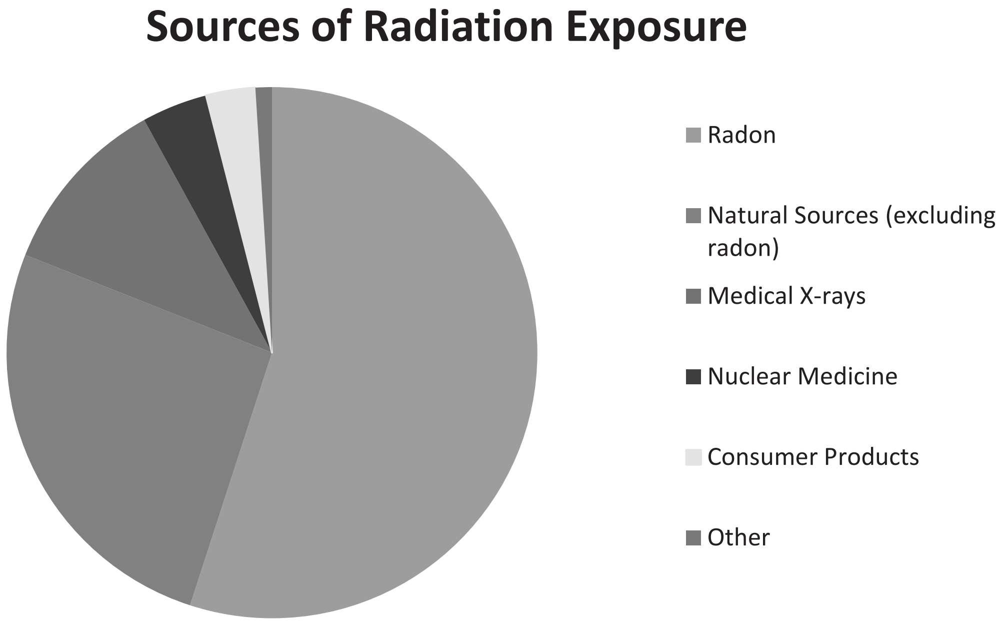
Man-made Sources of Radiation

A small fraction of background radiation comes from human activities. Trace amounts of radioactive elements have dispersed in the environment from nuclear weapons tests and accidents like the one at the Chernobyl nuclear power plant in Ukraine. Nuclear reactors emit small amounts of radioactive elements. Radioactive materials used in industry and even in some consumer products are also a source of small amounts of background radiation.

Various consumer commodities may contain radioactive materials. These would include some antiques, tobacco, some building materials and phosphate fertilizer. Antique flatware, watches and jewelry can contain radioactive materials that were added to give the pieces unique colors. Building materials such as brick, cement blocks, granite countertops, and glazed tiles may contain naturally occurring radiation.

Medical procedures account for almost 50% of the average dose a person receives (above background) each year. Radioactive materials are used in diagnosis, various therapies and in medical research. Diagnostic uses include CT scans, PET scans, X-rays and mammograms. Most therapeutic uses of radiation involve the treatment of cancer. Nuclear materials are used in medical research for such things as monitoring a human research subject’s response to a nonradioactive drug or device treatment as well as clinical trials to determine the safety or effectiveness of new radioactive drugs and devices.

Sources of Radiation Exposure



Measuring Radiation

There are a variety of ways of measuring radiation. In general, the units used measure radioactivity, ambient radiation levels and radiation dose.

Units – Radioactivity

Radioactivity refers to the amount of ionizing radiation released by a material. Whether it emits alpha or beta particles, gamma rays, x-rays, or neutrons, a quantity of radioactive material is expressed in terms of its radioactivity (or simply its activity). This represents how many atoms in the material decay in a given time period.

The units of measurement for radioactivity are the Curie. The Curie is U.S. unit used to measure radioactivity. One Curie is roughly the activity of one gram of Radium-226. The international unit is the Becquerel (Bq). The Becquerel is based on the number of disintegrations, or radioactive decays, per second. A Becquerel is 1 disintegration per second. A Curie is 37 billion disintegrations per second, which is the number of disintegrations per second in 1 gram of pure radium. A disintegrating atom can emit a beta particle, an alpha particle, a gamma ray, or some combination of all these. Becquerels or Curies measure the activity but don’t measure radiation dose.

Units – Ambient Level

Ambient radiation levels measure how much radiation is in the environment around us. The units for exposure are:

International units of measure

- Gray per hour (Gy/h)
- Sievert per hour (Sv/h)

U.S. units of measure

- Roentgen per hour (R/h)
- REM per hour (rem/h)

Units – Absorbed Dose

Disintegrating atoms emit different forms of radiation (alpha particles, beta particles, gamma rays, or x-rays). As radiation moves through the body, it dislodges electrons from atoms, disrupting molecules. Each time this happens, the radiation loses some energy until it escapes from the body or disappears. The energy deposited indicates the number of molecules disrupted. The energy the radiation deposits in tissue is called the dose (or more correctly, the absorbed dose). The units of measure for absorbed dose are the Gray (1 joule per kilogram of tissue) or the Rad (1/100 of a gray). The cumulative dose is the total absorbed dose or energy deposited by the body or a region of the body from repeated or prolonged exposures.

Absorbed dose describes the amount of radiation absorbed by an object or person. The U.S. unit used to measure absorbed radiation dose is the Rad . The international equivalent is the Gray (Gy). One hundred Rads are equal to 1 Gray. (U.S. unit) or the Gray .A Gray is the international unit used to measure absorbed dose (the amount of radiation absorbed by an object or person).

Alpha particles, beta particles, gamma rays, and x-rays affect tissue in different ways. Alpha particles disrupt more molecules in a shorter distance than gamma rays. Grays and Rads measure an absorbed dose but they don’t reflect the differences in biological effect of the different forms of ionizing radiation.

Units – Dose Equivalent

A measure of the biologic risk of the energy deposited is the dose equivalent. This describes the amount of radiation absorbed by person, adjusted to account for the type of radiation received and the effect on particular organs. The units of dose equivalent are Sieverts or REM (Roentgen equivalent man). (Dose equivalent is calculated by multiplying the absorbed dose by a quality factor.) The absorbed dose in Rads is equal to 1 REM (the U.S. measure). The absorbed dose in Grays is equal to 1 Sievert (the international unit).

One Sievert is equal to 100 REMs. More commonly, dose is measured in much smaller units: millirems or millisieverts.

Units of Measure for Radiation Exposure

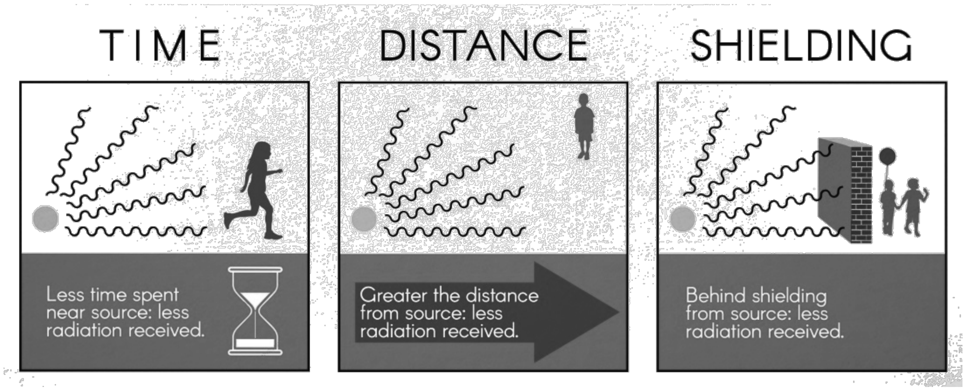
Unit	Symbol	Meaning
Becquerel	Bq	Represents a rate of radioactive decay equal to 1 disintegration per second, and 37 billion (3.7 x 1010) Bq equals 1 curie (Ci).
Curie	Ci	The amount of ionizing radiation released when an element spontaneously emits energy as a result of the radioactive decay (or disintegration) of an unstable atom. Also used to describe the rate at which radioactive material emits radiation, or how many atoms in the material decay (or disintegrate) in a given time period. 1 Ci is equal to 37 billion (3.7 x 10^{10}) disintegrations per second.
Gray	Gy	One of the two units used to measure the amount of radiation absorbed by an object or person. One gray (Gy) is the international system of units (SI) equivalent of 100 rads, which is equal to an absorbed dose of 1 Joule/kilogram. An absorbed dose of 0.01 Gy means that 1 gram of material absorbed 100 ergs of energy.
Radiation Absorbed Dose	Rad	The amount of energy (from any type of ionizing radiation) deposited in any medium (e.g., water, tissue, air). An absorbed dose of 1 rad means that 1 gram of material absorbed 100 ergs.

Roentgen Equivalent Man	REM	One of the two standard units used to measure the dose equivalent (or effective dose), which combines the amount of energy (from any type of ionizing radiation that is deposited in human tissue), along with the medical effects of the given type of radiation. For beta and gamma radiation, the dose equivalent is the same as the absorbed dose. By contrast, the dose equivalent is larger than the absorbed dose for alpha and neutron radiation, because these types of radiation are more damaging to the human body.
Roentgen	R	A unit of exposure to ionizing radiation. It is the amount of gamma or x-rays required to produce ions resulting in a charge of 0.000258 coulombs/kilogram of air under standard conditions.
Sievert	Sv	The international system (SI) unit for dose equivalent equal to 1 Joule/kilogram. 1 sievert = 100 rem.

Minimizing Exposure

The guiding principle of radiation safety is “ALARA”. ALARA stands for “as low as reasonably achievable”. This principle means that even if it is a small dose, if receiving that dose has no direct benefit, you should try to avoid it. The standard methods of avoiding excessive exposure to ionizing radiation use the principles of time, distance and shielding. During a radiological emergency (a release of radioactive material above the background level), we can use these principles to help protect responders and the public.

Methods of Reducing Exposure to Radiation



Time

"Time" simply refers to the amount of time you spend near a radioactive source. Limiting or minimizing the exposure time reduces the dose from the radiation source. Minimize your time near a radioactive source to only what it takes to get the job done. If you are in the exclusion zone in a radiological incident (the area where radiation levels are elevated above background) complete work as quickly as possible then leave the area.

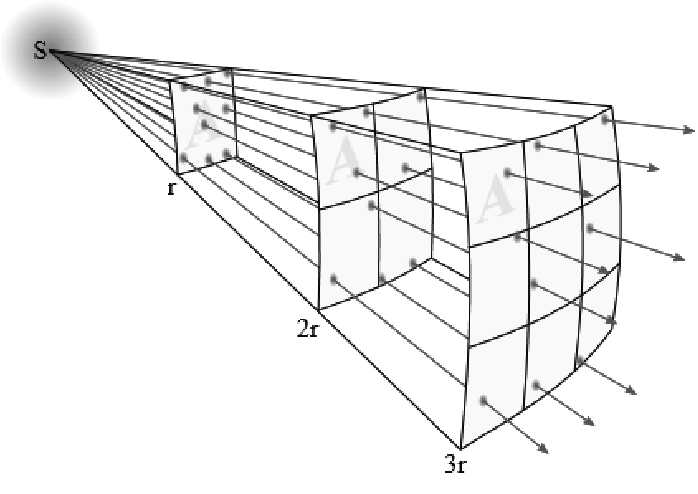
Distance

"Distance" refers to how close you are to a radioactive source. The dose of radiation decreases dramatically as you increase your distance from the source. Maximize your distance from a radioactive source as much as reasonably achievable. This is an easy way to protect yourself because distance and dose are inversely related. If you increase your distance, you decrease your dose dramatically.

Radiation will follow the inverse square law. That law governs how intense the radiation will be as you move away from the source. The radiation spreads out and becomes weaker as it travels away from the source. It becomes weaker because the same about of radiation is progressively spread over a larger area.

The decrease in intensity will lessen in proportion to the distance from the source (i.e. the intensity is inversely proportional to the distance from the source). In the case of energy sources such as light or radiation, the intensity will decrease inversely in proportion to the square of the distance from the source. For example: you are 10 feet away from a gamma source and your meter reads 4 Rads. If you move to 20 feet away from the source the intensity of the radiation will be 1 Rad.

Illustration of the Inverse Square Law



Shielding

To shield yourself from a radiation source, you need to put something between you and the radiation source. The most effective shielding will depend on what kind of radiation the source is emitting. Some radionuclides emit more than one kind of radiation. Barriers of lead, concrete, or water provide protection from penetrating gamma rays and x-rays. For example, certain radioactive materials are stored under water or in concrete or lead-lined rooms and dentists place a lead blanket on patients receiving x-rays of their teeth. Inserting the proper shield between you and a radiation source will greatly reduce or eliminate the dose you receive.

Exposure Limits

Radiation Workers

The Nuclear Regulatory Commission (NRC) regulates commercial nuclear power plants and other uses of nuclear materials, such as in nuclear medicine. It has regulations governing the occupational dose limits for adult radiation workers and the public. (10 CFR 20 Subpart A) The annual limits are:

- The total effective dose equivalent being equal to 5 rems (0.05 Sv); or
- The sum of the deep-dose equivalent and the committed dose equivalent to any individual organ or tissue other than the lens of the eye being equal to 50 rems (0.5 Sv).
- The annual limits to the lens of the eye, to the skin of the whole body, and to the skin of the extremities, which are:
- A lens dose equivalent of 15 rems (0.15 Sv), and
- A shallow-dose equivalent of 50 rem (0.5 Sv) to the skin of the whole body or to the skin of any extremity.

General Public

They also have limits for exposure for the public. They are:

The total effective dose equivalent to individual members of the public from the licensed operation shall not exceed 0.1 rem (1 mSv) in a year.

The dose in any unrestricted area from external sources shall not exceed 0.002 rem (0.02 millisievert) in any one hour.

Emergency Responders

The US EPA has made recommendations in their Protective Action Guidelines (PAG) for exposure limits for emergency responders. FEMA has equivalent recommendations. The following table summarizes those recommendations.

For all exposures, emergency workers must be fully informed of the risks of exposure, both acute and chronic, they may experience. This should include numerical estimates of the risk of delayed health effects. They must be trained, to the extent feasible, on actions to be taken. After this training and explanation of the risks each emergency worker should make an informed decision as to how much radiation risk they are willing to accept to complete a particular mission.

Guidelines for Radiation Exposure for Emergency Responders

Guideline	Activity
5 rem (0.05 Sv)	All occupational exposures. (All reasonably achievable actions have been taken to minimize dose.)
10 rem (0.1 Sv)	Protecting key resources/critical infrastructure necessary for public welfare (e.g., a power plant).
25 rem (0.25 Sv)	Lifesaving or protection of large populations. (All appropriate actions and controls have been implemented; however, exceeding 5 rem (0.05 Sv) is unavoidable.)
>25 rem (250 mSv)	Lifesaving or protection of large populations. (Only be undertaken with an understanding of the potential acute effects of radiation to the exposed responder and only when the benefits of the action clearly exceed the associated risks.)

Source: EPA-400/R-17/001 | January 2017 (www.epa.gov/radiation/protective-action-guides-pags)

Summary

Radiation occurs naturally and is present everywhere. Fortunately, there are few situations where responders are exposed to uncontrolled sources of radiation above background. Nevertheless, it is wise to be prepared and know what to do if such a situation arises.

Chapter Review

1. Some radionuclides go through a series of transformations before they reach a stable state. This process is called:
    - A. Anti-electron instability
    - B. Electron removal
    - C. Transmutation
    - D. Decay chain

2. Which form of ionizing radiation has the greatest penetrating power?
    - A. Lambda (λ)
    - B. Gamma (γ)
    - C. Beta (β)
    - D. Alpha (α)

3. Background radiation is the normal ionizing radiation present in the environment. Which of the following is a common source of background radiation in many locations?
    - A. Radon gas
    - B. Spent nuclear power plant fuel
    - C. Electrical storms
    - D. Processed uranium

4. There are a variety of ways of measuring radiation. In general, the units used measure radioactivity, ambient radiation levels and radiation dose. Check the appropriate box for each unit of measure to indicate what each unit measures.

Unit	Radioactivity/Ambient Level	Dose
Becquerel		
Curie		
Gray		
Radiation Absorbed Dose		
Roentgen Equivalent Man		
Roentgen		
Sievert		

5. Fill in the blank in the following phrases.

   No __________________________ effect.

   As low as _______________________________ achievable.

   Time _____________________ and shielding.

   Inverse _______________________ law.

   Radiation ________________________ does.

   Roentgen ____________________________ man.

   The time it takes for an atom to decay is measured in ________ lives.

   Radioactive materials are in DOT Hazard Class ____________ .

6. Which form of ionizing radiation is *not* naturally occurring?
   A. Neutron
   B. Gamma
   C. Beta
   D. Alpha

Chapter 15: Corrosive Materials – Hazard Class 8

Of all the DOT hazard classes, this is of the most common, both in terms of tonnage shipped and the frequency of shipment. Corrosive materials are some of the most common industrial commodities. The worldwide annual production of the most common corrosives is: sulfuric acid over 200 million tons, sodium hydroxide over 60 million tons and hydrochloric acid over 20 million tons.

Data from the federal government shows that 5 of the most 20 most commonly released hazardous substances are corrosives. Corrosive materials are involved in over 20% of all hazmat incidents. They are involved in over 50% of the incidents that result in injuries.

As a hazmat responder you can count on encountering corrosives on a regular basis.

DOT Hazard Class 8

49 CFR §173.136 Class 8—Definitions

(a) For the purpose of this subchapter, “corrosive material” (Class 8) means a liquid or solid that causes full thickness destruction of human skin at the site of contact within a specified period of time. A liquid, or a solid which may become liquid during transportation, that has a severe corrosion rate on steel or aluminum based on the criteria in §173.137(c)(2) is also a corrosive material. Whenever practical, *in vitro* test methods authorized in §173.137 of this part or historical data authorized in paragraph (c) of this section should be used to determine whether a material is corrosive.

§173.137 Class 8—Assignment of packing group.

The packing group of a Class 8 material is indicated in Column 5 of the §172.101 Table. When the §172.101 Table provides more than one packing group for a Class 8 material, the packing group must be determined using data obtained from tests conducted in accordance with the OECD Guideline for the Testing of Chemicals, Number 435, “*In Vitro* Membrane Barrier Test Method for Skin Corrosion” (IBR, *see* §171.7 of this subchapter) or Number 404, “Acute Dermal Irritation/Corrosion” (IBR, *see* §171.7 of this subchapter). A material that is determined not to be corrosive in accordance with OECD Guideline for the Testing of Chemicals, Number 430, “*In Vitro* Skin Corrosion: Transcutaneous Electrical Resistance Test (TER)” (IBR, *see* §171.7 of this subchapter) or Number 431, “*In Vitro* Skin Corrosion: Human Skin Model Test” (IBR, *see* §171.7 of this subchapter) may be considered not to be corrosive to human skin for the purposes of this subchapter without further testing. However, a material determined to be corrosive in accordance with Number 430 or Number 431 must be further tested using Number 435 or Number 404. The packing group assignment using data obtained from tests conducted in accordance with OECD Guideline Number 404 or Number 435 must be as follows:

(a) *Packing Group I.* Materials that cause full thickness destruction of intact skin tissue within an observation period of up to 60 minutes starting after the exposure time of three minutes or less.

(b) *Packing Group II.* Materials other than those meeting Packing Group I criteria that cause full thickness destruction of intact skin tissue within an observation period of up to 14 days starting after the exposure time of more than three minutes but not more than 60 minutes.

(c) *Packing Group III.* Materials, other than those meeting Packing Group I or II criteria—

(1) That cause full thickness destruction of intact skin tissue within an observation period of up to 14 days starting after the exposure time of more than 60 minutes but not more than 4 hours; or

(2) That do not cause full thickness destruction of intact skin tissue but exhibit a corrosion on either steel or aluminum surfaces exceeding 6.25 mm (0.25 inch) a year at a test temperature of 55 °C (130 °F) when tested on both materials. The corrosion may be determined in accordance with the UN Manual of Tests and Criteria (IBR, see §171.7 of this subchapter) or other equivalent test methods.

Examples of Corrosive Materials (Hazard Class 8).

Acids

- Acetic acid
- Ferric chloride
- Hydrochloric acid
- Nitric acid, red fuming
- Phosphoric acid

Bases

- Calcium oxide
- Hydrazine, anhydrous
- Lithium hydroxide
- Morpholine
- Potassium hydroxide
- Sodium Hydroxide

GHS Definitions

The Globally Harmonized System (GHS) defines corrosive materials as follows:

- A substance that is corrosive to skin when it produces destruction of skin tissue, namely, visible necrosis through the epidermis and into the dermis.
- pH less than 2 or greater than 11.5.
- A substance or mixture that by chemical action will materially damage or destroy metals.

NFPA Classifications

The National Fire Protection Association (NFPA) Code 704 "Standard System for the Identification of the Hazards of Materials for Emergency Response" has classified health hazards according to the probable severity of the effects of exposure to emergency response personnel. They categorize corrosive hazards as follows:

3: Materials that, under emergency conditions, can cause serious or permanent injury.

- Materials that are corrosive to the respiratory tract.
- Materials that are corrosive to the eye or cause irreversible cornea opacity.
- Materials that are corrosive to the skin.

Standards for Hazard Waste

Title 22 CCR §66261.22. Characteristic of Corrosivity

(a) A waste exhibits the characteristic of corrosivity if representative samples of the waste have any of the following properties:

(1) It is aqueous and has a pH less than or equal to 2 or greater than or equal to 12.5…

(2) It is a liquid and corrodes steel (SAE 1020) at a rate greater than 6.35 mm (0.250 inch) per year at a test temperature of 55° C (130° F)…

The US EPA uses identical criteria (40 CFR 261.22).

Corrosives – Basics

Corrosives are divided into two categories: acids and bases (also called "caustics"). Acids and bases are common solutions that exist everywhere. Almost every liquid, with the exception of water, has some acidic or basic properties.

Acids

In very general terms, an acid is a compound that dissolves in water to yield hydronium ions. In 1923 the Danish chemist Johannes Brønsted and the English chemist Thomas Lowry expanded on this definition. Their concept centers on the proton. When a hydrogen atom loses an electron the remaining particle is a proton. According to the Brønsted-Lowry model, a compound that donates a proton to another compound is called an acid, and a compound that accepts a proton is called a base. An acid-base reaction is the transfer of a proton from a proton donor (acid) to a proton acceptor (base). (The word acid from the Latin words *acidus* or *acere*, which mean "sour", since one of the characteristics of acids in water is a sour taste (e.g., vinegar or lemon juice).)

Bases

Bases are compounds that dissolve in water to yield hydroxide ions. They are often called caustics (or alkalis) and are proton accepters according to the Brønsted-Lowry model. Guillaume François Rouelle, was a French chemist and apothecary. In 1754 he introduced the concept of a base into chemistry, as a substance which reacts with an acid to give it solid form (as a salt). He noted that acids, which at that time were mostly volatile liquids (like acetic acid), turned into solid salts when combined with specific substances. Rouelle considered that such a substance serves as a "base" for the salt, giving the salt a "concrete or solid form" (i.e. a base). Bases react with acids to neutralize each other. (Note: Neutralizing acid spills with strong bases can cause a violent exothermic reaction. The resulting base can cause just as much damage as the original acid spill.)

Corrosive Material That Aren't Acids or Bases

According to the Brønsted-Lowry model a substance no longer needs to be composed of hydrogen (H^+) or hydroxide (OH^-) ions in order to be classified as an acid or base. There are many chemicals (both elements and compounds) that are classified by DOT as "corrosive" but aren't acids or bases. The following is a list of some of the most common.

- Amines: derivatives of ammonia. Used to make some dyes and pharmaceuticals. Also used to remove CO_2 from atmospheres (such as on submarines).
- Ammonia: precursor to many fertilizers. Widely used as a refrigerant.
- Benzoyl Chloride: used in the production of peroxides. Also used in the preparation of dyes, perfumes, pharmaceuticals, and resins.
- Bromine: very reactive and does not occur free in nature. Used to make flame retardants. Was used in many pesticides but many have been banned.
- Chlorine: extremely reactive and a strong oxidizer. About 15,000 chlorine compounds are used commercially.
- Hydrazine: highly toxic and unstable. Hydrazine is mainly used as a foaming agent in preparing polymer foams. Also used as a component in rocket fuels.
- Iodine: primarily used in nutrition. Also used as a catalysts in various processes.
- Mercury: used primarily for the manufacture of industrial chemicals or for electrical and electronic applications. It's being phased out of many traditional uses (e.g. thermometers) due to concerns about toxicity.
- Phosphorous Pentachloride: used as a chlorinating reagent. Reacts violently with water.
- Sulfur Trioxide: a precursor to sulfuric acid. Extremely corrosive.
- Titanium Chloride: catalyst for the manufacture of polyolefins (especially polyethylene).

It's important to remember that many substances fall into two or more DOT hazard classes. This is the case with many of the above.

Uses of Corrosives

Corrosive materials are some of the most commonly used, shipped and mass-produced substances. They are used in an endless variety of products and manufacturing processes.

Common acids and uses.

- Acetic acid: Component of vinegar.
- Boric acid: Used as a disinfectant or pesticide.
- Citric acid: Used as a flavoring and acidifier in food.
- Hydrochloric acid: Used to produce many organic materials.
- Hydrofluoric acid: Used to make fluorine compounds.
- Nitric acid, red fuming: Component of rocket fuels.
- Phosphoric acid: Component of many soft drinks.
- Sulfuric acid: Component of drain cleaners. Used in various industrial processes.

Common bases and uses.

- Ammonia: Used as a fertilizer and a refrigerant.
- Calcium hydroxide: Used as a flocculent in water treatment.
- Hydrazine, anhydrous: Precursor to several pharmaceuticals and pesticides.
- Lithium hydroxide: Used in breathing gas purification systems.
- Methylamine: Precursor to a variety of pharmaceuticals.
- Morpholine: Used for pH adjustment in steam generation systems.
- Potassium hydroxide: Precursor to other potassium compounds (e.g. fertilizers).
- Sodium Hydroxide: Countless uses.
- Zinc Hydroxide: Used as an absorbent in surgical dressings.

General Hazards of Corrosives

Corrosive chemical can attack human skin. They denature proteins or perform amide hydrolysis or ester hydrolysis. Amide hydrolysis damages proteins, which contain amide bonds. Lipids contain ester bonds and are attacked by ester hydrolysis.

In addition, a corrosive agent may participate in chemical reactions that dehydrate skin and/or produce heat. For example, sulfuric acid dehydrates carbohydrates in skin and releases heat, sometimes sufficient to cause a thermal burn in addition to the chemical burn.

Corrosive substances that attack other materials, such as metals, may produce rapid oxidation of the surface and damage the metal.

Types of Acids

Mineral Acids

A mineral acid or inorganic acid is any acid derived from an inorganic compound that dissociates to produce hydrogen ions (H^+) in water. Mineral acids are highly soluble in water, but tend to be insoluble in organic solvents. The inorganic acids are corrosive. Hydrochloric acid, sulfuric acid, and nitric acid are examples of mineral acids. Mineral acids are used in the chemical industry as feedstocks for the synthesis of other chemicals, both organic and inorganic. Large quantities of these acids – especially sulfuric acid, nitric acid, and hydrochloric acid – are manufactured for commercial use in large plants.

Organic Acids

An organic acid is an organic compound with acidic properties. In general, organic acids are weak acids. Citric acid, lactic acid, acetic acid and formic acid are examples of organic acids.

Oxyacids

An oxyacid is an acid that contains an oxygen atom bonded to a hydrogen atom and at least one other element. An oxyacid dissociates in water to form the H^+ cation and the anion of the acid. An oxyacid has the general structure X-O-H. Phosphoric acid is an example of an oxyacid.

Common Oxyacids

Acid	Formula	Description and Hazards
Chromic Acid	H_2CrO_4	A powerful irritant of skin, eyes, & mucous membranes. Attacks most metals, particularly copper and brass. A strong and corrosive oxidizing agent.
Boric Acid	H_3BO_3	A weak acid. Is only poisonous if taken internally or inhaled in large quantities. Long-term exposure can cause kidney damage and eventually kidney failure
Bromic Acid	$HBrO_3$	A colorless solution that turns yellow at room temperature as it decomposes to bromine. A powerful oxidizing agent.

Properties of Corrosives

General

Acids and bases are usually liquids but may be solids or gases. They have different properties and are able to neutralize each other to form water. Acids and bases can be defined by physical and chemical observations such as:

Basic Properties of Corrosives

Property	Acid	Base
Skin exposure	Produces a piercing pain.	Gives a slippery feel.
Taste	Sour	Bitter
pH	<7	>7
Texture	Sticky	Slippery
Reactivity	Reacts with metals to produce hydrogen gas.	Reacts with many fats and oils.
Litmus Paper	Changes to red.	Changes to blue.

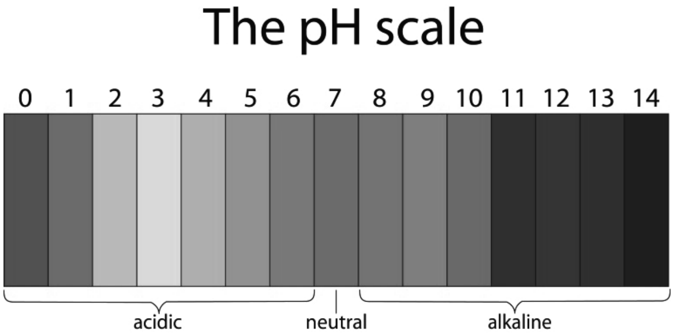
pH Scale

pH is a measure of hydrogen ion concentration, in other words, a measure of the acidity or alkalinity of a solution. The pH scale ranges from 0 to 14. Aqueous solutions at 25°C with a pH less than seven are acidic, while those with a pH greater than seven are basic (or alkaline). A pH level of is 7.0 at 25°C is defined as "neutral" because the concentration of H_3O^+ equals the concentration of OH^- in pure water. (Note: the pH scale only applies in aqueous solutions. No water, no pH.)

It is often assumed that "pH" stands for "power of hydrogen" but several scholars dispute that. The term was coined over 100 years ago by S.P.L. Sørensen, a Danish chemist.

Sørensen published a paper in 1909 introducing the term. In this paper, he stated "…I use the name "hydrogen ion exponent" and the notation for the numerical value of the exponent of this power." At that time the letter "p" was a common and simple mathematical convention for naming variables. The use of the term "power of hydrogen" has become conventional wisdom but it appears to have no basis in fact.

pH Scale



It is possible for a pH to be outside of the 0-14 range. According to a report from the U.S. Geological Survey mine waters from the Richmond Mine cleanup site in Iron Mountain, CA have been found to have pH values as low as -3.6. These extreme acid waters were formed primarily by pyrite oxidation and concentration by evaporation. Hot springs near the Ebeko volcano in Russia have estimated pH values as low as –1.7 from naturally occurring HCl and H_2SO_4.

Examples of pH Values of Common Chemicals

0 – Hydrochloric Acid (HCl)
1.0 – Battery Acid (H2SO4 sulfuric acid) and stomach acid
2.0 – Lemon Juice
2.2 – Vinegar
3.0 – Apples, Soda
3.0 to 3.5 – Sauerkraut
4.0 – Wine and Beer
4.5 – Tomatoes
7.0 – pure water (neutral)
7.4 – Human Blood
8.3 – Baking Soda (Sodium Bicarbonate)
11.0 – Ammonia
12.4 – Lime (Calcium Hydroxide)
13.0 – Lye
14.0 – Sodium Hydroxide (NaOH)

Because the scale is logarithmic, a pH difference of 1 between two solutions corresponds to a difference of a factor of 10 in their hydronium ion concentrations.

Strength of Acids and Bases

The strength of an acid refers to its ability or tendency to lose a proton (H+). A strong acid is one that completely ionizes (dissociates) in a solution. In contrast, a weak acid only partially dissociates. Examples in water include carbonic acid (H_2CO_3) and acetic acid (CH_3COOH). At equilibrium, both the acid and the conjugate base are present in solution. (It is important to not confuse the words strong and weak with the terms concentrated and dilute.)

pH is a measure of the concentration of hydrogen ions in a solution. Very strong acids may have a negative pH, while very strong bases may have a pH greater than 14.

There are many more weak acids than strong acids. The following is a list of common weak acids (and their formulas).

Acetic acid (ethanoic acid) (CH_3COOH)
Formic acid (HCOOH)
Hydrocyanic acid (HCN)
Hydrofluoric acid (HF)

Weak acids do not completely dissociate into their ions in water. For example, HF dissociates into the H^+ and F^- ions in water, but some HF remains in solution (i.e. does not completely dissociate in water), so it is not a strong acid. While technically a weak acid, hydrofluoric acid is extremely powerful and highly corrosive. It is so corrosive it dissolves glass. The fluoride ion attacks the silicon atom in silica glass while the proton is interacting with oxygen.

Weak Bases

Like weak acids, weak bases do not completely dissociate in aqueous solution. They react with water to produce the hydroxide ion. Examples of weak bases include ammonia, NH_3, and diethylamine, $(CH_3CH_2)_2NH$.

Strong Acids and Bases

Acids and bases that are completely ionized when dissolved in water are called strong acids and strong bases. There are only a few strong acids and bases. They are often used in industry and everyday life.

Relative to the number of strong acids, there are fewer strong bases. Most are alkali hydroxides. (Calcium oxide is considered a strong base, because it is completely, almost completely, ionized. However, the solubility of calcium hydroxide is very low.)

Examples of Strong Acids and Bases

Strong Acids	**Strong Bases**
Perchloric Acid ($HClO_4$)	Lithium Hydroxide (LiOH)
Hydrochloric Acid (HCl)	Sodium Hydroxide (NaOH)
Hydrobromic Acid (HBr)	Potassium Hydroxide (KOH)
Hydroiodic Acid (HI)	Calcium Hydroxide ($Ca(OH)_2$)
Nitric Acid (HNO_3)	Strontium Hydroxide ($Sr(OH)_2$)
Sulfuric Acid (H_2SO_4)	Barium Hydroxide ($Ba(OH)_2$)

Relative Strength of Some Common Acids

Relative Strength	**Formula**	**Name**
Strongest	$HClO_4$	Perchloric acid
↓	HNO_3	Nitric acid
	HCl	Hydrochloric acid
	H_2SO_4	Sulfuric acid
	H_3PO_4	Phosphoric acid
	CH_3COOH	Acetic acid
	H_2CO_3	Carbonic acid
Weakest	HCN	Hydrocyanic acid

Relative Strengths of Some Types of Bases

Relative Strength	**Ion**	**Base**
Strongest	OH^{-1}	hydroxides
↓	NH_3	ammonia
	NH_2^{-1}	amines
Weakest	CO_3^{-2}	carbonates

Concentration

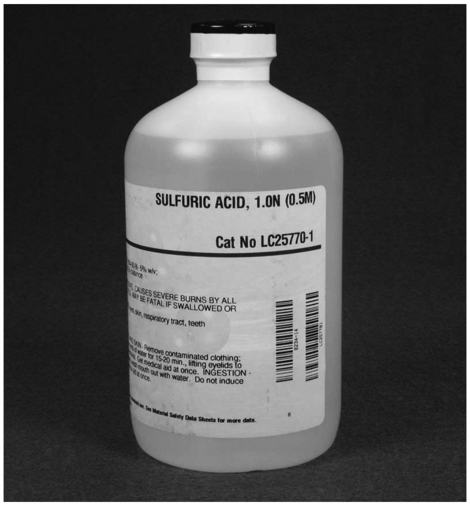
The standard unit of measure in chemistry for particles is the mole. A mole is 6.023×10^{23} particles. (The particles can be atoms, molecules, ions or electrons.) The mole is a unit of measure similar in concept to a dozen, a ream or a gross. It measures the amount of a specific thing but not the weight or size. For example, a dozen refrigerators takes up more space than a dozen apples and weighs vastly more. The same concept applies to atoms and molecules. The number of grams in the mass of 1 mole is the atomic weight of that element or molecule. Although one mole of hydrochloric acid contains the same number of molecules as one mole of sulfuric acid, the mole of sulfuric acid will have a greater mass since it has a greater molecular weight (HCl: 36.46, H_2SO_4: 98.08).

The most common unit of concentration is molarity. The molarity (M) is a common unit of concentration and is defined as the number of moles of solute present in exactly 1 L of solution. The molarity shows the concentration of the material. The higher the molarity, the greater the concentration.

Another common unit of measure for the concentration of corrosives is “normality” which is a concept similar to molarity. Molarity identifies the number of moles of a solute dissolved in one liter of solution. Normality on the other hand identifies the number of moles of reactive units per liter of solution. Where molarity describes the moles of a complete substance per liter of solution, normality describes only the moles of reactive species per liter of solution. Normality is always a multiple of molarity. For most corrosives normality will equal molarity. (In the case of sulfuric acid the normality is twice the molarity.)

The concentration of a corrosive may be expressed in per cent which is the amount of solute dissolved in the solution (in the case of corrosives, the solution is water). It’s not unusual to find labels on containers of corrosive materials that state the concentration is some combination of per cent, molarity (M) or normality (N).

Indications of Concentration



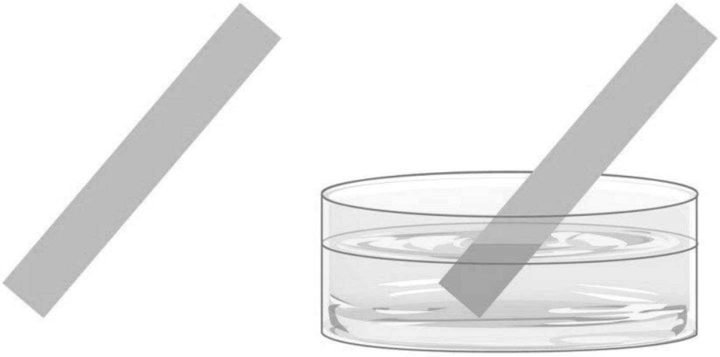
Responding to Incidents Involving Corrosive Materials

Detecting Corrosives

The most common method of detecting and measuring the pH of corrosives is through the use of paper strips impregnated with chemicals that change color when the pH changes.

One of the oldest methods of indicating pH is to expose the solution to litmus which is a water-soluble mixture of different dyes extracted from lichens. It is often absorbed onto filter paper to make it a usable tool. To use litmus paper you wet the paper then expose it to the solution or gas in question. The paper will change color to indicate whether the material is an acid or base.

Using Litmus Paper



Indicator strips that display the pH are called universal indicators. They are impregnated with various chemical dyes that change color over a range of pH values. They produce an easily recognizable different color for each pH unit. To use the strips you first wet them with water (preferable distilled water) than expose them to the gas or liquid to be tested. You then compare the indicator strip to the color matching chart supplied with the strips. The color change will show the approximate pH of the material tested.

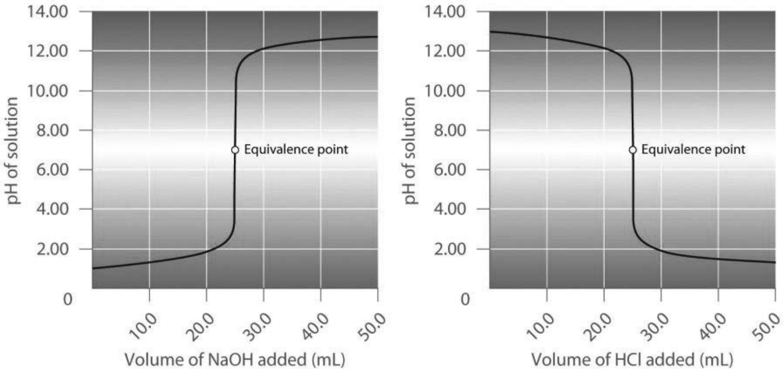
Examples of Universal Indicator Papers

Both litmus paper and universal indicator strips have limitations. On litmus paper, the color changes but doesn't produce precise measurements. Litmus paper *does not* measure the pH. It only shows whether the material is an acid or base. Universal indicator strips (commonly called "pH paper") display a range of pH values rather than a distinct and precise value. Also, some substances (e.g. chlorine) can bleach out the papers and render them unusable. With both systems the reactions produced by the different test strips are irreversible. They can only be used once.

Neutralizing Corrosive Solutions

Neutralizing an acid or base in a field setting is extremely difficult. Even in the laboratory, the change in pH in such reactions can be sudden and dramatic (see figure 4). This is exacerbated in situations where the exact identity and concentration of the material may be unknown. If responders attempt to neutralize a strong acid or base they may make the situation worse as the pH can shift suddenly and unpredictably. This is especially unpredictable when the concentration of the material is not known since the shape of the curves shown below varies greatly as the concentration changes.

Changes in pH During Neutralization



(a) Strong acid titrated with strong base **(b) Strong base titrated with strong acid**

Diluting Corrosives

In the case of hazmat incidents involving corrosive materials, dilution may not be the solution to pollution. Diluting a spill of an acid or base can be problematic.

- In general, adding water to an acid or base produces an exothermic reaction. These reactions can be vigorous and hazardous to anyone nearby. The standard practice is to add the acid to the water. In an incident that may be impossible.
- Many acids (e.g. sulfuric) are heavier and more viscous than water making them difficult to dilute.
- Diluting the material may bring the pH closer to neutral but that won't necessarily reduce the hazards from the material. Acids such as hydrochloric or hydrofluoric acid can still be toxic even when diluted. Other acids may react with water to give off toxic vapors. Some acids contain heavy metals which will still be present after the product is diluted.
- The physical properties of corrosives can vary greatly with concentration. Diluting a corrosive without knowing its concentration can have unpredictable results.
- The pH scale is logarithmic. Since it is a logarithmic scale, a difference of one pH unit is equivalent to a tenfold difference in hydrogen ion concentration. For example: You respond to an incident involving a 55 gallon spill of an acid with a pH of 1. If you want to get the pH to 2 you would have to dilute that 55 gallons of acid with over 500 gallons of water. If you want the pH to be 3 it would take over 5,000 gallons of water to do that.

Absorbing Corrosives

Another method of mitigating a spill of a corrosive liquid is to use an absorbent material to absorb, neutralize and/or solidify the liquid. There are a variety of commercial products available that can be used to absorb a spill of a corrosive liquid. They come in a variety of physical forms including pads, pillows and loose product. These products will have one or more of the following capabilities:

- Absorb the spilled material.
- Neutralize the spilled material. Some will give a color indication that the material has been neutralized.
- Solidify a spilled liquid.

There are some considerations to keep in mind when using absorbent material to mitigate a spill of a corrosive liquid.

- Some acids can ignite combustible material used in some absorbent products. Examples include oxidizing acids such as perchloric or chromic acid.
- It may be unsafe or impossible to absorb and/or neutralize some acids. Examples include hydrofluoric acid, chromic acid, perchloric acid, and fuming nitric acid.
- Some acids, such as hydrofluoric acid, may be incompatible with common absorbent material and require specialized absorbents.

Examples of Absorbent Materials

Pads

Socks

Granular

Assessing the Hazards of Corrosive Materials

Multiple hazards

As with all DOT hazard classes, materials in hazard class 8 can have multiple hazards and can fall into more than one DOT hazard class. The following is a summary of common acids and bases that have multiple hazards.

- Perchloric acid: oxidizer, water-reactive, not compatible with some absorbents.
- Nitric acid: strong oxidizer.
- Formic acid: flammable.
- Acetic acid: flammable.
- Hydrocyanic acid: flammable and an inhalation hazard.
- Bromine: toxic.

Unusual hazards

- Sulfuric acid: explosive or incompatible with an enormous array of substances. Strongly hygroscopic.
- Sodium hydroxide: reacts with various metals to generate hydrogen gas.
- Hydrochloric acid: reacts with a wide variety of materials exothermically to generate various toxic gases.
- Hydrofluoric acid: extremely toxic. Skin absorptive. Dissolves glass.
- Hydroiodic acid: reacts exothermically with wide variety of materials to generate hydrogen gas.
- Phosphoric acid: Reacts with cyanide compounds to release gaseous hydrogen cyanide.
- Oxalic Acid: hygroscopic and sensitive to heat.

Summary

Corrosive materials are ubiquitous. They are used in every industry and are present in nearly every retail setting. Responders should expect to regularly see them in incidents.

Chapter Review

1. In general, adding water to an acid or base produces a/an __________ reaction.
   A. Oxidization/Reduction
   B. Vigorous
   C. Exothermic
   D. Endothermic

2. Fill in the blanks about the basic properties of corrosive materials.

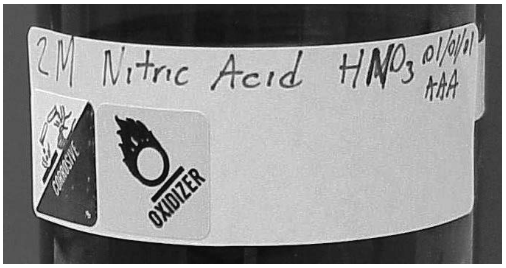
Property	**Acid**	**Base**
Chemical behavior	Dissolves in water to yield ____________ ions	Dissolves in water to yield ____________ ions
pH	__________ than 7	__________ than 7
Litmus Paper reaction	Changes to ________.	Changes to _______.

3. The US DOT defines a “corrosive material” (Class 8) as a liquid or solid that:
   A. Has a pH less than or equal to 2 or greater than or equal to 12.5.
   B. Causes full thickness destruction of human skin.
   C. Will materially damage or destroy metals by chemical action.
   D. Causes irreversible cornea opacity.

4. How does litmus paper indicate pH?
   A. Alarm bell
   B. Color change
   C. Turns black
   D. Paper dissolves

5. In general, organic acids are ______________ acids.
   A. Strong
   B. Weak
   C. Flammable
   D. Oxidizing

6. What does the “2M” on the label below indicate?



   A. The NFPA rating.
   B. The medicinal properties.
   C. How many metric tons the bottle holds.
   D. The molarity of the substance.

7. Which of the following acids is capable of dissolving glass?
   A. Hydroiodic
   B. Boric
   C. Hydrochloric
   D. Hydrofluoric

8. Which of the following materials has the highest pH?
   A. Calcium hydroxide
   B. Sodium Bicarbonate
   C. Sodium hydroxide
   D. Ammonia

9. Fill in the name of the corrosive materials that corresponds to the formula listed.

Formula		Name
HCN		
HCl		
H_2SO_4		
HF		
NaOH		
HNO_3		
NH_3		

Chapter 16: Miscellaneous Hazardous Materials – Hazard Class 9

This DOT hazard class is in the “none-of-the-above” category. The materials in this hazard class don’t meet the criteria for any of the other 8 classes.

In some cases, materials that were previously not considered to be hazardous were involved in serious incidents that resulted in a loss of life.

Lithium Batteries

On September 3, 2010 a Boeing 747 operated by United Parcel Service crashed in Dubai. The cause of the crash was a fire in the main deck cargo compartment. The fire was caused by lithium batteries that overheated and ignited adjacent combustible materials.

The flight deck quickly filled with toxic smoke killing the Captain. The dense smoke made it impossible for the First Officer to see any of the instruments. As he attempted to fly the aircraft to a nearby airport the fire burned through various control cables making it impossible to control the aircraft. The First Officer lost control of the aircraft and it crashed.

Although the lithium batteries were classified as a Miscellaneous Hazardous Material (Hazard Class 9) the packing regulations in effect at that time did not address the total or potential fire risk. These batteries have the potential of rapid discharge, in which the batteries produce very high currents. This can cause rapid overheating and explosion.

Molten Sulfur

On the morning of January 19, 1985, in Benicia, California, a truck pulling two tank trailers loaded with molten sulfur was crossing the Benicia Bridge. It struck the concrete median and overturned into the opposite lanes. One trailer was destroyed and one breached. The molten sulfur was ejected across the roadway and a large amount splashed into a car with two occupants. The driver of the truck and the driver of the car were both killed. The product caught fire and burned for 3 hours.

At that time molten sulfur was not classified as a hazardous material. (DOT has since put molten sulfur into Hazard Class 9.) The trailers weren’t placarded and the responding firefighters had difficulty identifying the product and determining appropriate tactics to mitigate the effects of the spill.

There are scores of other products in Hazard Class 9 that responders wouldn’t normally consider to be hazardous. In each case they have unusual and/or specific hazards that may not be obvious.

DOT Hazard Class 9

49 CFR §173.140 Class 9—Definitions

For the purposes of this subchapter, *miscellaneous hazardous material* (Class 9) means a material which presents a hazard during transportation but which does not meet the definition of any other hazard class. This class includes:

(a) Any material which has an anesthetic, noxious or other similar property which could cause extreme annoyance or discomfort to a flight crew member so as to prevent the correct performance of assigned duties; or

(b) Any material that meets the definition in §171.8 of this subchapter for an elevated temperature material, a hazardous substance, a hazardous waste, or a marine pollutant.

§171.8 Definitions and Abbreviations.

Elevated temperature material means a material which, when offered for transportation or transported in a bulk packaging:

(1) Is in a liquid phase and at a temperature at or above 100 °C (212 °F);

(2) Is in a liquid phase with a flash point at or above 38 °C (100 °F) that is intentionally heated and offered for transportation or transported at or above its flash point; or

(3) Is in a solid phase and at a temperature at or above 240 °C (464 °F).

Hazardous substance for the purposes of this subchapter, means a material, including its mixtures and solutions, that—

(1) Is listed in the appendix A to §172.101 of this subchapter;

(2) Is in a quantity, in one package, which equals or exceeds the reportable quantity (RQ) listed in the appendix A to §172.101 of this subchapter; and

(3) When in a mixture or solution—

(i) For radionuclides, conforms to paragraph 7 of the appendix A to §172.101.

(ii) For other than radionuclides, is in a concentration by weight which equals or exceeds the concentration corresponding to the RQ of the material, as shown in the following table:

	Concentration by weight	
RQ pounds (kilograms)	**Percent**	**PPM**
5000 (2270)	10	100,000
1000 (454)	2	20,000
100 (45.4)	0.2	2,000
10 (4.54)	0.02	200
1 (0.454)	0.002	20

The term does not include petroleum, including crude oil or any fraction thereof which is not otherwise specifically listed or designated as a hazardous substance in appendix A to §172.101 of this subchapter, and the term does not include natural gas, natural gas liquids, liquefied natural gas, or synthetic gas usable for fuel (or mixtures of natural gas and such synthetic gas).

Hazardous waste, for the purposes of this chapter, means any material that is subject to the Hazardous Waste Manifest Requirements of the U.S. Environmental Protection Agency specified in 40 CFR part 262.

Marine pollutant, means a material which is listed in appendix B to §172.101 of this subchapter (also see §171.4) and, when in a solution or mixture of one or more marine pollutants, is packaged in a concentration which equals or exceeds:

(1) Ten percent by weight of the solution or mixture for materials listed in the appendix; or

(2) One percent by weight of the solution or mixture for materials that are identified as severe marine pollutants in the appendix.

Examples of Miscellaneous Hazardous Materials (Hazard Class 9).

Asbestos. A naturally occurring mineral. It’s composed of millions of microscopic fibrils. Although asbestos is inert and resistant to flame, inhaling asbestos fibers can cause serious and fatal illnesses including lung cancer, mesothelioma, and asbestosis (a type of pneumoconiosis).

Carbon dioxide, solid (dry ice). So-called “dry ice” is the solid form of carbon dioxide. It is non-combustible, non-toxic and inert. However, it sublimes rapidly and can release large quantities of carbon dioxide gas. If it’s packaged in a container that does not allow for release of the gas the container may explode. If the carbon dioxide gas is emitted in a confined space, or other unventilated area (e.g. cold room) may create an oxygen deficient atmosphere. Also, it is a cryogenic material that causes severe frostbite upon contact with skin.

Cotton. Cotton stored in bulk can spontaneously combust. It’s especially prone to this if it’s wet. These fires are a well-known hazard in areas where cotton is grown.

Fish meal or Fish scrap. Many types of fish meal have high fat contents and, when shipped in bulk, are capable of self-heating and spontaneous combustion.

Polychlorinated biphenyls. Polychlorinated biphenyls (PCB) are a family of organic chlorine compounds. They were once widely used as dielectric and coolant fluids in electrical apparatus, carbonless copy paper and in in heat transfer fluids. They have since been replaced by other compounds. Although they are not corrosive or flammable, PCBs are toxic and highly persistent in the environment.

Sulfur (including molten sulfur). Sulfur is an element that can exist in solid, liquid or gaseous form. In addition, it forms over 30 solid allotropes, more than any other element. Although it doesn’t meet the definitions of other hazard classes, each physical state of sulfur can have significant hazards. It’s capable of combusting and emitting toxic gases. When shipped in the molten state it can cause severe burns upon contact with skin.

GHS Definitions

The Globally Harmonized System (GHS) doesn’t incorporate US DOT Hazard Class 9.

NFPA Classifications

The National Fire Protection Association (NFPA) Code 704 “Standard System for the Identification of the Hazards of Materials for Emergency Response” doesn’t have a specific category for Hazard Class 9. The hazards of the material in question would be covered by existing NFPA 704 criteria.

Summary

There are substances that have specific hazards that don’t fall into the definitions of the other eight DOT hazard classes. In many cases the hazards manifest themselves when the Hazard Class 9 material is stored in a certain manner or in a specific physical state. Responders will intuitively know that some substances are hazardous (e.g. asbestos) even though it doesn’t fall into any of the other DOT hazard classes. In other cases, responders will be surprised a material is in this hazard class. In many of those cases, that’s due to how the material is handled or stored (e.g. cotton).

Chapter Review

1. DOT Hazard Class 9 means a material which presents a hazard during transportation. What is the other criteria that would cause a substance to be included in Hazard Class 9?
   A. The concentration of the substance wouldn't cause adverse effects.
   B. It isn't regulated by the United Nations.
   C. It doesn't meet the definition of any other hazard class.
   D. The substance is only transported in aircraft.

2. A liquid substance would be classified as an *Elevated temperature material* if the temperature of the material is:
   A. Higher than normal
   B. Above its flash point
   C. Above 100 °F
   D. Above 100 °C

3. Which of the following is an example of a Miscellaneous Hazardous Materials (Hazard Class 9)?
   A. Chlorine
   B. Asbestos
   C. Methyl-ethyl diforsuranol
   D. Aluminum powder

4. The term "Miscellaneous Hazardous Materials *doesn't* include:
   A. Organic food products
   B. Binary acids
   C. Low vapor pressure liquids
   D. Petroleum products

Chapter 17: Introduction to Toxicology

Toxicology is the study of the adverse effects of chemicals on living organisms. (Note: it isn't the study of "poisons" since substances not classed as a "poison" will still have potential toxic effects. This includes substances in nearly every hazard class.) "Adverse effects" can range from life-threatening to mildly irritating.

For Emergency Responders, toxicology is the key to understanding how a substance affects a person when they are exposed to it. Understanding the terminology associated with this field is critical to making decisions about how to protect responders and the public. Decisions such as this can include; what kind of chemical protective ensemble to wear, what kind of air monitor(s) to use and whether to evacuate a population or shelter them in place.

This chapter will provide an overview of toxicological terminology, how it applies to toxins in general and it will provide some of the tools needed to complete a hazard and risk assessment.

The tools this chapter will identify include some of the limits placed on exposure to hazardous materials. Some of these limits are OSHA regulations and some are consensus standards developed by industry experts. There is some overlap, a few inconsistencies and an occasional disagreement between these experts. These exposure limits provide the responder with a range of options for use in making response decisions.

Toxicity

The Dose Makes the Poison

Paracelsus, a Swiss physician who lived in the 16th Century, is generally considered to the father of toxicology. He advocated using various minerals and chemical compounds to treat diseases. Other physicians objected saying the substances were too toxic to be used as therapeutic agents. He responded, "All things are poison and nothing is without poison; only the dose makes a thing not a poison."

Every substance is toxic, it's all a matter of dose. For example, humans need water and oxygen to survive. In high enough doses, though, both can kill.

Water

Although water is one of the least toxic substances known, it is capable of causing harm if consumed in sufficient quantities.

Water intoxication, also called hyperhydration, is a condition caused by consuming excessively large quantities of water. It causes undue retention of water with a resulting decrease in sodium concentration and other electrolytes. The result is a disturbance of brain functions. It can cause lethargy, nausea, vomiting, and mild mental aberrations; in severe cases there may be convulsions, coma and even death.

Oxygen

The result of breathing increased partial pressures of oxygen is hyperoxia, an excess of oxygen in body tissues. Oxygen toxicity is a well-known hazard in diving and in hyperbaric oxygen treatment.

Breathing pure O_2 has a number of deleterious effects. It can impair pulmonary gas exchange, decrease cardiac output and can have toxic effects on the central nervous system. Severe cases can result in cell damage and death.

Terminology

Basic terms

- Acute: Adverse effects of a substance that result either from a single exposure or from multiple exposures in a short period of time (usually less than 24 hours).
- Adverse effect: Change in biochemistry, morphology, physiology, growth, development, or lifespan of an organism which results from exposure to a contaminant.
- Carcinogen: A substance, agent, radionuclide or form of radiation that promotes the formation of cancer.
- Chronic: Adverse effects as a result of long term exposure to a contaminant.
- Ca: Potential occupational carcinogen.
- Concentration: Amount of toxin or substance present in a given volume of air.
- Dose: Amount of toxin or substance inhaled, ingested, injected into the body or absorbed through the skin.
- Exposure: Amount or intensity of a contaminant that reaches the target population.
- Irritant: A chemical, which is not corrosive, but which causes a reversible inflammatory effect on living tissue by chemical action at the site of contact. (Note: This definition usually doesn’t include corrosives.)
- LC_{50}: Median concentration lethal to 50% of a test population.
- LD_{Lo}: Minimum lethal dose (injected, ingested or absorbed through the skin).
- LC_{Lo}: Minimum lethal concentration (inhaled).
- LD_{50}: Median lethal dose to 50% of a test population.

  (Note: X_{Lo}, X_{20}, X_{50}: Subscripts indicate the percent of the population effected or other information, Lo indicates first effected, 20 indicates 20%, etc.)
- LOC: Level of concern. Level (threshold concentration) of exposure to a chemical above which there may be serious and immediate health effects, to any person exposed for a defined length of time (exposure duration). Generally, the lower the LOC value for a substance, the more toxic the substance is. (Also may be referred to as exposure limits, exposure guidelines, or toxic endpoints.)
- Mg/Kg: milligrams per kilograms: milligrams of material per kilograms of body weight.
- mg/m^3: milligrams per cubic meter: milligrams of chemical per cubic meter of air.

- Mutagen: A physical or chemical agent that causes a mutation in the genetic material, usually DNA, of an organism.
- ppb: parts per billion or 1/1,000,000,000
- ppm: parts per million or 1/1,000,000
- REL: Recommended Exposure Limit. Level that NIOSH believes would protect worker safety and health over a working lifetime.
- Sensitizer: A material that may cause little or no reaction upon first exposure but which on repeated exposure may cause more severe reactions.
- STEL: Short Term Exposure Limit. An employee exposure to an airborne contaminant, expressed as a 15-minute time-weighted average concentration.
- Teratogen: Any agent that causes an abnormality in the developing embryo following fetal exposure during pregnancy.
- TWA: Time-weighted average concentration of a particular substance. Usually measured over an 8 hour period.

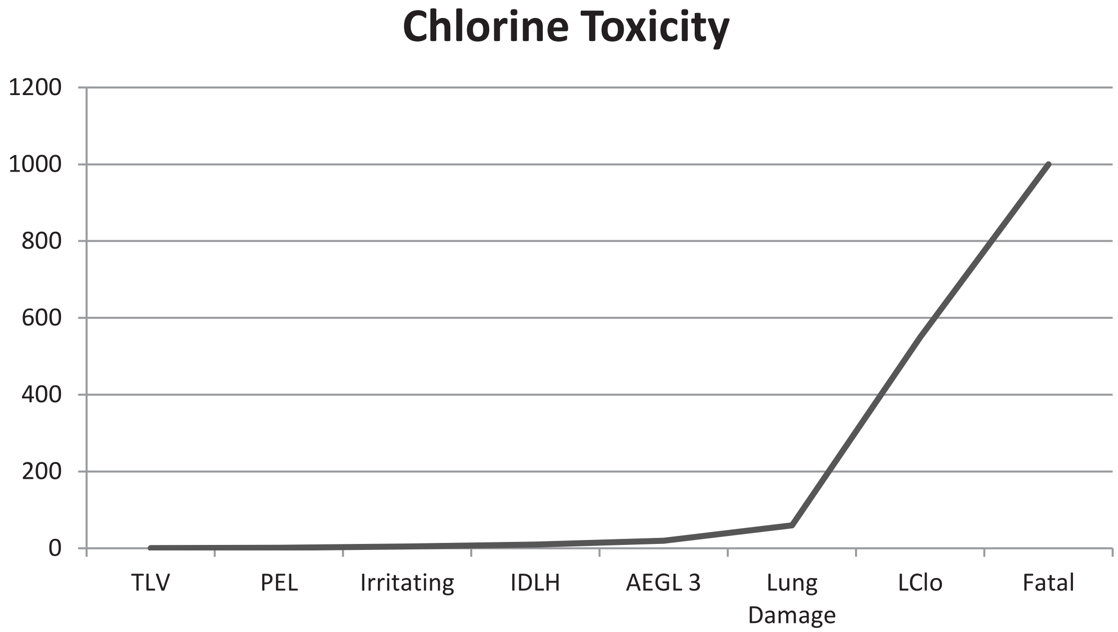
Terms used to quantify exposures.

- IDLH: Immediately Dangerous to Life and Health. Maximum concentration above which only a highly reliable breathing apparatus providing maximum worker protection should be permitted. Exposures above this level may impair the ability of a worker to escape without loss of life or irreversible health effects. This includes certain transient effects, such as severe eye or respiratory irritation, disorientation, and incoordination, which could prevent escape.
- PEL: Permissible Exposure Limit. The maximum permitted 8-hour time-weighted average concentration of an airborne contaminant. (This is a legal limit set by OSHA.)*
- TLV$^{©}$: Threshold Limit Value. Level to which a worker can be exposed day after day for a working lifetime without adverse effects.*
- TLV$^{©}$-C: Threshold Limit Value-Ceiling. The maximum concentration of an airborne contaminant to which an employee may be exposed at any time.*
- TLV$^{©}$-STEL: Threshold Limit Value-Short Term Exposure Limit. Spot exposure for a duration of 15 minutes, that cannot be repeated more than 4 times per day with at least 60 minutes between exposure periods.*
- TLV$^{©}$-TWA: Threshold Limit Value – Time Weighted Average. Average exposure on the basis of an 8h/day, 40h/week work schedule.*

("TLV" is a proprietary term owned and copyrighted by the American Conference of Governmental Industrial Hygienists (ACGIH). They are a recommended level set by ACGIH.)

*Note: these measures are used to manage chronic occupational exposures over a worker's lifetime. They aren't appropriate for use in managing brief acute exposures such as those encountered in emergency response.

Exposure Levels – Graphically



Measuring Levels of Contaminants

Each of the preceding terms measures exposures in terms of how much of a hazard an individual is exposed to. They can apply to a variety of hazards, not just hazardous materials. In the case of TLVs, they can also apply to other hazards such as noise exposure, vibration, ionizing and non-ionizing radiation exposure and heat and cold stress. This course will focus on evaluating exposures from airborne hazardous materials (gases, vapors and particulates).

The health effects of any toxic substance are related to the dose (i.e. level of exposure). Because many substances are toxic at very low doses it's important to have units of measure that can quantify dilute concentrations (both in air and in liquids) in a uniform manner. We can use these units to compare the toxicity of one substance to another.

The standard measures of toxicity cited above quantify effects at very low levels of exposure. The units used in toxicology are generally measures of concentration (i.e. the amount of one material in a larger amount of another material). The following standard units of measure are used to describe and quantify toxic airborne exposures:

- mg/m^3: milligrams per cubic meter, milligrams of chemical per cubic meter of air. The weight of a substance present in a cubic meter or air. (Primarily used to measure the amount of particulates present.)
- mg/kg: milligrams per kilograms, milligrams of material per kilograms of body weight. (Primarily used to measure oral doses.)
- ppb: parts per billion or 1/1,000,000,000. (Primarily used to measure gases and vapors.)
- ppm: parts per million or 1/1,000,000. (Primarily used to measure gases and vapors.)

Both parts per million and parts per billion are "volume in volume" measures and have no inherent dimensions. Milligrams per cubic meter on the other hand express a specific mass of a substance in a specific volume of air (1 cubic meter).

Acute Exposure Guideline Levels (AEGL)

The exposure levels described above are intended to be used to evaluate and manage *workplace* exposures. They apply to healthy adult workers. They don't take into account how people who *aren't* healthy adults will react to exposures. Because of this, the levels cited above are often poorly suited to use in making decisions about protecting the general population from the adverse effects of exposure to hazardous materials.

AEGLs are exposure guidelines that estimate the concentrations at which most people—including sensitive individuals such as old, sick, or very young people—will begin to experience health effects if they are exposed to a hazardous chemical for a specific length of time (duration). AEGLs give responders a quantitative tool for assessing the hazards and risk to the general public from emergencies involving a hazardous airborne chemical. This makes them useful in evaluating the need for protective actions in a hazmat incident. (Note: AEGLs are the default level of concern for the ALOHA air dispersion model.)

AEGLs are established by the US EPA with input from various groups. These groups include federal and state government agencies, universities and other academic organizations, labor unions and private industry groups. EPA publishes draft AEGLs in the Federal Register. This allows the general public and interested parties to officially review and comment on the proposals.

There are three AEGL values, each of which corresponds to a specific tier of health effects. They are defined as follows:

- **AEGL-3** is the airborne concentration, expressed as parts per million (ppm) or milligrams per cubic meter (mg/m^3), of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening health effects or death.
- **AEGL-2** is the airborne concentration (expressed as ppm or mg/m^3) of a substance above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape.
- **AEGL-1** is the airborne concentration (expressed as ppm or mg/m^3) of a substance above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic nonsensory effects. However, the effects are not disabling and are transient and reversible upon cessation of exposure.

All three tiers (AEGL-1, AEGL-2, and AEGL-3) are calculated for five exposure periods: 10 minutes, 30 minutes, 60 minutes, 4 hours, and 8 hours. (The ALOHA air model defaults to the 60 minute exposure level.)

Typically, the AEGL values will be different for each exposure duration. This is because the physical effects are typically related to dose (that is, concentration over exposure duration). However, in some cases, the AEGL values will be the same for all durations. This usually occurs when the effects depend only on concentration—not on the length of time people are exposed.

Routes of entry

There are four routes of entry: Inhalation, ingestion, absorption and injection. The effects of an exposure can vary greatly depending on the route of entry. For example, swallowing liquid mercury would cause no acute harm while inhaling mercury fumes can cause severe brain damage. Few substances are toxic by all routes of exposure.

If a material is toxic by more than one route of entry the toxic effects for each route of entry can be completely different. When a substance is ingested it’s routed through the digestive system. The material will usually get absorbed in the small intestine and the body will then metabolize the substance. It will then make its way into various organs. If a material is absorbed through the lungs or skin it will enter the blood stream immediately and be transmitted directly to various organs.

Reference material used in hazmat response will identify the toxic effects of a substance. They will usually specify the route of entry for the effect identified. This is important information to use when making decisions about what level of PPE to use and how to protect the public. In general, the more routes of entry a substance has, the more hazardous it is. (Note: many chemical reference sources will use the terms “oral” and “dermal” in lieu of ingestion and absorption.)

Inhalation

Inhalation exposures result from breathing air that is contaminated with hazardous particulate matter (e.g., dust), gases, vapors, or aerosols.

The physiology and anatomy of respiratory system makes it well-suited to allow contaminants to enter the body and produce toxic effects.

- The respiratory system is structured to quickly get gases into the body.
- Adults breathe 12-18 times per minute and can’t go more than 3-4 minutes without breathing. This allows contaminants to rapidly enter the body, often before an individual is aware it’s happening.
- Air enters the lungs (in order) via the mouth, trachea and bronchial tubes. The bronchial tubes lead to the lobes of the lungs. (The right lung has three lobes; the left lung has two.) The lobes are filled with small, spongy sacs called alveoli. This is where the gas exchange occurs. The alveolar walls are extremely thin and are composed of a single layer of tissues called epithelial cells and pulmonary capillaries. Oxygen enters the blood stream by diffusing through these capillaries. The large surface area of the lungs and the thin walls of the alveoli allow gases to quickly get to the blood stream and cause systemic damage to the body.
- The lungs have a large surface, especially in comparison to the skin. The skin of adults generally has 20 ft^2 of surface area while the lungs have about 750 ft^2 of surface area.

Inhaled substances may directly injure or irritate the pulmonary epithelium at various locations of the respiratory tract. They may also be absorbed through the lungs resulting in systemic toxicity. (Some substances may produce both effects.) The following identifies the effects various commons substances have on the respiratory system:

- Chlorine. Chlorine is highly reactive. When it enters the respiratory system it becomes hydrochloric acid, hypochlorous acid or chloramines. They damage the airway tissue by irritating the respiratory mucus membrane which leads to pulmonary edema.
- Ammonia. Ammonia reacts with water in lung mucosa to form a strong alkali, ammonium hydroxide (NH_4OH). This can cause severe chemical burns that result in airway obstruction and edema.
- Hydrogen fluoride (and hydrofluoric acid). Hydrogen fluoride (HF), a colorless, highly irritating gas with a pungent odor. It easily dissolves in water to form hydrofluoric acid. It penetrates deeply into body tissues causing both local cellular destruction and systemic toxicity. When inhaled the effects have a very rapid onset due to the rapid transport of the gas into the bloodstream.
- Oxides of nitrogen. The oxides of nitrogen, i.e. nitrogen oxides, are composed of a mixture of nitrogen and oxygen type of gases. The most toxic nitrogen oxides are nitric oxide (NO) and nitrogen dioxide (NO_2). When inhaled, these substances are converted to nitric (HNO_3) and nitrous (HNO_2) acids in the distal airways, directly damaging certain structural and functional cells in the respiratory system.
- Hydrogen sulfide. Hydrogen sulfide is a broad-spectrum poison, meaning that it can poison several different systems in the body, although the nervous system is most affected. It is a potent cytotoxic asphyxiant, impairing cytochrome oxidase and cellular respiration. The toxicity of H2S is comparable with that of carbon monoxide. It binds with iron in the mitochondrial cytochrome enzymes, thus preventing cellular respiration.

Ingestion (Oral)

Responders don't eat hazardous materials, intentionally. Responders may ingest a hazardous substance if they eat or drink some something that has been contaminated by that substance. Such exposures would be inadvertent.

Ingestion exposures wouldn't necessarily be a result of eating or drinking something contaminated with a hazardous material. Normal human behavior such as nail biting or touching your face with your hands/fingers can cause you to ingest contaminants on your hands. On average, people touch their faces with their hands four times an hour. Stress (such as that caused by a response) can cause that rate to double.

Most inadvertent ingestion exposure would be caused by hand-to-mouth and object-to-mouth means. The Safety Officer will use a Site Safety Plan to implement administrative controls to prevent exposures like this.

The human gastrointestinal (GI) tract consists of the mouth, esophagus, stomach and intestines (small and large). The function of the GI tract is to process ingested food by mechanical and chemical means, extract nutrients and excrete waste products. The areas of the GI tract that are most at risk from ingesting a hazardous material are the perioral area (outside of the mouth), oral cavity and the stomach.

In general, the properties of a hazardous material will determine the harm it will cause. Corrosives will physically damage the mouth and esophagus but (usually) not reach the other areas of the GI tract. Toxic substances will generally be absorbed by the stomach and/or small intestine and cause systemic poisoning. Radioactive alpha and beta particles can enter the GI tract through inadvertent ingestion and become lodged at various points in the tract.

Absorption (dermal)

Relatively few materials can be absorbed through intact skin. Human skin is generally impermeable to solid materials, most inorganic substances and radioactive particles (alpha or beta). If the skin is damaged due to disease, abrasion or other injury it will have less resistance to exposure to hazardous materials.

In general, this route of entry refers to chemicals that enter the blood stream after passing through intact skin. (Contaminants can also be absorbed through the cornea. This is usually not a significant hazard to responders since the cornea has a fraction of the surface area of the skin.) There are a variety of materials that can damage the skin upon contact, especially corrosives. However, they typically don’t pass through the skin and enter the blood stream. This is not the case, though, with hydrofluoric acid. It is one of the few corrosives capable of systemic toxicity through dermal exposure. Once absorbed into blood through the skin, it reacts with blood calcium and may cause cardiac arrest.

Chemicals that can be absorbed through the skin include benzene, aniline, styrene, toluene, carbon disulfide, acrylonitrile, carbon tertrachloride. chloroform and nitrobenzene. Many pesticides such as Aldrin, Carbofuran, Chlordane and Dursban are also skin-absorptive.

This route of entry may be a hidden hazard. In many cases, absorption of chemicals through the skin can occur without a person noticing. Because of this, dermal absorption may be a significant exposure pathway.

There are three ways dermal absorption can occur: intercellular lipid pathway, transcellular permeation and penetration through the appendages (hair follicles, glands).

Intercellular Lipid Pathway

The outer layer of the skin is the stratum corneum. It consists of cells known as corneocytes. The spaces between the corneocytes are filled with substances such as fats, oils, or waxes known as lipids. Some chemicals can penetrate through these lipid-filled intercellular spaces through diffusion.

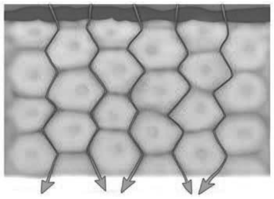
Transcellular Permeation/Diffusion

Another pathway for chemicals to be absorbed into and through the skin is transcellular, or cell-to-cell, permeation whereby molecules diffuse directly through the corneocytes.

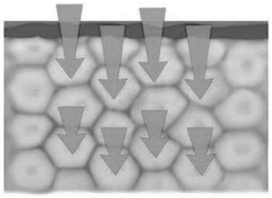
Penetration through Appendages (hair follicles, glands)

The third pathway for diffusion of chemicals into and through the skin is skin appendages (i.e., hair follicles and glands). This pathway is usually insignificant because the surface area of the appendages is very small compared to the total skin area. However, very slowly permeating chemicals may employ this pathway during the initial stage of absorption. (This is why it's important to wear some sort of head covering when using field identification systems such as 5-Step ™ or HazCat ™.)

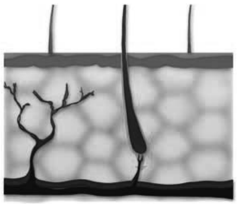
Intercellular Lipid Pathway



Transcellular Permeation



Penetration



Chemical protective clothing (CPC) is designed to interrupt and/or prevent dermal exposure. The toxicity and properties of the material involved will determine the type of suit material required and the extent to which the CPC covers the body.

(Note: Dermal absorption is not the same thing as contact dermatitis, an inflammation of the skin caused by direct damage to the skin following exposure to a hazardous agent or by an immunologic reaction triggered by dermal contact to a skin allergen.)

Injection

Injection is a less common route of exposure. It can occur when a contaminated object punctures the skin and injects a chemical (or other agent) into the bloodstream. This can also occur when a chemical is sprayed at the body at high pressure such as from a leak in a hydraulic line. Adverse effects can then occur as the substance is circulated in the blood and deposited in the target organs. Injection effectively bypasses the protection provided by intact skin and provides direct access to the bloodstream, and thus, to internal organ systems. Injection may occur through mishaps with needles, wires, when handling biting animals, or through accidents with broken glass or other sharp objects that have been contaminated.

Factors Influencing Toxic Effects

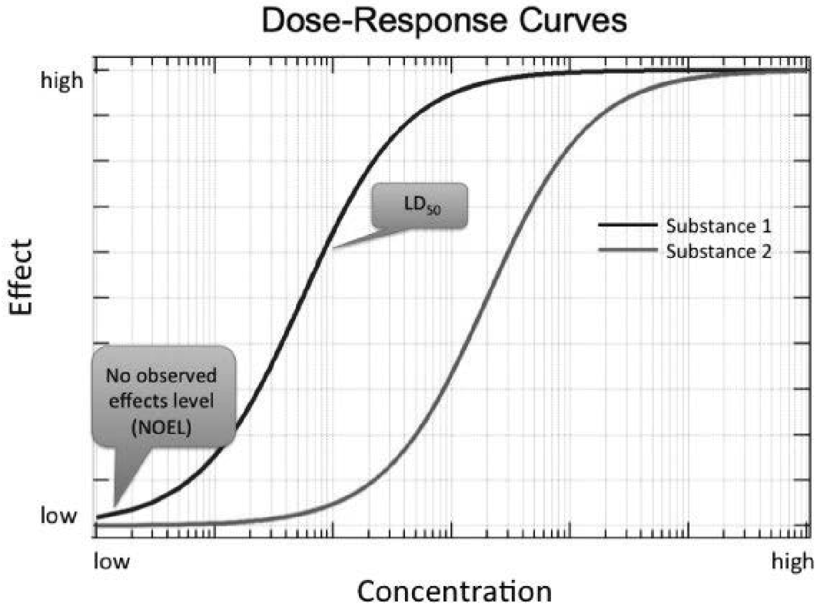
There are a variety of factors that affect how toxic a substance will be. The toxic effects of a given substance vary with the dose, length of exposure and the route of entry. Biological variation will cause even greater differences. The effects of a specific dose at a given route of entry and a specific length of exposure will be affected by the age of the person exposed and their general level of health. For example, an adult could easily tolerate an acute large dose of table salt (sodium chloride) but the same dose could be fatal for an infant.

Dose (Exposure) Response Relationship

The dose response relationship is the correlation between the dose (or exposure) and the magnitude of the biological change produced (measured in appropriate quantifiable units). It describes the change in biological effect resulting from differing levels of exposure. A dose response relationship exists if a change in the dose of a chemical causes a quantifiable change in the effect observed.

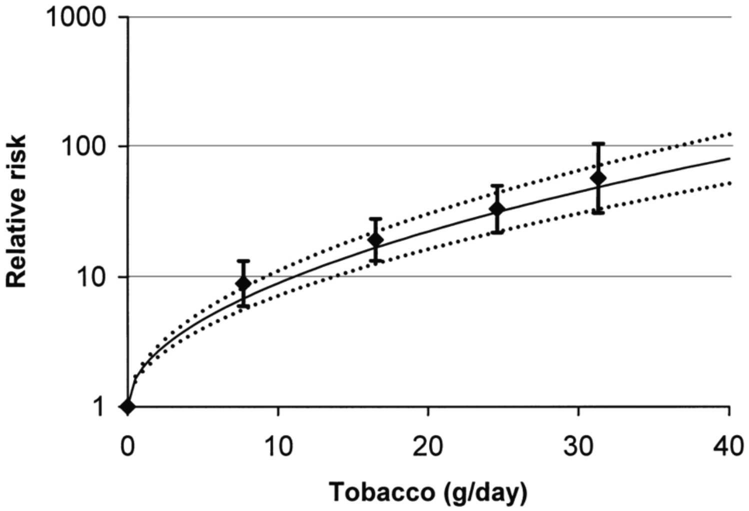
For most substances, small doses are not toxic. The point at which toxicity first appears is known as the threshold dose level. From that point, the curve increases with higher dose levels. Most dose response curves are "S" shaped but some may be linear.

Typical Dose Response Curves



This is an important concept in pharmacology. Researchers will test medications to determine when they begin to exhibit an effect (threshold dose level). They will increase the dose to identify the most effective dose for a given population. They plot the results on a graph. This model will help to determine dosages that are safe and effective. This helps them to determine the most effective dose. (Note: In the area of clinical pharmacology, they use the term "dose" while in hazmat response we use the term "exposure." In pharmacology, dose means dosage or amount of the medication administered to a person.)

Dose Response Curve for Tobacco Use



Individual Variability

Sex

Males and females exhibit different responses to exposure to hazardous materials but the main differences in effects of exposure occur in the reproductive systems. There is little to no data on how the effects of human exposures will vary by sex. Numerous animal studies show differences between the sexes but, as always, it's impossible to know if these studies would show similar results in humans.

Age

There is little empirical data on the human effects of the vast majority of hazardous materials. Most toxicological studies are done on animals that may or may not respond to a contaminant the same way a human will. This is particularly true for age differences in humans. Most exposures to hazardous materials take place in the workplace; therefore, toxicological data on human exposures is for adult males. There is very little data on the effects of exposures to children.

Acute Effects

"Acute" effects refer to the ability of a substance to cause adverse effects within a short time of dosing or exposure. These adverse effects result either from a single dose/exposure or from multiple doses/exposures in a short period of time (usually less than 24 hours). The exposure is of a finite duration occurring within a short time (up to 14 days).

The majority of exposures to responders will be acute exposures.

Chronic Effects

"Chronic" health effects are those that persist over a long period of time whether or not they occur immediately upon exposure or are delayed. Chronic adverse effects occur as a result of repeated long term exposure to a contaminant(s).

Summary

A good understanding of this subject will help you to make more informed decisions about several aspects of hazmat response such as: selecting personal protective equipment, assessing the hazards of a given material, evaluating the need for protective actions and in formulating procedures to protect responders.

Chapter Review

1. Which of the following is an example of a procedure-based response?
   A. Assessing the risks of a proposed response tactic.
   B. Evaluating the toxicity of a substance.
   C. Following a standard checklist.
   D. Weighing risks versus gains.

2. Fill in the blank.

There are _______ routes of entry.

“PPM” is an acronym for parts per ___________________.

LD_{50} is the median lethal ___________ to 50% of a test population.

A ____________ health effect is one that persists over a long period of time.

“IDLH” is an acronym for Immediately _______________ to Life and Health.

A cytotoxic ___________________ impairs cellular respiration.

The __________________ makes the poison.

TLV measures ____________________ workplace exposures.

3. Water can be toxic if consumed in excessive quantities. Which of the following is one of the toxic effects of extreme water intake?
   A. Decrease in sodium concentration and other electrolytes.
   B. Impairment of pulmonary gas exchange.
   C. Intercellular lipid deficiency.
   D. Non-ionizing cellular damage.

4. Which of the following substances can be toxic by dermal absorption?
   A. Sodium hydroxide.
   B. Anhydrous ammonia.
   C. Poison ivy.
   D. Carbon tertrachloride.

5. AEGLs are exposure guidelines that estimate the concentrations of specific substances at which most people will begin to experience adverse health effects if they are exposed for a specific duration. Which of the following AEGL levels indicates that people exposed to the substance could experience life-threatening health effects or death?
   A. AEGL-1
   B. AEGL-2
   C. AEGL-3
   D. AEGL-4

6. For most substances small doses are not toxic. The point at which toxicity first appears is known as the threshold dose level. What is the term used to describe this effect?
   A. Acute/chronic variation
   B. Partial-pressure effect
   C. Route of entry
   D. Dose-response relationship

7. Which of the following routes of entry is the *least* likely to occur in hazmat response activities?
   A. Ingestion
   B. Inhalation
   C. Absorption
   D. Injection

Chapter 18: Hazard Assessment and Risk Analysis

Risk-Based Response

There are two basic types of response strategies: procedure-based response and risk-based response. A procedure-based response involves following checklists and predetermined processes. A risk-based response requires responders to assess the hazards and analyze the risks and implement tactics that will minimize risks.

All decisions about a response should be based on a thorough analysis of the hazards present in the incident and the potential risks involving those hazards.

The basic steps in Risk-Based Response are:

- Analyze a problem involving hazmat.
- Assess the hazards.
- Evaluate the potential consequences (i.e. risk).

Without a firm grasp of basic chemistry it would be difficult to perform these tasks.

Hazard Assessment

The most critical part of hazard assessment in hazmat response is to identify or recognize hazards that are present (or that can be anticipated).

“Hazards” are real or potential conditions that can cause injury, illness or death to personnel or can degrade, damage or destroy equipment or property. The type of hazards present and their degree of hazard will determine how a response proceeds. The hazard assessment process will affect all aspects of a response such as PPE selection, size and orientation of control zones, protective actions needed and the development of a monitoring strategy.

Hazard assessment in hazmat response is an ongoing process. New hazards can crop up as containment systems become compromised or materials react with each other. Recognizing and assessing these hazards continues through all phases of a response.

The hazard assessment process answers several questions.

- What will this material do?
- Will it do something bad right now?
- How can it hurt me?
- How can I protect myself?

Steps in Hazard Assessment. What will this material do?

The first step in deciding what the material will do is to identify the material. It sounds obvious but it's often a complex process with a lot of potential pitfalls.

There are a variety of systems and tools designed to help responders identify the materials involved in a hazmat incident. As seen in previous chapters, US DOT and GHS have specific definitions for hazardous materials/substances and have tools to help identify them. There are other tools such as monitoring instruments and field identification systems that help to identify or confirm the identity of hazardous materials. (They will be covered in subsequent modules of hazmat technician training.)

As discussed in Chapter 2, hazardous materials can be elements, pure substances or mixtures. Identifying a material that is a mixture can be a difficult and complex process depending on the makeup of the material and whether or not it's homogenous or heterogeneous.

Steps in Hazard Assessment. What will this material do?

The second step in deciding what the material will do is to identify the hazard(s).

As discussed in previous chapters, US DOT, GHS and NFPA 704 try to indicate the major hazards. The definitions these systems use encompass a wide array of hazards. A critical part of the hazard assessment process is to identify *all* of the potential hazards the material presents. None of the systems used to communicate hazards to responders is perfect and there are always substances that will fall between the cracks. These systems may identify a major hazard but not a hazard that doesn't meet the definitions used by these systems.

In many cases, the name of the material can help identify the hazards. For example:

- Hydroxide: caustic in solution with water. (e.g. Sodium hydroxide)
- Peroxide: oxidizer, unstable. (e.g. Calcium peroxide)
- Cyanide: toxic. (e.g. Sodium cyanide)
- Hydrocarbon ending in "ane:" flammable (e.g. Propane)

Steps in Hazard Assessment. Will something bad happen *right now*?"

In some cases the answer will be, "It already has!"

The first task in assessing whether or not something bad will happen now is to predict the behavior of the material.

A substance's basic "behavior" is determined by the type of change it undergoes. As discussed in Chapter 2, there are two fundamental types of change that matter can undergo: physical and chemical. There are some types of chemical/physical change that have "red flags" in their descriptions. Some examples:

- BLEVE: catastrophic container failure as contents change from liquid to vapor state.
- Exothermic: reaction that gives off heat.
- Polymerization: rearrangement of molecules that can result in a container failure.
- Combustion: substance reacts rapidly with oxygen and gives off heat.

The type of material (organic or inorganic) and the type of bonds (metallic, covalent, ionic or resonant) will influence the behavior of a material. For example:

- An ionically bonded material will often be water-soluble.
- Organic compounds are often flammable.
- A material with covalent bonds will often not be water-soluble.
- Resonant bonds will usually make a substance very stable.

The periodic table can be useful in predicting behavior. For example:

- Alkali metals (Group 1): often water-reactive.
- Halogens (Group 7/17): some are highly reactive.
- Noble gases (Group 8/18): tend to be inert.

As discussed in detail in Chapter 7, the properties of a substance will determine in detail how it behaves. If you have a thorough understanding of chemical and physical properties you'll be able to accurately and reliably predict what a hazardous material will do. Assessing the properties should answer the four questions posed earlier.

There are other variables that influence the behavior (and therefore the risk) of a given material. Chief among them is weather. Several physical and chemical properties (e.g. vapor pressure) are what is called "temperature dependent" so their effect on the incident will vary according to the ambient temperature. Relative humidity can influence chemical reactions and the wind will affect how a material disperses in air.

Steps in Hazard Assessment. How can it hurt me?

Answering this question requires you to decide how hazardous is hazardous. This course has covered a nearly endless array of categories, types and classes of hazardous materials. How do you quickly evaluate the degree of hazard a given material presents?

The US DOT regulations in 49 CFR lists and defines the nine hazard classes. 49 CFR §172.504 *General Placarding Requirements* lays out the requirements for placarding shipments of hazardous materials. It divides the placarding requirements into two categories and puts them into two tables. The two tables are divided by the degree of hazard. The hazard classes in Table 1 are, in general, more hazardous than those in Table 2.

Table 1

Hazard Class or Division Number	Placard Name
1.1	Explosives 1.1
1.2	Explosives 1.2
1.3	Explosives 1.3
2.3	Poison gas
4.3	Dangerous when wet
5.2	Organic peroxide
6.1	Poison inhalation hazard
7 (Radioactive Yellow III label only)	Radioactive

Table 2

Hazard Class or Division Number	Placard Name
1.4	Explosives 1.4
1.5	Explosives 1.5
1.6	Explosives 1.6
2.1	Flammable gas
2.2	Non-flammable gas
3	Flammable
Combustible liquid	Combustible
4.1	Flammable solid
4.2	Spontaneously combustible
5.1	Oxidizer
5.2	Organic peroxide
6.1	Poison
6.2	(None)
8	Corrosive
9	Class 9
ORM-D	(None)

Historic data can also assist responder in ranking hazards. There are two federal agencies that collect and publish data on hazmat incidents. They are US DOT and the Agency for Toxic Substances and Disease Registry (ATSDR). The data from these two agencies consistently show that the conditions that kill and injure people are fire and explosion. These incidents mainly involve flammable gases and liquids. Their data shows that corrosives account for the most injuries (primarily from skin contact).

As discussed in Chapter 17, all substances are toxic. That's interesting information but isn't useful for hazard assessment. Fortunately, there are hard numbers that we can use to determine the relative toxicity of substances. Chapter 17 lists the standard terms used to quantify the risk of exposure. In general, smaller numbers mean the substance is more toxic. The historic data gathered by various government agencies may give a distorted picture of relative toxicity. Their data consistently shows that the toxic substances that cause the most deaths are anhydrous ammonia and chlorine. There are gases that are more toxic but they aren't produced or shipped in anywhere near the quantities that ammonia and chlorine are.

Risk Analysis

A risk assessment is a process that identifies potential hazards and analyzes what could happen if a hazard occurs. The process of risk analysis answers two questions:

- What bad thing(s) may happen?
- How likely is it that this bad thing will occur?

A "risk" is the potential loss or adverse impact from exposure to hazards; the chance of injury or property damage probability and severity of accident or loss from exposure to various hazards, including injury to people and loss of resources.

Risk generally is a function of severity and probability. Severity: the potential adverse consequences an event. (Adverse: damage, injury, or impact on a mission or task.) Probability: the likelihood an individual event will occur.

There are a variety of factors that affect risk. They fall into some general categories: material involved, containment system used, potential areas of impact and stressors present.

Material involved.

- Physical and chemical properties of the product involved.
- Quantity of material (inside and out of the container).

Containment system.

- Design and construction features of the container.
- Are the pressure relief devices (PRDs) functioning?
- Is the containment system stable?

Stressors present.

- Mechanical stress.
- Thermal stress (Fire).
- Is there direct impingement or radiant heat?
- Chemical stress.

Potential areas of impact.

- Proximity of exposures.
- Surrounding environment and terrain.
- Expected direction of travel of any spilled material.
- Adjacent tracks and/or roads.
- Utilities within the area.

Summary

Implementing a risk-based response requires a hazard and risk assessment founded on what you've learned in this course. The subjects covered in this course are tools that you can use to evaluate the substances involved in an incident and respond safely according to the risks the materials present.

Chapter Review

1. Which of the following is an example of a procedure-based response?
    - A. Assessing the risks of a proposed response tactic.
    - B. Evaluating the hazards of a substance.
    - C. Following a standard checklist.
    - D. Weighing risks versus gains.

2. US DOT categorizes hazardous materials into nine hazard classes. Those nine hazard classes are divided into two tables. What information do these tables provide that can help us to assess the hazards of a given material?
    - A. Materials in Table 2 evaporate faster than other materials.
    - B. A material in Table 1 requires a larger placard than one in Table 2.
    - C. Each Table will refer you to specific sections of the DOT ERG.
    - D. Substances in Table 1 are generally more hazardous than those in Table 2.

3. The periodic table can be useful in predicting the general behavior of a substance. If an element is in Group 18 (Noble Gases) it would tend to be:
    - A. Inert
    - B. Reactive
    - C. Toxic
    - D. Water-reactive

4. A ____________ is the potential loss or adverse impact from exposure to hazards; the chance of injury or property damage probability and severity of accident or loss from exposure to various hazards, including injury to people and loss of resources.
    - A. Hazard
    - B. Risk
    - C. Harm
    - D. Menace

5. The type of bonds a molecule has will often influence the behavior of a material. If a material has ionic bonds it will tend to be:
    - A. Water soluble
    - B. Flammable
    - C. Explosive
    - D. Unstable

6. A container will fail when it's stressed by external forces. Which of the following would be an example of a chemical stressor?
   A. Exposure to ultraviolet light
   B. Exposure to a corrosive material
   C. Impact from a meteorite
   D. Flame impingement

7. The hazard assessment process will affect all aspects of a response. Which of the following would be an example of a chemical stressor?
   A. Exposure to ultraviolet light
   B. Exposure to a corrosive material
   C. Impact from a meteorite
   D. Flame impingement

8. The hazard assessment process will affect all aspects of a response. One of the steps in this process is to identify the substance involved. The following table lists some general categories of materials. Match them with the task in a response that this material is most likely to affect.

Material	Task			
	PPE Selection	Selecting Protective Actions	Selecting Monitoring Instrument	Determining Sizes of Control Zones
Hydroxides				
Peroxides				
Name ends with "ane"				
Name contains "cyanide"				
Material in Hazard Class 2.1				
Fulminates				
Name ends with "ate"				
Ethers				
Carbamates				

Hazard Assessment and Risk Analysis Case Studies

Risk-Based Response

A risk-based response requires responders to assess the hazards and analyze the risks and implement tactics that will minimize risks. The following case studies will give you practice in making decisions about incident response using the risk-based response tools.

Read the case study the instructor assigns to you. Be prepared to address the following topics about this incident.

- Identify the hazards present.
- Assess those hazards.
- Identify and evaluate the potential consequences (i.e. risk) of those hazards.

Present your findings to the rest of the class when directed to do so.

Case Study – Kansas City ANFO Explosion

On November 29, 1988 at 0340 hours security guards at a construction site in Kansas City, Missouri called the Fire Department and reported that there was a “small pickup truck” burning. In the background a woman could be heard saying “the explosives are on fire.” The woman was later identified as another security guard. KCFD dispatched two engines and a battalion chief. They arrived on scene within minutes. When firefighters arrived they found two separate arson fires at the site. They immediately began to extinguish the fires.

The construction site was an area near the intersection of U.S. Highway 71 and 87th Street in Kansas City, Missouri. The project required moving substantial quantities of limestone that was routinely broken up by drilling holes into the rock, placing a blasting agent in the holes, and then detonating it. Kansas City has large quantities of limestone throughout the area. There were several limestone quarries operating in the area.

The blasting agent used at the site was a mixture of ammonium nitrate and fuel oil. The common name for the product is ANFO. If a more powerful explosive is needed, aluminum dust or pellets can be blended in. This creates a “hotter” load. Reportedly, of the approximately 50,500 pounds of ammonium nitrate/fuel oil mixture involved in these explosions, 47,000 pounds contained the mixture of 5 percent aluminum.

The construction project used between 10,000 and 16,000 pounds a day on the average. The material came in 30-pound socks that were placed into the drilled holes, then detonated with a device such as a blasting cap. The material was divided between two trailers/magazines less than 100 feet apart.

The ammonium nitrate mixtures were stored in two appropriate “Type 5” trailers/magazines specifically designed to transport and store blasting agents. The trailers were in the open, not enclosed in any fencing. The trailers were not placarded. (The DOT regulations in effect then required placarding only when the material is transported. DOT regulations were later changed to require shippers to leave placards on vehicles after they were delivered.)

Case Study – Kansas City ANFO Explosion Outcome

At 0408 hours, approximately 22 minutes after the first engine company arrived on the scene and approximately 16 minutes after the second company arrived on the scene a catastrophic explosion occurred. All six firefighters assigned to both companies were killed.

Approximately 40 minutes later, a second explosion occurred, followed by several minor explosions. The explosions broke windows far from the site and were heard through a wide area. There were two large craters found where the two trailers had been. The first trailer explosion created a swimming pool-like crater, with a “deep part” 80 feet in diameter and eight feet deep connected to a smaller crater 20 feet in diameter and six feet deep. The second trailer explosion created a crater approximately 100 feet in diameter and eight feet deep.

Properties of Ammonium nitrate-fuel oil mixture; Class 1.1D; UN 0331

Physical State: Solid

Molecular Weight: not available

Boiling Point: n/a

Freezing Point: n/a

Solubility: n/a

Vapor Pressure: n/a

Ionization Energy: n/a

Flash Point: n/a

Upper Explosive Limit: n/a

Lower Explosive Limit: n/a

Relative Gas Density: n/a

OSHA PEL: TWA: n/a

IDLH: n/a

Case Study – Hydrogen Fluoride Acid Release

At 0238 hours the county 9-1-1 call center received a report of a tractor trailer rollover with unknown injuries. A cell phone caller reported a tractor trailer overturned on the highway. The caller stated "It looks like a person is trapped in the vehicle." The caller also reports "lots of smoke visible" at the scene.

The first-arriving state police officer found an overturned tractor trailer blocking both southbound lanes of a four-lane, limited-access highway. In this area of the highway, cement barriers separate the north-bound and south-bound lanes.

The officer saw a black and white placard on the trailer with "1052" on the placard.

The conditions at the scene are:

- Clear skies.
- 28°F, 53 percent humidity.
- Winds slight NNE at 1 mile per hour.
- Sloped, hilly terrain.

The vehicle involved is a modified MC-312 carrying 33,000 pounds (approximately 4,000 gallons) of hydrogen fluoride, aqueous, United Nations (UN) ID# 1052. It failed to negotiate a sharp curve in a limited access highway. It hit the shoulder and rolled over.

At daybreak responders reported small puffs of white gas visible at the rear of the trailer. At 0900 hours a private hazmat cleanup crew, hired by the trucking company performed a damage assessment. The crew reported the following:

- The trailer appeared to be in good structural condition. The damage appeared to be cosmetic.
- The dome cover was damaged and could not be opened. This made it difficult, if not impossible, to offload the cargo. (According to the cleanup crew it would take about 40 hours to offload the cargo.)
- There was a small drip, approximately every 30 seconds that vaporized and dissipated. The leak was in the vapor line, which at that point contained liquid due to the position of the truck.
- The leak could have been from a spring loaded relief valve or a ¼ turn ball valve that was bent or cracked.

Cleanup company personnel with colorimetric tubes detected readings of 2.0 parts per million (ppm) at 3 feet off the ground when the material vaporized.

Case Study – Hydrogen Fluoride Acid Release Outcome

At 1038 hours the entry crew removed the ball valve handle and closed the valve using vise grip pliers. The leak was stopped. Personnel performed additional air monitoring with nothing detected. At 1501 hours the tanker was uprighted and reevaluated for damage and/or leaks. None were found. The tanker was placed on a lowboy trailer for removal to its original destination. The truck and trailer left the scene at 1618 hours.

Properties of Hydrogen Fluoride, Anhydrous; Class 8; UN 1052

Physical State: Solid

Molecular Weight: 20.01

Boiling Point: 67.1° F

Freezing Point: −118.5° F

Solubility: Miscible

Vapor Pressure: 400 mm Hg at 36.5° F

Ionization Energy: 15.98 eV

Flash Point: Not flammable

Upper Explosive Limit: Not flammable

Lower Explosive Limit: Not flammable

Relative Gas Density: 0.7

OSHA PEL: TWA: 3 ppm

IDLH: 30 ppm

Case Study – Chlorine Release

About 0503 hours, central daylight time, on Monday, June 28, 2004, a westbound Union Pacific Railroad (UP) freight train traveling on the same main line track as an eastbound BNSF Railway Company (BNSF) freight train struck the midpoint of the 123-car BNSF train as the eastbound train was leaving the main line to enter a parallel siding. The accident occurred at the west end of the rail siding at Macdona, Texas, on the UP's San Antonio Service Unit. The collision derailed the 4 locomotive units and the first 19 cars of the UP train as well as 17 cars of the BNSF train.

As a result of the derailment and pileup of railcars, the 16th car of the UP train, a pressure tank car loaded with liquefied chlorine, was punctured. Chlorine escaping from the punctured car immediately vaporized into a cloud of chlorine gas that engulfed the accident area to a radius of at least 700 feet before drifting away from the site. (This determination was based on the extent of foliage kill in the area.) In addition to the chlorine release there was a small fire involving spilled fuel, a release of nitrogen fertilizer solution, 1000 gallons of lubricant oil and 10,000 gallons of diesel fuel. The nitrogen fertilizer solution was off-gassing ammonia.

The initial notification to local emergency response authorities came via a 911 call placed at 0506 hours from a residence on Nelson Road to the Bexar County 911 Emergency Call Center. The caller reported difficulty breathing and the presence of white smoke outside the residence. The caller also, in what could be described as a weak voice, referred to a train derailment. The 911 operator heard the word "smoke" and understood that the caller was experiencing breathing difficulty but apparently did not recognize the words "train derailment," and the caller was transferred to a fire department dispatcher. The caller again reported "train derailment" and "smoke," but the fire dispatcher also did not recognize that the incident involved a train derailment. Various other callers to 911 mentioned "train derailment" or "train wreck." However the dispatcher(s) apparently only picked up on the words "smoke" and "difficulty breathing." The response was thus processed as a "difficulty breathing and smoke in the residence" response action.

When fire department responders approached the accident site in darkness about 0515 hours, they began to have difficulty breathing as they became exposed to the vapor cloud of chlorine from the punctured railcar. Access to the scene was blocked by the derailed train. Entry teams were forced to travel approximately 3/4 mile through the crash site to the trapped residents. A short time later, responders determined that the derailment wreckage at the grade crossing prevented access to residences at the west end of Nelson Road, one of which was their dispatch destination. The obstructed grade crossing also prevented the immediate rescue of three individuals who were reported to be trapped in their residence by the vapor cloud several hundred feet to the south of the emergency dispatch destination.

Case Study – Chlorine Release Outcome

Three persons, including the conductor of the UP train and two local residents, died as a result of chlorine gas inhalation. The UP train engineer, 23 civilians, and 6 emergency responders were treated for respiratory distress or other injuries related to the collision and derailment. Damages to rolling stock, track, and signal equipment were estimated at $5.7 million, with environmental cleanup costs estimated at $150,000.

Properties of Chlorine; Class 2.3; UN 1017

Physical State: Gas

Molecular Weight: 70.9

Boiling Point: -21°F

Freezing Point: -150° F

Solubility: 0.7%

Vapor Pressure: 6.8 atm

Ionization Energy: 11.48 eV

Flash Point: n/a (Gas)

Upper Explosive Limit: n/a

Lower Explosive Limit: n/a

Relative Gas Density: 2.47

OSHA PEL: TWA: 0.5 ppm C: 1 ppm

IDLH: 10 ppm

Case Study – Vinyl Chloride Release

On Friday, November 30, 2012, at 0652 hours, southbound freight train arrived and stopped on the main track at the Paulsboro moveable bridge near milepost 13.7. A red signal aspect was displayed and did not change to green when the radio signal command was executed by the train crew, indicating that the bridge was not prepared for train movement.

Despite multiple attempts by the train crew to remotely execute a radio signal command to align and lock the bridge, the signal aspect remained red and did not turn green. The conductor inspected the bridge and erroneously concluded it was properly locked to prevent movement. The engineer informed the dispatcher of the conductor's findings. The dispatcher then gave permission for the train to pass the red signal aspect and cross the bridge.

The swing span locking mechanism was not engaged at the east end of the bridge. The bridge span rotated under the moving train and misaligned the running rails. About 0702 hours, as the train traveled over the bridge, 7 cars derailed, the 6th through the 12th cars. Four tank cars that derailed on the bridge came to rest partially in Mantua Creek. Three of the derailed tank cars that entered the creek contained vinyl chloride and one contained ethanol. One tank car was breached and released about 20,000 gallons of vinyl chloride. Eyewitnesses reported that a vapor cloud engulfed the scene immediately following the accident.

At 0701 hours, the communications center received the first 911 call from the home of the Paulsboro deputy fire chief, which is located adjacent to the derailment site with a direct line of sight to the bridge. The deputy fire chief's wife told the 911 operator that a train had derailed and that the Paulsboro train bridge had collapsed. She said she watched the train derail and that there was "smoke everywhere." The deputy fire chief then took the phone and told the 911 operator the train derailed into Mantua Creek and was "spewing out all kind of gas."

The first police officer arrived about 0705 hours, followed shortly thereafter by two other police officers. The officers reported that a "heavy cloud was hovering over Mantua Creek" near the Paulsboro moveable bridge

Case Study – Vinyl Chloride Release Outcome

The train crew and numerous emergency responders were exposed to concentrations of vinyl chloride that were over 500 times the recommended exposure limit (REL). As many as 680 residents were evacuated from their homes as a result of the vinyl chloride release. 28 area residents sought medical attention for possible vinyl chloride exposure.

Equipment damage estimates were $451,000. The emergency response and remediation costs totaled about $30 million. It took over two weeks to remove the wreckage.

Properties of Vinyl Chloride Stabilized; Class 2.1; UN 1086

Physical State: Gas

Molecular Weight: 62.5

Boiling Point: 7°F

Freezing Point: -256°F

Solubility: 0.1%

Vapor Pressure: 3.3 atm

Ionization Energy: 9.99 eV

Flash Point: n/a (Gas)

Upper Explosive Limit: 33.0%

Lower Explosive Limit: 3.6%

Relative Gas Density: 2.21

OSHA PEL: TWA: 1 ppm C: 5 ppm [15-minute]

IDLH: A potential occupational carcinogen.

Case Study – Ammonia Release

On July 15, 2009, about 0740 hours, a driver and trainee began a transfer of anhydrous ammonia began from a Werner Transportation Services, Inc. (Werner) cargo tank truck to a storage tank at the Tanner Industries, Inc. (Tanner) facility in Swansea, South Carolina.

Just before 0800 hours, about 7 or 8 minutes after the transfer had begun, the trainee heard a pop sound followed by a loud rush of gas. He looked underneath the truck and saw a rupture in the transfer hose assembly directly in front of him. He stated that he saw anhydrous ammonia pluming upward from the rupture, forming a dense white cloud. The trainee immediately pushed the emergency shutdown button on the rear of the cargo tank. Upon doing this, he noticed that movement of the ammonia cloud quickly shifted in the direction of Highway 321. He then turned to the facility manifold to find a shutdown switch, but he did not see one because the white ammonia cloud was surrounding the manifold. He then evacuated through the south gate and ran west into a wooded area. Eventually he heard the hose stop and saw the cloud lift soon after.

The driver stated that he also heard a loud pop about 0800 hours and saw a cloud of gas outside the driver’s side window. He then turned off the engine to stop the trailer pump; put on his half- face respirator; got out of the truck on the passenger side; and escaped through the white cloud in front of the building along the fence, exited through a gate, and followed the railroad tracks.

At 0757 hours, the Lexington County Communications Center received the initial 911 call from a Tanner employee at the facility reporting a release of 100 to 500 pounds of anhydrous ammonia. The first Lexington County Fire Service unit arrived on scene at 0807 hours. A Tanner representative recommended to the Emergency Management Department that the community should shelter-in-place as a precautionary measure after the anhydrous ammonia release. Fire service search teams found that most residents had self-evacuated.

The South Carolina Department of Health and Environmental Control (DHEC) arrived on scene at 0950 hours and began taking air samples. By 1125 hours, the DHEC reported their instruments could no longer detect any ammonia and declared the area safe for the public.

Case Study – Ammonia Release Outcome

A motorist traveling north on the highway drove into the ammonia cloud, apparently tried to get away from the cloud, then got out of her car and died of ammonia poisoning. Fourteen people reported experiencing minor respiratory problems or dizziness as a result of the anhydrous ammonia release and were evaluated by emergency medical services (EMS) on scene. Of those 14, 7 displayed symptoms that required EMS to transport them for further evaluation at an emergency department; they were treated and released the same day.

Properties of Ammonia, Anhydrous; Class 2.2; UN 1005

Molecular Weight: 17

Boiling Point: -28°F

Freezing Point: -108°F

Solubility: 34%

Vapor Pressure: 8.5 atm

Ionization Energy: 10.18 eV

Flash Point: n/a (Gas)

Upper Explosive Limit: 28%

Lower Explosive Limit: 15%

Relative Gas Density: 0.60

OSHA PEL: TWA: 50 ppm

IDLH: 300 ppm