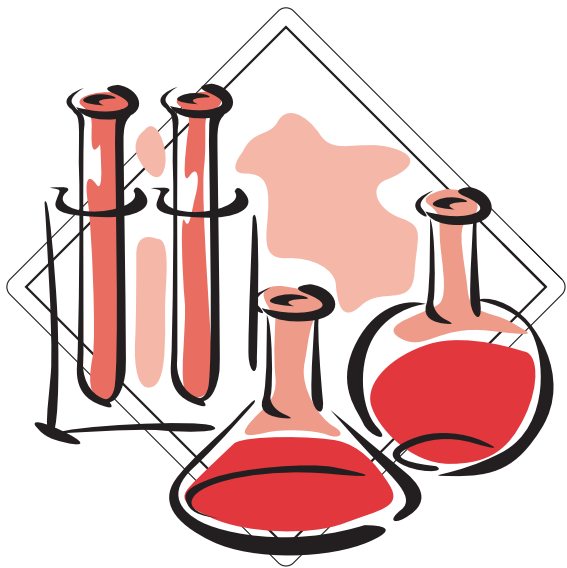


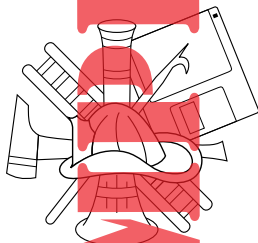
# The Hazmat Chemistry Pocket Pal



Jill Meryl Levy  
Firebelle Productions

# **The Hazmat Chemistry Pocket Pal**

**by Jill Meryl Levy**



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by Jill Meryl Levy

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## Important Message to My Readers

This book contains a simplified review of the most important concepts taught in hazmat chemistry classes nationwide. The topic is obviously more complex, and there are many exceptions not covered in this book.

Be smart and be safe. Use this book to brush up on the basics, but supplement it with other resources for a more thorough understanding of hazmat chemistry.

BE  
SAFE



# Acknowledgments

The following people provided valuable input for my *Hazmat Chemistry Study Guide*, which was the basis for this book: Dieter Heinz, Brian Heinz, Kevin Smith, Robert Delaney, Richard C. Dufek, Bryan Callowhill, Todd Spellman, and the late Chris Waters. Most of them continue to provide peer review for my books and reference cards.

I'm also grateful to David Ghilarducci, Dale Foster, and Doug Hansen who, in addition to Dieter Heinz and Brian Heinz, were my hazmat chemistry instructors years ago.

## Dedication

To Robert Charles Innis,  
who sparked my imagination in junior high school  
and inspired in me a passion for writing.  
He always brings out the best in me.

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# SAMPLE

# Terms and Definitions

## Vapor Pressure

**Vapor pressure** is the force exerted by the vapors of a product against the atmosphere or the sides of a container. It is a significant factor in determining how readily a material evaporates and how readily its vapors become airborne—and how easily those vapors can endanger us at a hazmat incident.

Vapor pressure is normally measured in millimeters of mercury (mmHg) at 68°F (20°C). Two other common units for measuring vapor pressure are pounds per square inch (psi) and atmospheres (atm). Although there are others, these are the ones we see most often in the hazmat arena.

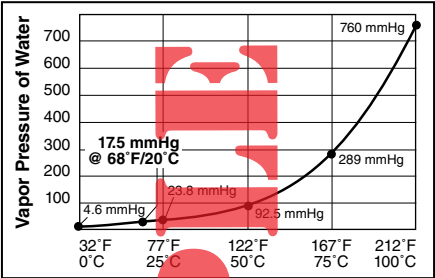
$$760 \text{ mmHg} = 14.7 \text{ psi} = 1 \text{ atm}$$

If the vapor pressure of a liquid or solid reaches 760 mmHg (atmospheric pressure) at sea level, the material will reach its *boiling point*—the point of maximum vapor production.

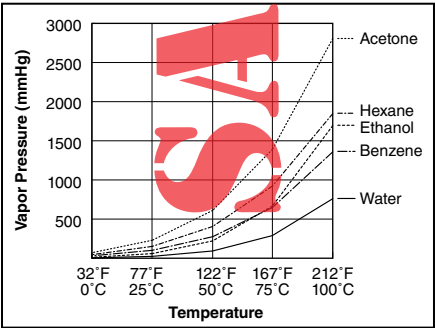
While there is no official dividing line between a “safe” vapor pressure and an “unsafe” vapor pressure, common sense tells us that a product whose vapor pressure is less than that of water probably isn’t going to “reach out and touch someone” who follows the basic principles of “isolate and deny entry.” Water has a vapor pressure of 17.5 mmHg at 68°F (20°C).

Obviously, you must look at a product’s other properties and at incident-specific factors to evaluate overall risk, but if you know the material has a low vapor pressure, it should take your stress level down a notch.

Vapor pressure is temperature-dependent. The higher the temperature, the higher the vapor pressure. The chart below shows the vapor pressure of water at different temperatures.



The chart below compares water with four other substances. Notice that while they're all fairly close at 32°F (0°C), their vapor pressures vary widely as the temperature increases. The higher the vapor pressure at any given temperature, the greater the potential risks.



The higher the vapor pressure, the more volatile a material is and the more readily it will evaporate. A material is considered **volatile** if it evaporates quickly.

*Caution:* The nerve agent sarin is often described as being “volatile,” because sarin has the highest vapor pressure of the nerve agents. However, with a vapor pressure of only 2.1 mmHg, it is far less “volatile” than water. It’s a good reminder of why it’s important to look beyond the sometimes misleading English descriptions to determine the chemical and physical properties of a substance.

## Vapor Density

**Vapor density** is the relative weight of a vapor or a gas compared with a like volume of air. All vapors and most gases are heavier than air. Only a handful of gases are lighter than air:

Gas	Vapor Density
Hydrogen	0.07
Helium	0.138
Natural Gas *	0.550
Methane	0.553
Ammonia **	0.589
Hydrogen Fluoride	0.690
Neon	0.696
Acetylene	0.898
Hydrogen Cyanide	0.932
Diborane	0.954
Nitrogen	0.966
Ethylene	0.967
Carbon Monoxide	0.967

\* Natural gas consists mostly of methane, with varying amounts of other gases and odorizers.

\*\* Ammonia becomes heavier and will hover near the ground if it absorbs moisture.

Vapor density can be calculated by dividing the molecular weight of an element or compound by 29 (the molecular weight of air). **Molecular weight** is the combined weight of all atoms in a compound. The atomic weight of each element is indicated on the periodic table of elements. (This will be explained in Chapter 2.)

Vapor density is independent of other factors. However, external conditions can affect where a vapor or gas is found.

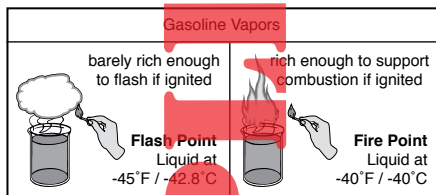
- Because temperature affects vapor pressure, temperature also affects the rate at which gases and vapors disperse.
- Moisture in the atmosphere can be absorbed by gases and vapors, causing them to be less buoyant.
- The lower atmospheric pressures at higher elevations will allow gases and vapors to disperse more readily.
- Wind and air currents can affect how well gases and vapors mix with the atmosphere and how easily they disperse.
- Lower concentrations of gases and vapors disperse more readily than higher concentrations do.

## Flammability

**Flash point** is the minimum temperature at which a liquid produces enough vapor to form an ignitable mixture in air. The vapors may ignite if an ignition source is present. However, the flame does not continue to burn when the source of ignition is removed; rather, the vapors flash and are consumed by the flame.

Flash point is generally considered the most important property in assessing flammable liquids. The lower the flash point, the greater the hazard.

**Fire point** is the temperature at which enough vapors are given off to support continuous burning after the source of ignition has been removed. The fire point is generally just a few degrees above flash point.



Flash point and fire point refer to the temperature of the liquids rather than to the vapors they produce. The flash point of mixtures, such as kerosene and diesel fuel, may be listed as a range of temperatures instead of a single temperature, because the flash point can vary depending on composition. Reference sources will sometimes also list flash points for volatile solids—solids that evolve enough flammable vapors under ambient conditions to pose a flammability risk. Flash point and fire point don't apply to gases.

**Ignition temperature** is the minimum temperature required to cause self-sustained combustion, independent of an ignition source. Simply put, it's the minimum temperature to which a material must be exposed before it will ignite. It is also the temperature the ignition source must be. (See also pages 64 and 65 for the relation between molecular size, flash point, and ignition temperature.)



Ignition temperature is sometimes difficult to measure and should be considered an approximation. Ignition comes in two forms:

- *Pilot ignition* involves an external ignition source (e.g., a water heater pilot light or a lit cigarette igniting gasoline vapors).
- *Autoignition* is caused by an elevated temperature. In a fire, for example, convection carries hot air and gases to other parts of a building. When the atmosphere becomes hot enough that these gases reach their ignition temperatures, they will ignite without the introduction of any other ignition source. This is called *flashover*.

A few substances are subject to **spontaneous ignition**. Animal and vegetable oils (e.g., mink oil and linseed oil) are good examples. The oil will slowly oxidize when exposed to air, generating heat in the process. If the heat cannot dissipate fast enough, it will accelerate the production of flammable vapors, then spontaneously ignite those vapors. This is why oily rags left lying in a pile are a fire hazard.

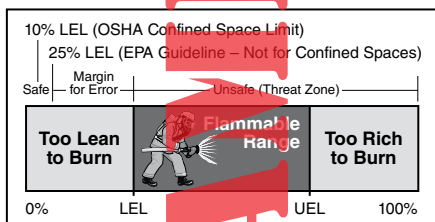
**Flammable (explosive) range** is the percentage of vapor in air within which ignition is possible.

- Below the **lower explosive limit (LEL)**, vapors are too lean to burn.
- Above the **upper explosive limit (UEL)**, vapors are too rich to burn.

Sometimes you will see the terms *lower flammable limit (LFL)* and *upper flammable limit (UFL)* instead. They mean the same thing as lower and upper explosive limits.

The wider the flammable range, the greater the span at which ignition is possible and the greater the risk. Conversely, products with narrower flammable ranges will present less of a fire hazard. Other factors, like flash point and vapor pressure, also affect the overall flammability risk. However, all things being equal, the greater the flammable range, the greater the fire danger.

Only atmospheres well below the LEL are safe to enter. OSHA prohibits working in confined space atmospheres with more than 10% of the LEL. The EPA's recommended limit for other environments is 25% of the LEL. Both limits (10% and 25%) leave a good margin of error to guard against everything from fluctuations in the chemical concentration to defective monitors or errors in interpreting the meter readings.



Even though the vapors are too rich to burn above the UEL, never consider that to be a safe atmosphere, because the vapor concentration may drop to within the flammable range during emergency operations.

The distinction between flammable and combustible liquids is in their flash points. The U.S. Department of Transportation (DOT) uses a cutoff of 140°F (60°C), which comes from the hazardous materials regulations sponsored by the United Nations for international transportation.

- **Flammable liquids** are generally defined as those with flash points not more than 140°F (60°C).
- **Combustible liquids** are those that do not meet the definition of any other hazard class and have flash points above 140°F (60°C) but below 200°F (93.3°C).

In contrast, the National Fire Protection Association (NFPA) and the Occupational Safety and Health Administration (OSHA) define a flammable liquid as one whose flash point does not exceed 100°F (37.8°C) and a combustible liquid as one whose flash point is 100°F (37.8°C) or higher.

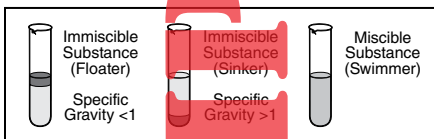
Another way to think of it is that flammable liquids can ignite easily at ambient temperatures, whereas combustible liquids must be heated first. This is not a precise definition, but it's a handy approximation for field use.

Note: The word **inflammable** is a confusing term, because the prefix *in-* is often used to mean “not.” However, *inflammable* means *flammable*. It does *not* mean nonflammable.

## Water Behavior

**Specific gravity** is the weight of a liquid compared to an equal volume of water. Water weighs 8.345 pounds per gallon. However, since it is the standard against which all other liquids are measured, it is said to have a specific gravity of 1. Specific gravity is generally reported as a number relative to the weight of water (e.g., benzene is 0.88).

In general, an immiscible substance with a specific gravity less than one ( $<1$ ) will float on water. It is a *floaters*. An immiscible substance with a specific gravity greater than one ( $>1$ ) will sink in water. It is a *sinker*. A miscible substance is a *swimmer*.



Notice that water behavior is affected by both specific gravity and miscibility. The terms *miscibility* and *solubility* are often used interchangeably. However, **miscibility** refers to the ability of products to mix, or form a uniform blend. **Solubility** refers to the ability of a product to dissolve.

Chemicals that mix in water are called *miscible*, *soluble* (water-soluble), or *polar*, while those that don't are called *immiscible*, *insoluble*, or *nonpolar*. (Polarity is explained on the following page.) Miscibility may be indicated with relative descriptions (e.g., "slightly soluble") or by percentages.

Solubility is determined by **polarity**, which is a reflection of how strongly one atom attracts the electrons of another atom in a compound. Magnets make a good analogy for polarity. With their positive and negative poles, magnets are strongly attracted to each other.



**Polar** substances have positive and negative poles in the form of atoms that differ in their electronegativity; the electrons between them are drawn more strongly to one element in the compound than to the others. Such is not the case in **nonpolar** substances.

Polarity is directly related to miscibility. Since “like dissolves like,” water will dissolve other polar substances (like most alcohols) but not nonpolar substances (like hydrocarbons). Thus polar substances are water-soluble.

Nonpolar substances are not water-soluble, but they may be soluble in other nonpolar substances. For example, wax will dissolve in gasoline.

Temperature affects solubility. In general, the warmer the **solvent** (the substance used to dissolve something else into solution), the greater its capacity to dissolve the **solute** (the substance added to a solvent). For example, it is easier to dissolve sugar into hot tea than into iced tea. Thus a hazardous material may be more soluble on a hot day than it is on a cold one.

Gases behave differently; the warmer the solution, the less soluble gases become. Carbonated beverages, for example, go flat (lose carbon dioxide) more quickly when warm than when cold.

Understanding water behavior can sometimes help you assess the dangers even when dealing with an unknown substance. Products that are lighter than water are usually flammable or combustible hydrocarbons. Those that are heavier than water are usually toxic. Of course, these are generalizations, not hard-and-fast rules you should stake your life on. But when no other details are yet available and you need some direction from which to develop an initial action plan, these little tidbits of information provide a fairly reliable starting point.

Water reactivity is another concern, but we'll look at that shortly, when we get to chemical reactivity.

## Physical Change / Physical Reaction

In a **physical reaction**, materials undergo a change in form (solid, liquid, or gas), but not in chemical composition. The causative factor in physical change is usually temperature.

- **Melting** is a change from solid to liquid (e.g., ice turning to water). The temperature at which it happens is called the *melting point*.
- **Freezing** is a change from liquid to solid (e.g., water turning to ice). The temperature at which it happens is called the *freezing point*.
- **Vaporization** is a change from liquid to vapor (e.g., water turning to steam). The point of maximum vaporization is called the *boiling point*.

- **Condensation** is a change from vapor to liquid (e.g., steam from a hot shower condensing on a mirror).
- **Sublimation** is a change from solid to vapor without the material ever passing through the liquid state (e.g., as seen with dry ice).
- **Deposition** is a change from gas to solid. It's a rare reaction associated with nuclear blasts.

As indicated on the previous page, **boiling point** is the point of maximum vapor production. More specifically, it is the temperature at which the vapor pressure at the surface of the liquid is equal to or slightly greater than atmospheric pressure, meaning that individual molecules are able to easily break through the surface of the liquid in vapor form, escaping into the atmosphere. The lower the boiling point, the greater the hazard potential.

Temperature can change the thickness of a liquid—its **viscosity**—without changing its physical state. Viscous liquids (those with high viscosity) are thicker liquids, like heavy oils. Thinner liquids, like water, are less viscous.

## Chemical Change / Chemical Reaction

In a **chemical reaction**, materials undergo a change in composition. A new substance is formed—one that has its own chemical and physical properties and hazards. For example, when methane ( $\text{CH}_4$ ) burns, the molecule breaks apart. However, the individual atoms combine with oxygen in the air to yield hydrogen ( $\text{H}_2$ ), carbon monoxide (CO), carbon dioxide ( $\text{CO}_2$ ) and water vapor ( $\text{H}_2\text{O}$ ).

**Incompatible chemicals** are those that react with each other in ways that generally produce negative consequences. The reactions can range from relatively mild to catastrophic, depending on the type and quantity of chemicals involved. Acids and bases, for example, are incompatible with each other. If the two mix, they can generate a tremendous amount of heat. However, under controlled conditions, weak corrosives can be added to neutralize a spill of the opposite pH.

Materials that are **air-reactive** will ignite, decompose, or release energy when exposed to air. Some of these reactions can be quite violent. Air-reactive materials are also called **pyrophoric**.

Technically, pyrophoric materials are those that react in dry air versus moist air. However, never assume that the word *pyrophoric* on a warning label, on a material safety data sheet (MSDS), or in a hazardous materials reference source is meant to exclude reactivity to moist air. Not everyone writing these documents will check the precise definition of a word before using it. Assume that pyrophoric materials will also react with moisture until you've determined otherwise by checking at least three reference sources.

**Water reactivity** is the tendency of a material to react, or chemically change, upon contact with water. Reactions can range from mild to severe. The more reactive chemicals can release flammable gases, toxic gases, and/or corrosive solutions, generating a lot of heat in the process. (A reaction that generates heat is called **exothermic**.) Some materials can react explosively when exposed to water, ripping the water molecules apart to liberate oxygen.



**Polymerization** is a chemical reaction in which small compounds (*monomers*) react with themselves to form larger molecules (*polymers*). Double bonds between carbon atoms (below left) are not as stable as single bonds. However, open bonding sites (unpaired electrons—below right) is an unstable condition that nature won't allow for long. So when the double bond is broken, the monomer will react (bond) with other monomers to form new compounds—polymers.

$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{C} = \text{C} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ -\text{C} - \text{C}- \\   \quad   \\ \text{H} \quad \text{H} \end{array}$
Ethylene Monomer ( $\text{C}_2\text{H}_4$ )	Ethylene Monomer in Transition
$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \quad   \quad   \quad   \quad   \quad   \quad   \quad   \\ (\text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C})_n \\   \quad   \quad   \quad   \quad   \quad   \quad   \quad   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	
Polyethylene Polymer	

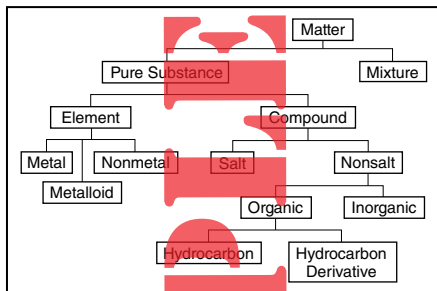
Compounds with double bonds between carbon atoms are prone to polymerization. Human intervention is not required. However, **catalysts** can be used to initiate or speed up a reaction, whereas **inhibitors** can be used to slow or stop a reaction.

Uncontrolled polymerization is very dangerous. Polymers are not as dense as monomers; they take up more space. The reaction also generates heat. Overpressurization and heat can cause catastrophic container failure. Once the reaction begins, it cannot be stopped.

# Elements and Compounds

## Matter

**Matter** can be organized as illustrated below.



Initially, matter is divided into pure substances and mixtures:

- A **pure substance** is a homogenous one—every sample of the same substance is identical in composition.
- A **mixture** consists of two or more elements or compounds that are physically mixed but not chemically bonded. Consequently, mixtures can vary from one sample to another.

Although most hazardous materials we encounter are mixtures, hazmat chemistry classes usually focus on pure substances, because it is far easier to make generalizations about them. (This book also focuses on pure substances.) However, when a pure substance is the major component of a particular mixture, you are well on your way to understanding its hazards and characteristics.

Pure substances are divided into elements and compounds:

- **Elements** are represented by a single capital letter or by a capital letter followed by a lowercase letter. Examples: hydrogen (H), oxygen (O), sodium (Na), and chlorine (Cl).
- **Compounds** (molecules) consist of two or more elements that are chemically bonded. Compounds are represented by formulas showing multiple elements. Examples: water (H<sub>2</sub>O) and sodium chloride (NaCl).

Compounds can be broken down to release simpler substances (the individual elements), whereas elements can't be broken down into anything simpler without getting into the atomic structure (protons, neutrons, and electrons).

Elements are divided into metals, nonmetals, and metalloids (or semimetals):

- **Metals** generally have a lustrous (shiny) appearance and are good conductors of heat and electricity. They are malleable (can be hammered into sheets) and ductile (can be drawn into wires). Most metals are solids in their natural states. The exceptions are mercury (Hg), cesium (Cs), and francium (Fr), all of which are liquids.
- **Nonmetals** generally are not lustrous, are not good conductors, and are neither malleable nor ductile. All of the nonmetals are either solids or gases, with the exception of the liquid element bromine (Br).

Metals and nonmetals are arranged on the periodic table of elements as shown on page 26.

While periodic tables draw a definite distinction between metals and nonmetals, the distinction is not as absolute as it appears to be.

- **Metalloids** (or **semimetals**) are elements immediately surrounding the dividing line between metals and nonmetals. They tend to have properties of each. The metalloids are boron (B), silicon (Si), germanium (Ge), arsenic (As), antimony (Sb), tellurium (Te), and polonium (Po). Further discussion of metalloids is beyond the scope of this book.

Sometimes two or more metals are mixed to create **metal alloys**, such as brass. Some alloys, such as steel, contain a small percentage of nonmetal elements. Further discussion of alloys is beyond the scope of this book.

Compounds are divided into salts and nonsalts:

- Most **salt compounds** consist of a metal element bonded to one or more nonmetal elements. (A few exceptions have no metal elements in them. They are discussed in Chapter 4.)
- **Nonsalt compounds** consist solely of nonmetal elements.

Nonsalt compounds are either organic or inorganic:

- **Organic compounds** are derived from living (or once living) organisms. Almost all of them contain carbon-hydrogen bonds.
- **Inorganic compounds** are not derived from living (or once living) organisms and do not contain carbon-hydrogen bonds.

It's commonly considered that organic compounds are those containing carbon, whereas inorganic compounds are those without carbon. However, several compounds containing carbon are classified as inorganic. Examples include carbon dioxide ( $\text{CO}_2$ ), sodium cyanide ( $\text{NaCN}$ ), calcium carbonate ( $\text{CaCO}_3$ ), and carbon tetrachloride ( $\text{CCl}_4$ ). So it's more accurate to use the definitions on the previous page.

Organic compounds are either hydrocarbons or hydrocarbon derivatives.

- **Hydrocarbons** contain only carbon and hydrogen atoms.
- Most **hydrocarbon derivatives** contain carbon and hydrogen, along with other nonmetal elements, such as oxygen, nitrogen, or chlorine. However, these materials are all derived from the basic hydrocarbons; hence the name hydrocarbon derivatives.

## The Periodic Table of Elements

The periodic table of elements displays elements according to their atomic structure. Periodic tables typically show the following information:

- Atomic number
- Atomic weight
- Element symbol
- Element name

An element's position on the periodic table provides some basic information on its basic characteristics. We'll look at a few examples in the following pages.

Alkali Metals  
1 • I

Alkaline  
Earth Metals  
2 • II

Noble Gases  
18 • VIII

2	4.003	Halogens																			
He	Helium	10	20.180	Ne	Neon	18	39.948	Ar	Argon	36	83.798	Kr	Krypton	54	131.29	Xe	Xenon	86	222	Rn	Radon

1008 H Hydrogen	4 9.012 Li Lithium	6.941 Be Beryllium	12 24.305 Na Sodium	20 40.078 Mg Magnesium	23 50.942 V Vanadium	24 51.996 Cr Chromium	25 54.938 Mn Manganese	26 55.845 Fe Iron	27 58.933 Co Cobalt	28 58.693 Ni Nickel	29 63.546 Cu Copper	30 65.409 Zn Zinc	31 69.723 Ga Gallium	32 72.64 Ge Germanium	33 74.922 As Arsenic	34 78.960 Se Selenium	35 79.904 Br Bromine	36 83.798 Kr Krypton
37 85.468 Rb Rubidium	38 87.620 Sr Strontium	39 88.502 Y Yttrium	40 91.224 Zr Zirconium	41 92.906 Nb Niobium	42 95.940 Mo Molybdenum	43 98.0 Tc Technetium	44 101.07 Ru Ruthenium	45 102.91 Rh Rhodium	46 106.42 Pd Palladium	47 107.87 Ag Silver	48 112.41 Cd Cadmium	49 114.82 In Indium	50 118.71 Sn Tin	51 121.76 Sb Antimony	52 127.60 Te Tellurium	53 126.90 I Iodine	54 131.29 Xe Xenon	55 132.91 Cs Cesium
56 137.33 Ba Barium	57 178.49 La Lanthanum	58 175.05 Ce Cerium	59 173.04 Pr Praseodymium	60 144.24 Nd Neodymium	61 144.24 Pm Promethium	62 150.36 Sm Samarium	63 151.96 Eu Europium	64 157.25 Gd Gadolinium	65 158.93 Tb Terbium	66 162.50 Dy Dysprosium	67 164.93 Ho Holmium	68 167.26 Er Erbium	69 168.93 Tm Thulium	70 173.04 Yb Ytterbium	71 174.97 Lu Lutetium	72 175.04 Hf Hafnium	73 178.49 Ta Tantalum	74 180.95 W Tungsten
87 223 Fr Francium	88 226 Ra Radium	89-103 Ac Actinium	104 261 Rf Rutherfordium	105 262 Db Dubnium	106 266 Sg Seaborgium	107 264 Bh Bohrium	108 277 Hs Hassium	109 268 Mt Meitnerium	110 271 Ds Darmstadtium	111 272 Rg Roentgenium	112 285 Cn Copernicium	113 284 Nh Nihonium	114 289 Fl Flerovium	115 288 Mc Moscovium	116 292 Lv Livermorium	117 294 Ts Tennessine	118 294 Og Oganesson	119 304 Uu Ununennium

Key to Periodic Table	Atomic Number	Atomic Weight	Symbol
1	1.008	H	Hydrogen
Name			

**Metals** are located on the left side of the periodic table; **nonmetals**, on the right. (Notice the dividing line between metals and nonmetals.) Hydrogen, which is located in the upper left-hand corner above the thick dividing line, is also a nonmetal.

I	II							III	IV	V	VI	VII	VIII
(Nonmetal)								Nonmetals					
		Metals											

Elements become **heavier** and larger as you look lower on the table, which is significant with respect to vapor density, **specific gravity**, and other related properties.

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

1	2							13	14	15	16	17	18
I	II							III	IV	V	VI	VII	VIII
Representative Elements		Transition Metals						Representative Elements					
		3	4	5	6	7	8	9	10	11	12		
		Transition Metals (Rare Earth Elements)											

Roman numerals above each column in the representative elements indicates the number of outer shell electrons for each element. The number of electrons in the outermost shell is the characteristic that most influences chemical bonding (reactivity). This will be explained in the next chapter.

Elements are grouped vertically in **families** based on their chemical behaviors. All members of the same family have similar chemical characteristics, though each will also have its own unique properties.

The four families highlighted below are the most predictable; the similarities between each member of the family are greater than within other families. It is primarily because each member has the same number of electrons in its outermost shell.

Alkali Metals												Noble Gases	
↓												↓	
I	II											VII	VIII
Li	Be											F	Ne
Na	Mg											Cl	Ar
K	Ca											Br	Kr
Rb	Sr											I	Xe
Cs	Ba											At	Rn
Fr	Ra												

**Group I - The alkali metals** are lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), and francium (Fr).

These elements are flammable and highly reactive. When in contact with water, they produce flammable hydrogen gas, a strong caustic runoff, and excessive heat. These elements are quite soft compared to the metal goods we're used to seeing. They can be cut with a knife, much as one would cut through a block of clay.



Sodium and potassium, the most common of the alkali metals, will ignite spontaneously if exposed to moist air. Sodium will ignite even on contact with dry air. Contact between these metals and water rips apart the water molecules, allowing other compounds to be formed from the individual elements. Sodium and potassium combine with free oxygen and hydrogen atoms to form the highly corrosive sodium hydroxide (NaOH) and potassium hydroxide (KOH) solutions, respectively. Free hydrogen atoms combine to form the highly flammable hydrogen ( $H_2$ ) gas. The heat generated from this violent reaction with water is enough to melt the metal and ignite both the hydrogen gas and nearby combustibles.

**Group II - The alkaline earth metals** are beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra).

These elements are flammable and often water-reactive, though less so than the alkali metals (Group I). The alkaline earth metals are harder than the alkali metals, but still soft compared to many other metals. Some compounds containing these elements are very toxic.

A common example from this group is magnesium, which burns with an intense white flame. With an ignition temperature of 1202 F (650°C), magnesium is relatively difficult to ignite in block form. However, the risk of ignition increases in proportion with the amount of surface area exposed to air, so powder, dust, chips, and shavings present a significant fire hazard. Magnesium is very water-reactive when burning. Water will intensify the fire as the water molecule is broken down to form oxygen ( $O_2$ ) and hydrogen ( $H_2$ ). Even water molecules not ripped apart can be instantly converted to steam by the heat of the fire, causing a steam explosion.

**Group VII - The halogens** are fluorine (F), chlorine (Cl), bromine (Br), iodine (I), and astatine (At).

These elements are highly reactive and toxic. They are nonflammable, but they are powerful oxidizers that support combustion.

Chlorine, with its characteristic suffocating odor, is the most common halogen. Chlorine gas reacts with moisture in the lungs or on the skin to form corrosive hydrochloric acid (HCl). Even more destructive to human tissue is hydrofluoric acid (HF), which is formed when fluorine reacts with water. Again, these gases don't burn. However, chlorine and fluorine in particular are such powerful oxidizers—more powerful than oxygen itself—that fires can burn intensely in their presence even when no oxygen is present.

**Group VIII - The noble gases** are helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), and radon (Rn).

These gases are inert, nonreactive simple asphyxiants that are often stored and transported as cryogenic liquids (colder than  $-130^{\circ}\text{F}/-90^{\circ}\text{C}$ ).

The primary risks associated with these gases in an uncontrolled release are frostbite and asphyxiation from oxygen displacement. The high expansion ratios associated with cryogenic liquids greatly increase the risk of catastrophic container failure in the event of a fire or other scenario where the product temperature is elevated beyond the capacity of pressure-relief devices.

## Dieter's Top 13 Nonmetals and Metals

The periodic table can be overwhelming. Thus in his hazmat chemistry classes, respected instructor Dieter Heinz uses “Dieter’s Top 13” to help focus attention on substances most commonly encountered and/or of greatest significance to hazmat technicians. Your community may see more of some elements than others, depending on the industries present. However, narrowing the focus to the elements most abundant in or significant to your community makes the periodic table much less intimidating.

**Dieter's Top 13 Nonmetals** are grouped based on their most common usage:

- Carbon (C) and hydrogen (H) are found in many chemicals, particularly fuels.
- The halogens—fluorine (F), chlorine (Cl), bromine (Br), and iodine (I)—are most often found in oxidizers. Oxygen (O), of course, is also an oxidizer.
- Agricultural chemicals and those used in weapons of mass destruction most often contain phosphorus (P), nitrogen (N), and/or sulfur (S).
- The elements most often encountered in the hi-tech industry are boron (B), silicon (Si), and arsenic (As).

[illegible]

Carbon and hydrogen deserve special mention. As emphasized earlier, almost all of the compounds classified as organic are those containing carbon-hydrogen bonds. It's estimated that about 90% of all known compounds are organic, and more than 95% of all known compounds contain carbon. It's not because carbon is the most abundant element. Rather, it's a very versatile element, as you'll see in the chapter on chemical bonding. It can bond with up to four other atoms, including other carbon atoms. It can form double and triple bonds. It can bond in long chains or ring structures. So it's no coincidence that hazmat chemistry classes put such a heavy emphasis on hydrocarbons and hydrocarbon derivatives.

**Dieter's Top 13 Metals** have many uses. Some of the common ones are highlighted below:

A periodic table diagram showing the positions of the elements Cu, Ag, and Au. Red arrows point to these elements, which are highlighted in red. The elements are arranged in a grid, with Cu, Ag, and Au in the same column, and Au and Hg in the same row. The element Th is also visible in the bottom left.

- Metals used to conduct electricity (AC or DC) include aluminum (Al), copper (Cu), gallium (Ga), lithium (Li), silver (Ag), and sodium (Na).
- Metals commonly used in nuclear energy applications (for example, to transfer heat out of nuclear reactors) include sodium (Na), thorium (Th), and zirconium (Zr).

- Metals and their alloys commonly used in the construction of buildings, vehicles, and aircraft include aluminum (Al), beryllium (Be), gold (Au), lithium (Li), and zirconium (Zr).
- Metals and their alloys commonly used in tools and utensils include aluminum (Al), beryllium (Be), chromium (Cr), copper (Cu), and silver (Ag).
- Metals used in the medical and dental industries for diagnostic or treatment purposes include barium (Ba), lithium (Li), mercury (Hg), silver (Ag), and sodium (Na).
- Metals commonly used in jewelry include gold (Au) and silver (Ag).

## Element Form

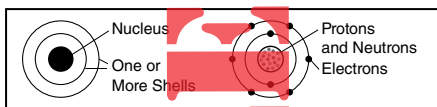
Most elements exist as **solids** in their natural states. The elements that exist as **gases** are hydrogen, nitrogen, oxygen, chlorine, fluorine, and the noble gases (helium, neon, argon, krypton, xenon, and radon). Periodic tables generally identify bromine, cesium, francium, and mercury as **liquids**. However, some elements are borderline and may exist in different forms, depending on ambient temperature.

If a periodic table is printed in color, solid elements are generally printed in black, gaseous elements in red, and liquid elements in blue. (Some printers may use other color schemes.)

## Atomic Structure

The basic building block of any substance is the **atom**. Each atom has a **nucleus** (center) and one or more **shells**.

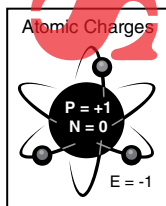
Within the nucleus are **protons** and **neutrons**. Every element has a specific number of protons, which corresponds to the atomic number of the element. Some elements have an equal number of protons and neutrons, but it's not unusual for elements to have more neutrons than protons.



**Electrons** orbit the nucleus much the way planets orbit the sun. These electrons are said to reside in shells (sometimes called *orbits* or *rings*). How elements interact with one another is primarily a function of their electrons. This will be explained in more detail in the next chapter.

An atom's **atomic weight** comes from its protons and neutrons. Electrons are so light that they are considered essentially weightless. Protons and neutrons each weigh what is referred to as one (1) atomic mass unit, or simply "1." Molecular weight is the combined weight of all elements in a compound or molecule.

Protons and electrons are electrically charged, protons positively (+1) and electrons negatively (-1). Neutrons have no electrical charge; they are neutral.



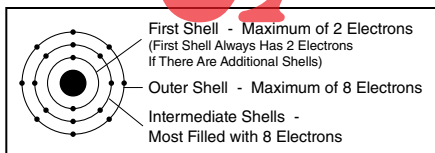
Atoms must have an equal number of protons and electrons to ensure a balance between positive and negative charges—to ensure the atom is electrically neutral. But when some atoms react (bond) with other atoms, they either gain or lose electrons, becoming “charged” in the process. These charged atoms are called *ions*. (Chemical bonding is covered in the next chapter.)

Periodic tables show the predominant, or most stable, form of each element. However, many elements have two or more isotopes. **Isotopes** are variations of the same element, the difference being the number of neutrons in the nucleus.

Isotopes of the same element have the same chemical properties, but their physical properties may vary. For example, carbon-14 (with six protons and eight neutrons) is radioactive, whereas carbon in its predominant form (with six of each) is not.

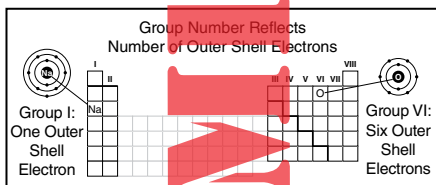
Again, an atom can have several shells surrounding the nucleus. The number of electrons in the outermost shell is the characteristic that most influences chemical bonding (chemical reactivity). These outermost shell electrons are also known as *valance electrons*.

Hydrogen and helium are so small that they each have only one shell. Hydrogen has one electron on that shell, while helium has two. All other elements are large enough to have two or more shells.



The shell closest to the nucleus can hold no more than two electrons, regardless of how big the atom is. The outer (or outermost) shell can have up to eight electrons. Most intermediate shells have eight electrons. (Some metals play by slightly different rules and can have differing numbers of electrons on their intermediate shells, but that is beyond the scope of this book. The outermost shell is the one we care about in hazmat chemistry.)

The periodic table identifies the number of outer shell electrons in the representative elements. It is indicated by the Roman numeral group numbers at the top of the table. Elements in Group I have one outer shell electron, elements in Group II have two, and so forth.



Elements in Group VIII, the noble gases, are the only elements whose outermost shells are filled to maximum capacity. As such, the noble gases won't bond with other elements. Only those elements whose outermost shells aren't filled to the maximum are eligible to play the bonding game.



# SAMPLE

# Chemical Bonding

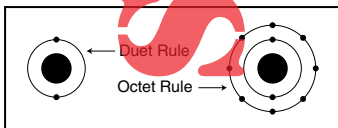
## Why Elements Bond

All atoms must have an equal number of protons and electrons to be *electrically neutral*. However, to be *stable*, an atom must have a completely filled outer shell (two electrons on hydrogen and helium, eight on all others). Herein lies a conflict and thus the basis for chemical reactivity.

Elements in Group VIII, the noble gases, already have filled outer shells; thus they have no reason to react (bond) with other elements. They are inert. (Inert doesn't mean harmless. Remember, these gases are simple asphyxiants that are often stored or transported as cryogenic liquids, making them a thermal hazard with high expansion ratios.)

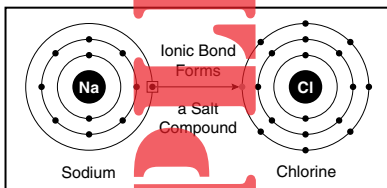
All elements other than the noble gases have outer shells that aren't filled with the maximum number of electrons, so they must bond with others to create a full outer shell.

Hydrogen, with only one shell, needs one more electron to obtain a total of two. This is called the **duet rule**. All other atoms will attempt to achieve eight electrons on their outermost shells. This is called the **octet rule**.



## Types of Bonds

**Ionic bonds** are formed by the transfer of electrons from a metal element to a nonmetal element. Metal elements donate electrons from the outermost shell, essentially shedding the outer shell and exposing a filled shell beneath it. Nonmetal elements accept the donated electrons, also ending up with filled outer shells. Shown below is sodium chloride (NaCl).

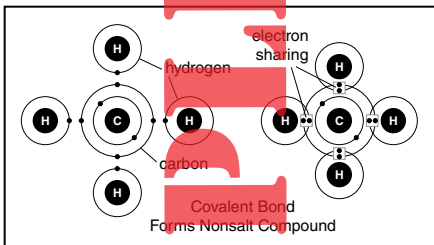


While the two elements are now stable, they're no longer electrically balanced. When the metal element donates electron(s), it's left with a net positive charge (protons outnumber electrons). Conversely, when the nonmetal element accepts electrons, it's left with a net negative charge (electrons outnumber protons). A charged atom is called an **ion**. Positively charged ions (metals) are **cations**, while negatively charged ions (nonmetals) are **anions**.

<u>Element</u>	<u>Electron Transfer</u>	<u>Ion Formed</u>	<u>Charge</u>
metal	donates	cation	positive
nonmetal	accepts	anion	negative

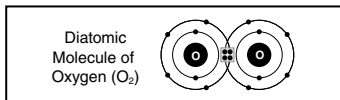
Oppositely charged ions attract each other, forming a strong bond that holds them together. Although there has been a transfer of electrons, the atoms involved cannot stray far because the ions can't exist by themselves. The union of a metal element and one or more nonmetal elements creates a **salt compound**. (Salts are covered in Chapter 4.)

**Covalent bonds** are formed between two or more nonmetal elements. These elements share electrons rather than transfer electrons. Their outermost shells overlap so that electrons seem to belong to each atom at the same time. The result is a **nonsalt compound**. The nonsalt compound pictured on this page is the hydrocarbon known as methane ( $\text{CH}_4$ ). (Hydrocarbons are covered in Chapter 5.)

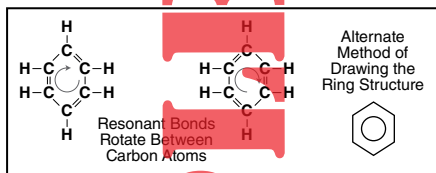


Covalent compounds are comprised of nonmetal elements only. Most of the ones hazmat technicians encounter consist solely of carbon, hydrogen, and oxygen in various combinations. The bulk of the covalent compounds that contain other elements are limited to nitrogen, phosphorus, sulfur, and the halogens (chlorine, fluorine, bromine, and iodine).

A covalent compound existing as a molecule of two identical atoms is called a **diatomic molecule** (or, in the case of gases, a **diatomic gas**). Diatomic molecules include oxygen ( $\text{O}_2$ ), hydrogen ( $\text{H}_2$ ), nitrogen ( $\text{N}_2$ ), fluorine ( $\text{F}_2$ ), chlorine ( $\text{Cl}_2$ ), bromine ( $\text{Br}_2$ ), and iodine ( $\text{I}_2$ ).



When compounds contain **resonant bonds**, the electrons rotate or alternate very rapidly between the carbon atoms as illustrated with the compound benzene ( $C_6H_6$ ) below. Benzene's ring structure can be represented either by elements connected with dashes or by a ring within a hexagon. (These **aromatic hydrocarbons** are also nonsalt compounds.)



The chart below summarizes the types of bonds.

<u>Bond</u>	<u>Composition</u>	<u>Electrons</u>	<u>Result</u>
ionic	metal + nonmetal	transfer	salt
covalent	nonmetals only	share	nonsalt
resonant	nonmetals only	share	nonsalt

Each bond stores energy (bond energy) that is released when the bond is broken. The amount of energy released will depend on the amount and type of elements that comprise the bond and on what causes the bond to be broken. Some compounds can release a tremendous amount of energy (in the form of heat and light) when their bonds are broken.

## Relation to Four Families of Elements

Now that you've seen the relation between outer shell electrons and chemical bonding, let's go back to the periodic table and to the four families of elements considered so important to your understanding of hazardous materials.

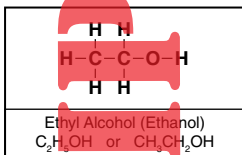
- **Group I - The alkali metals** were described as *highly reactive*. Any element with just one electron on its outer shell is so close to the ideal (stable) condition of having a filled outer shell that it reacts vigorously to donate that one outer shell electron to any element that needs it.
- **Group II - The alkaline earth metals** are also fairly reactive, but not to the same degree as alkali metals. It takes more effort to shed two outer shell electrons than it does to shed one, so these elements aren't quite as "motivated."
- **Group VII - The halogens** are also one electron away from having a filled outer shell, so they're highly reactive too. However, they're different from the alkali metals. They have seven electrons on their outer shells, so they'll readily grab one more electron from any metal element with one or more to donate in an ionic bond. But they'll also share electrons with nonmetal elements to form covalent bonds.
- **Group VIII - The noble gases** have filled outer shells already. They have no reason to react with other elements. They are inert.

Alkali Metals												Noble Gases	
I	II	Alkaline Earth Metals										VII	VIII
												F	He
Li	Be											Cl	Ar
Na	Mg											Br	Kr
K	Ca											I	Xe
Rb	Sr											At	Rn
Cs	Ba												
Fr	Ra												

## Chemical Formulas and Illustrations

Chemistry textbooks often contain illustration styles that look considerably different from those you will see in this book or in a hazmat chemistry class. It's because we're not looking at *chemistry* per se. We're looking at *concepts* that explain the behavior of hazardous materials.

**Dash style illustrations** are the simplest for presenting the concepts most important to the study of hazardous materials. The example below is ethyl alcohol (ethanol). Dashes represent the bonds between atoms. Most are single (—). Some are double (=) or triple (≡).

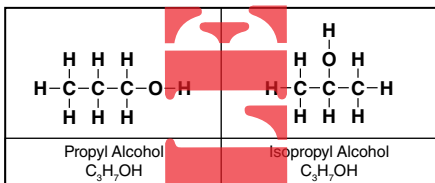


Chemical formulas can take several forms:

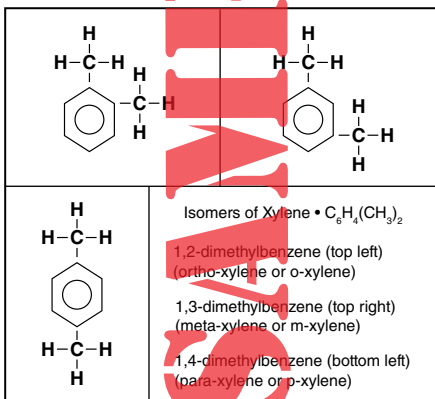
- The illustration above for ethyl alcohol is its **structural formula**.
- Ethyl alcohol is most often written as  $C_2H_5OH$ , but its **condensed structural formula** ( $CH_3CH_2OH$ ) identifies how the atoms are arranged.
- A **molecular formula** ( $C_2H_6O$ ) identifies only how many atoms of each element are present. Molecular formulas don't distinguish between different compounds with the same ratio of elements. For example, ethyl alcohol ( $C_2H_5OH$ ) and dimethyl ether ( $CH_3OCH_3$ ) have the same molecular formula ( $C_2H_6O$ ), but the atoms are arranged differently.

## Isomers

Some products can have the same molecular *formula* but different molecular *structures*. These products are known as **isomers** of each other. Shown below are propyl alcohol and isopropyl alcohol.



Shown below are isomers of xylene.



These illustrations are provided to give you a visual idea of what isomers are. You don't need to know what isomers look like. Rather, you need to understand what isomers are.



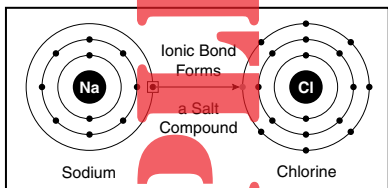
The following are some additional key points to know about isomers:

- Despite having the same formulas, isomers can have measurably different characteristics and hazards. These differences can be slight or significant. Even a 20°F difference in flash point, for example, is enough to change the risks at a hazmat incident.
- Names matter. Some materials have more than one name. For example, propyl alcohol and propanol are the same thing. However, propyl alcohol and isopropyl alcohol are *not* the same substance. So make sure you get the names correct at a hazmat incident.
- Prefixes matter. Sometimes those prefixes are only a single letter, as illustrated on the previous page. Even *iso-* can be shortened to *i-*. Don't dismiss this as extraneous noise when looking at chemical names.
- Numbers matter. The numbers used in the xylene examples on the previous page identify where the bonds are located on the ring structure. You don't need to know where the bonds are located, but you do need to know that the numbers mean something. Again, don't dismiss this as extraneous noise when looking at chemical names.

# Salts

## General Overview of Salts

Most salt compounds are formed through an **ionic bond** between a metal element and one or more nonmetal elements, like sodium chloride (NaCl), which we know more commonly as table salt.



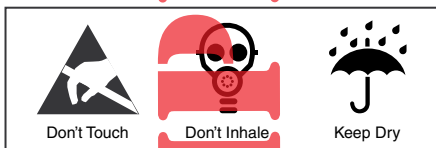
Only a few salts don't contain a metal element. Examples include ammonium chloride ( $\text{NH}_4\text{Cl}$ ) and ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ). That's because the ammonium ion ( $\text{NH}_4^+$ ) behaves like a metal element in the way it forms an ionic bond with other nonmetals. This will become clearer later in the chapter.

Let's start with characteristics that are common to *most* salts. Remember, however, that there are exceptions to any generalization.

- Salts are solid.
- Salts are nonflammable.
- Most are water-soluble.
- Many are water-reactive and will produce a flammable gas, a toxic gas, a caustic solution, and/or heat when in contact with water.

- Salts are electrolytes; they conduct electricity when in a molten state or when dissolved in water.
- Salts generally range from being mildly toxic to very toxic.
- Some salts cause severe environmental damage.

Based on these common hazards, it's safe to assume that you should avoid contact with and inhalation of salts and that you should keep them dry if possible. Some may require greater precautions; others, less. However, you can't go wrong if you apply these guidelines.



## Introduction to Names and Formulas

We'll focus on six types of salts, the first five of which are easily recognized by names ending in *-ide*. Some are more specific (*cyanide, oxide, hydroxide, or peroxide*).

Like many hazardous materials, salts can have multiple names. However, the IUPAC (International Union of Pure and Applied Chemists) naming system is universally accepted in chemical references, formal chemistry courses, and scientific and forensic laboratories. The IUPAC naming system identifies salts according to the elements that comprise them, starting with the metal element and ending with the nonmetal element(s).

Salt	Composition	Naming
Binary Salt	metal + nonmetal (not otherwise listed)	metal + nonmetal root (ends in <i>ide</i> )
Metal Cyanide	metal + cyanide	metal + <i>cyanide</i>
Metal Oxide (Binary Oxide)	metal + oxygen	metal + <i>oxide</i>
Metal Hydroxide	metal + hydroxide	metal + <i>hydroxide</i>
Metal Peroxide	metal (Group I or II) + peroxide	metal + <i>peroxide</i>
Metal Oxsalt	metal + element + oxygen	metal + oxyradical (ends in <i>ate</i> or <i>ite</i> ) (may include prefix <i>per</i> or <i>hypo</i> )

The following examples will make the chart clearer:

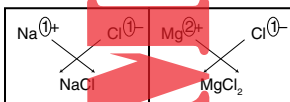
Type	Example	Formula
binary	sodium chloride	NaCl
cyanide	sodium cyanide	NaCN
oxide	sodium oxide	Na <sub>2</sub> O
hydroxide	sodium hydroxide	NaOH
peroxide	sodium peroxide	Na <sub>2</sub> O <sub>2</sub>
oxsalt	sodium hypochlorite	NaClO

Again, five types of salts have names ending in *-ide*. The last type, oxsalts, have names ending in *-ate* or *-ite*. So when you see chemical names ending in *-ide*, *-ate*, or *-ite*, think “salt.” Then check to see if the name also contains a metal element (or the ammonium ion—NH<sub>4</sub>). If so, it’s a salt. If not, it’s a nonsalt. (See also “Naming Similarities on page 89.)



The ratio between metal and nonmetal elements is based on the rules of chemical bonding covered in the last chapter. That chapter provided the example of sodium chloride (NaCl), where sodium (Na) and chlorine (Cl) bonded in a one-to-one ratio because they had one and seven electrons, respectively, on their outer shells. However, magnesium (Mg) has two electrons on its outer shell. It would have to bond with two atoms of chlorine (Cl) to create a balanced compound—magnesium chloride ( $\text{MgCl}_2$ ).

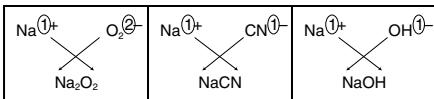
The easiest way to determine the formula of a salt compound is to apply something called the **criss-cross rule**. Draw a simple diagram like the one below, identifying the electrical charges associated with each ion. Then cross the numbers as shown. The electrical charge of one ion becomes the subscript number for the opposite ion. (Where the number is 1, no subscript is needed.)



Reduce the subscripts to the lowest possible numbers without changing the ratio in which the elements are present. For example, calcium ( $\text{Ca}^{2+}$ ) and oxygen ( $\text{O}^{2-}$ ) form calcium oxide ( $\text{CaO}$ , *not*  $\text{Ca}_2\text{O}_2$ ).

Some salts have **polyatomic ions**, where two or more atoms bonded together act as a single ion. The crisscross rule is applied the same way, except that the polyatomic ion is treated like one unit.

<u>Ion</u>	<u>Charge</u>	<u>Example</u>
peroxide ( $\text{O}_2$ )	2-	$\text{Na}_2\text{O}_2$
cyanide (CN)	1-	NaCN
hydroxide (OH)	1-	NaOH



Oxysalts also have polyatomic ions. However, the oxysalts are complex enough that we'll look at them separately later in the chapter.

The elements that comprise salts typically do so only in specific ratios. For example, aluminum chloride ( $\text{AlCl}_3$ ) consists of aluminum and chlorine only in a 1 to 3 ratio. So it is unnecessary to use prefixes such as *mono-*, *di-*, or *tri-* (e.g., aluminum trichloride) to indicate how many atoms are present. The oxysalts are an exception, but the prefixes and endings associated with them are unique. Again, we'll look at them later in the chapter.

## Types of Salts

This section provides more detail on each of these salts and their common characteristics. (These generalizations apply primarily to salts containing alkali metals and alkaline earth metals. In general, when salts contain transition metals, toxicity and environmental damage are common concerns and reactivity is usually less of a problem.)

**Binary salts** contain two elements—one metal and one nonmetal (other than oxygen).

### Examples of Binary Salts

sodium chloride (table salt) –  $\text{NaCl}$

calcium carbide –  $\text{CaC}_2$

lithium sulfide –  $\text{Li}_2\text{S}$

aluminum chloride –  $\text{AlCl}_3$

The toxicity can vary from nontoxic (e.g., sodium chloride) to very toxic (e.g., sodium fluoride). The worst binary salts are water-reactive (especially the nitrides, carbides, hydrides, phosphides, and some chlorides). In contact with water, binary salts will produce a flammable and/or toxic gas, a caustic solution, and heat.

Metal sulfides, a subdivision of binary salts, are comprised of a metal element and sulfur. These salts are very reactive with acid, producing highly toxic hydrogen sulfide gas ( $\text{H}_2\text{S}$ ).

**Metal oxide salts** (binary oxide salts) consist of a metal element bonded to oxygen.

#### Examples of Metal Oxide Salts

sodium oxide –  $\text{Na}_2\text{O}$

potassium oxide –  $\text{K}_2\text{O}$

calcium oxide –  $\text{CaO}$

magnesium oxide –  $\text{MgO}$

The worst of the metal oxides are caustic (corrosive), particularly those containing alkali (Group I) metals. They are water-reactive. Metal oxides containing alkali metals react violently with water to produce a caustic solution and a lot of heat. However, metal oxides *don't* release a gas in contact with water. And despite the name, most are not oxidizers. Many metal oxide salts are toxic.

**Metal cyanide salts** consist of a metal element bonded to a complex ion of carbon and nitrogen (CN).

#### Examples of Metal Cyanide Salts

sodium cyanide –  $\text{NaCN}$

potassium cyanide –  $\text{KCN}$

Cyanide salts are highly toxic. They react with acids to produce hydrogen cyanide (HCN), which is a very toxic and flammable gas.

**Metal hydroxide salts** consist of a metal element bonded to a complex ion of oxygen and hydrogen (OH).

#### Examples of Metal Hydroxide Salts

sodium hydroxide – NaOH  
potassium hydroxide – KOH  
calcium hydroxide –  $\text{Ca(OH)}_2$

Like many hazardous materials, these compounds can have multiple names. Because some of the most common corrosives are metal hydroxides, it's important to recognize their frequently used trivial (slang) names.

- Sodium hydroxide – caustic soda, lye
- Potassium hydroxide – caustic potash, potash lye
- Calcium hydroxide – caustic lime, slaked lime

The worst of the metal hydroxides are caustic (corrosive). Those made with alkali (Group I) metals are some of the most destructive chemicals known. Metal hydroxides will react with, attack, corrode, and dissolve many substances. They are extremely destructive to skin and other body tissues. They are water-reactive. Many are toxic.

**Metal peroxide salts** consist of a metal element bonded to a peroxide radical (two oxygen atoms covalently bonded to each other).

#### Examples of Metal Peroxide Salts

sodium peroxide –  $\text{Na}_2\text{O}_2$   
potassium peroxide –  $\text{K}_2\text{O}_2$   
calcium peroxide –  $\text{CaO}_2$



Metal peroxides are very strong oxidizers and can react with fuels. They are water-reactive, producing a caustic solution, heat, and oxygen gas when in contact with water. Some react violently.

**Metal oxysalts** consist of a metal element, oxygen, and a third element. The third element is most often a nonmetal, but not always. Sodium permanganate ( $\text{NaMnO}_4$ ) and potassium permanganate ( $\text{KMnO}_4$ ) are examples of oxysalts with two metal elements.

#### Examples of Metal Oxysalts

sodium hypochlorite –  $\text{NaClO}$

potassium nitrate –  $\text{KNO}_3$

calcium carbonate –  $\text{CaCO}_3$

The worst of the oxysalts are very strong oxidizers and will react readily in contact with fuels. Oxysalts formed with halogens are the most hazardous.

Naming oxysalts is more complex than naming other salts. Like the others, oxysalts start with the metal element, followed by the root of the second element. However, they end in either *-ate* or *-ite*, not *-ide*, and may contain the prefixes *per-* or *hypo-*. The prefixes and endings are directly related to the amount of oxygen in the compound.

#### Common Naming Scheme for Oxysalts

Metal + “per (nonmetal) ate”

Metal + “(nonmetal) ate”

Metal + “(nonmetal) ite”

Metal + “hypo (nonmetal) ite”

The two nonmetal elements in an oxysalt form an **oxyradical**. The normal (most stable) state of an oxyradical is its **base state**. The following chart shows the base states of various oxyradicals.

## Base States of Various Oxyradicals

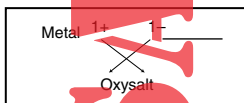
<u>With 3 Oxygen Atoms</u>		<u>With 4 Oxygen Atoms</u>	
Chlorate	$\text{ClO}_3$	Sulfate	$\text{SO}_4$
Bromate	$\text{BrO}_3$	Chromate	$\text{CrO}_4$
Iodate	$\text{IO}_3$	Phosphate	$\text{PO}_4$
Nitrate	$\text{NO}_3$	Arsenate	$\text{AsO}_4$
Manganate	$\text{MnO}_3$		
Carbonate	$\text{CO}_3$		

The chart below provides an example of how the addition or subtraction of oxygen atoms is reflected in the changing names of oxysalts.

### Examples of Oxysalt Naming

<u>Oxygen Content</u>	<u>Example</u>	<u>Formula</u>
1 extra atom	sodium <u>perchlorate</u>	$\text{NaClO}_4$
base state	sodium <u>chlorate</u>	$\text{NaClO}_3$
1 less atom	sodium <u>chlorite</u>	$\text{NaClO}_2$
2 less atoms	sodium <u>hypochlorite</u>	$\text{NaClO}$

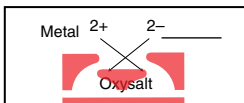
Oxyradicals are polyatomic ions, like the ones shown earlier. Oxyradicals having a charge of 1- must be paired with a metal element that has one electron on its outer shell. Examples include potassium nitrate ( $\text{KNO}_3$ ) and sodium bicarbonate ( $\text{NaHCO}_3$ ).



### Examples of Oxyradicals with 1- Charge

Hypochlorite	$\text{ClO}$	Permanganate	$\text{MnO}_4$
Chlorite	$\text{ClO}_2$	Bicarbonate	$\text{HCO}_3$
Chlorate	$\text{ClO}_3$	Acetate	$\text{CH}_3\text{COO}$
Perchlorate	$\text{ClO}_4$	Bisulfate	$\text{HSO}_4$
Nitrite	$\text{NO}_2$	Bromate	$\text{BrO}_3$
Nitrate	$\text{NO}_3$		

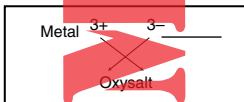
Oxyradicals with a charge of 2- must be paired with an element (or elements) with a 2+ charge. Examples include calcium carbonate ( $\text{CaCO}_3$ ) and sodium carbonate ( $\text{Na}_2\text{CO}_3$ ).



### Examples of Oxyradicals with 2- Charge

Carbonate	$\text{CO}_3^{2-}$	Chromate	$\text{CrO}_4^{2-}$
Sulfite	$\text{SO}_3^{2-}$	Dichromate	$\text{Cr}_2\text{O}_7^{2-}$
Sulfate	$\text{SO}_4^{2-}$	Oxylate	$\text{C}_2\text{O}_4^{2-}$
Persulfate	$\text{S}_2\text{O}_8^{2-}$		

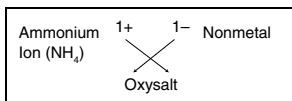
Oxyradicals with a charge of 3- must be paired with something that provides a 3+ charge. Trisodium phosphate ( $\text{Na}_3\text{PO}_4$ ) is an example.



### Examples of Oxyradicals with 3- Charge

Phosphate	$\text{PO}_4^{3-}$
Arsenate	$\text{AsO}_4^{3-}$
Borate	$\text{BO}_3^{3-}$

Most polyatomic ions have negative charges. However, the ammonium ion ( $\text{NH}_4^+$ ) has a positive charge (1+), so it behaves like a metal element in the ionic bonding process. That's why there are a handful of salts, such as ammonium chloride ( $\text{NH}_4\text{Cl}$ ) and ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ), that don't contain a metal element.



All of the metal elements discussed so far have only one charge associated with their ions. However, many of the transition metals have more than one **oxidation state**, meaning that they can donate different numbers of electrons. For example, iron (Fe) can form either ferrous chloride ( $\text{FeCl}_2$ ) or ferric chloride ( $\text{FeCl}_3$ ). Below are examples of other ions with multiple oxidation states. However, further discussion is beyond the scope of this book.

<u>Element</u>	<u>Ion Name</u>	<u>Symbol</u>
Chromium	Chromium (II) or chromous	$\text{Cr}^{2+}$
	Chromium (III) or chromic	$\text{Cr}^{3+}$
Manganese	Manganese (II) or manganous	$\text{Mn}^{2+}$
	Manganese (III) or manganic	$\text{Mn}^{3+}$
Iron	Iron (II) or ferrous	$\text{Fe}^{2+}$
	Iron (III) or ferric	$\text{Fe}^{3+}$
Copper	Copper (I) or cuprous	$\text{Cu}^+$
	Copper (II) or cupric	$\text{Cu}^{2+}$
Mercury	Mercury (I) or mercurous	$\text{Hg}^{2+}$
	Mercury (II) or mercuric	$\text{Hg}^{2+}$
Tin	Tin (II) or stannous	$\text{Sn}^{2+}$
	Tin (IV) or stannic	$\text{Sn}^{4+}$
Lead	Lead (II) or plumbous	$\text{Pb}^{2+}$
	Lead (IV) or plumbic	$\text{Pb}^{4+}$

It's important to recognize the different types of salts and the hazards associated with them. The rest is more nice-to-know information at the emergency responder level.

# SAMPLE

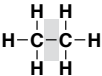


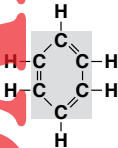
# Hydrocarbons

## The Four Types of Hydrocarbons

Hydrocarbons contain only two elements (hydrogen and carbon) in different ratios and configurations. The four main types of hydrocarbons are distinguished by the bonds between carbon atoms.

Hydrocarbon	Bond
alkane	single
alkene	double
alkyne	triple
aromatic	resonant

Here's a pictorial representation of the bonds:

Alkane (single bonds)	Alkyne (triple bonds)
	
Example: Ethane ( $C_2H_6$ )	Example: Ethyne ( $C_2H_2$ )
Alkene (double bonds)	Aromatic (resonant bonds)
	
Example: Ethene ( $C_2H_4$ )	Example: Benzene ( $C_6H_6$ )

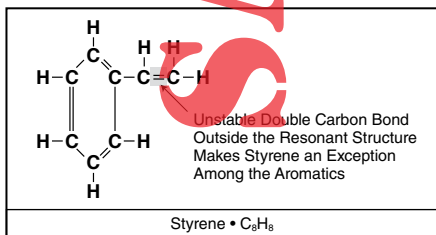
All hydrocarbons have common characteristics.

- All are flammable.
- All have some degree of toxicity.
- All are floaters (specific gravity less than 1).

Differences in behavior between the types of hydrocarbons are based primarily on the bonds between carbon atoms. Single and resonant bonds are stable, whereas double and triple bonds are not. Therefore:

- Most **alkanes** are relatively stable.
- **Alkenes** are reactive and prone to polymerization, particularly the smaller compounds.
- **Alkynes** are highly unstable. They have explosive potential.
- Most **aromatics** are very stable, even though they appear to have three double bonds, because the electrons rotate between elements (resonant bonds). As a group, aromatics are fairly toxic. They burn with sooty smoke that often has a spider web appearance. Some are carcinogenic.

Remember that these are generalizations only and that the information does not necessarily apply to all chemicals in a given category. For example, styrene ( $C_8H_8$ ) differs from other aromatic hydrocarbons in that it has an unstable double carbon bond outside the resonant structure. That makes it prone to polymerization.



**Saturated** hydrocarbons are those containing only single bonds between the carbon atoms (alkanes). In effect, the alkanes are saturated with as many hydrogen atoms as they can possibly hold, because every available bonding site is filled with hydrogen.

The other hydrocarbons are **unsaturated**, because the multiple bonds leave less room for hydrogen atoms. (The term **polyunsaturated** means there is more than one carbon-carbon double bond.)

Saturated	Unsaturated
<pre>       H   H   H                 H - C - C - C - H                       H   H   H           </pre>	<pre>       H   H   H                       C = C - C - H                       H       H           </pre>
Propane (C <sub>3</sub> H <sub>8</sub> )	Propene (C <sub>3</sub> H <sub>6</sub> )

## Hydrocarbon Names and Formulas

Hydrocarbon types can often be identified by name. Alkanes and alkynes use *-ane* and *-yne* endings, respectively. The *-ene* ending may indicate either an alkene or an aromatic, depending on the prefix.

Type	Ending	Examples
alkane	<i>-ane</i>	methane, ethane
alkene	<i>-ene</i>	ethene, propene *
alkyne	<i>-yne</i>	ethyne, propyne
aromatic	<i>-ene</i>	benzene, toluene

\* The alkenes *ethene*, *propene*, and *butene* are also known as *ethylene*, *propylene*, and *butylene*.




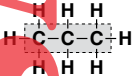
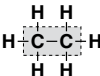
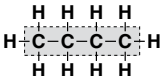


As with any other naming system, there are exceptions. For example, despite the *-ene* ending, acetylene ( $C_2H_2$ ) is an alkyne with a highly unstable triple bond between carbon atoms. (Acetylene is also known as *ethyne*.)

Alkanes, alkenes, and alkynes use common prefixes based on the number of carbon atoms in the formula.

# Carbon Atoms	Prefix	Example
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

The following is a visual representation of the information above ... *meth-*, *eth-*, *prop-*, *but-*, etc. signify the number of carbon atoms in the compound. The illustration shows only four examples, but the others follow the same pattern.

	
Methane ( $CH_4$ )	Propane ( $C_3H_8$ )
	
Ethane ( $C_2H_6$ )	Butane ( $C_4H_{10}$ )

The aromatic hydrocarbons have *-ene* endings, but they have different prefixes than the other hydrocarbons do.

### Five Aromatics

<u>Name</u>	<u>Formula</u>
Benzene	$C_6H_6$
Toluene	$C_7H_8$
Xylene	$C_8H_{10}$
Styrene	$C_8H_8$
Cumene	$C_9H_{12}$

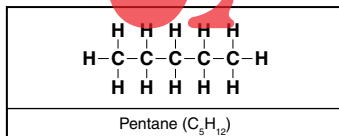
Hydrocarbons can also be recognized by formula. First, they contain only carbon and hydrogen. Second, the four types of hydrocarbons have formulas that follow certain patterns, as shown below. (The letter "n" represents the number of carbon atoms in the structure.)

### Hydrocarbon Formulas

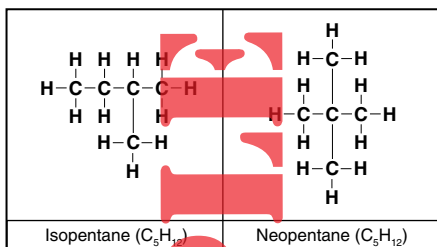
<u>Type</u>	<u>Formula</u>	<u>Example</u>
Alkane	$C_nH_{2n+2}$	$C_2H_6$ (Ethane)
Alkene	$C_nH_{2n}$	$C_2H_4$ (Ethene)
Alkyne	$C_nH_{2n-2}$	$C_2H_2$ (Ethyne)
Aromatic *	$C_nH_{2n-6} \text{ (} n \geq 6 \text{)}$	$C_6H_6$ (Benzene)

\* Styrene ( $C_8H_8$ ) is an exception. It doesn't follow the pattern of other aromatics.

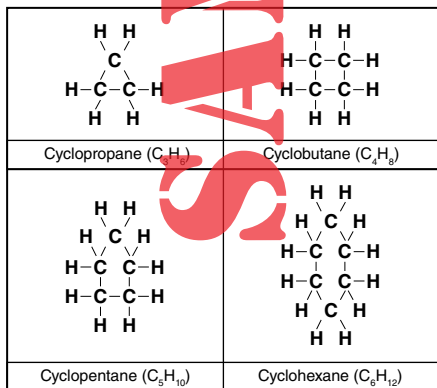
**Straight-chain hydrocarbons** have all the carbon atoms arranged in a row.



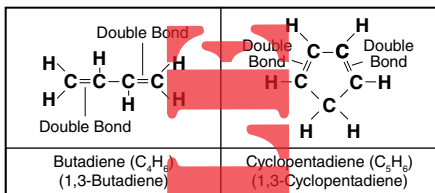
The **branched hydrocarbons** shown below are isomers of each other (and isomers of pentane, which was pictured on the previous page). Remember, isomers have the same molecular formula, but different molecular structures.



**Cyclo compounds** appear to have a ring structure like the aromatics, but they have single bonds (not resonant bonds) between carbon atoms. Cyclo compounds can have different properties than their straight-chain cousins do. (They also don't follow the same formula patterns.)



If one double bond between carbon atoms is reactive and unstable, **multiple double bonds** in the same compound are much worse. Butadiene ( $C_4H_6$ ) and cyclopentadiene ( $C_5H_6$ ) are examples of dangerous, highly unstable compounds.



Butadiene, a flammable and toxic monomer used in the plastics industry, will polymerize so easily that DOT regulations prohibit shipping it without the addition of an inhibitor. (It is usually shipped as a liquefied compressed gas.) Cyclopentadiene is so reactive that it explodes if heated.

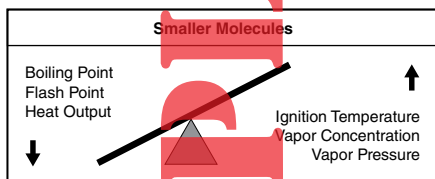
Note that the names butadiene and cyclopentadiene above still give us clues to formula and structure. *But-* and *pent-* indicate four and five carbon atoms, respectively. The *-ene* ending signals an alkene (double bond), with the prefix *cyclo* in cyclopentadiene further indicating a cyclo compound. The secondary prefix *di-* in each name warns of two double bonds between carbon atoms versus just one.

## The Effect of Molecular Size

The more carbon and hydrogen in the compound, the larger the molecule. Molecular size has a direct effect on physical and chemical properties, including those related to flammability. Many of these properties are directly or indirectly proportional to one another.

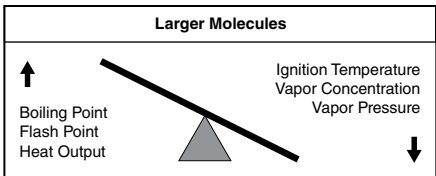
The comparisons below assume that one is comparing similar compounds, such as all straight-chain hydrocarbons. When comparing different types of compounds, chemical composition has a greater bearing on physical and chemical properties than molecular size does.

**Smaller compounds** are more active, so they produce more vapor (have a higher vapor content) and have a higher vapor pressure than do larger compounds.



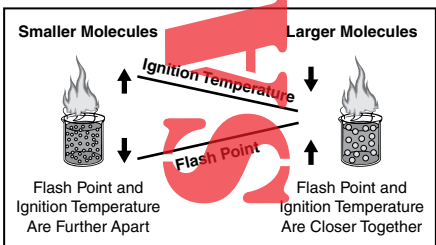
The flash point is lower in smaller compounds, because it takes less heat to raise the temperature of the liquid to where it produces sufficient vapors to form an ignitable mixture in air. But it takes more heat energy (ignition temperature) to ignite those vapors, because they contain less hydrogen (fuel) than do the vapors produced by larger molecules. Thus flash point and ignition temperature are further apart in relation to each other. Smaller compounds will output less heat because they have less fuel.

**Larger compounds** are less active, so they produce less vapor (have a lower vapor content) and have a lower vapor pressure than do smaller compounds.



The flash point is higher in larger compounds, because it takes more heat to raise the temperature of the liquid to where it produces sufficient vapors to form an ignitable mixture in air. But it takes less heat energy (ignition temperature) to ignite those vapors, because they contain more hydrogen (fuel) than do the vapors produced by smaller molecules. Thus flash point and ignition temperature are closer together in relation to each other. Larger compounds will output more heat because they have more fuel.

Although flash point and ignition temperature are inversely proportional, they will never cross. The ignition temperature of a product will always be higher than the flash point.



# SAMPLE

# Hydrocarbon Derivatives

## Hydrocarbon Derivatives Defined

**Hydrocarbon derivatives** are compounds derived from hydrocarbons. Hydrocarbon derivatives consist of one or more *hydrocarbon radicals* attached to a *functional group*.

Hydrocarbon Radical	+	Functional Group	=	Hydrocarbon Derivative
$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}- \\   \\ \text{H} \end{array}$		$-\text{O}-\text{H}$		$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{O}-\text{H} \\   \\ \text{H} \end{array}$
Methyl ( $\text{CH}_3$ )		Hydroxyl (OH)		Methyl Alcohol ( $\text{CH}_3\text{OH}$ )
$\begin{array}{cc} \text{H} & \text{H} \\   &   \\ \text{H}-\text{C} & -\text{C}- \\   &   \\ \text{H} & \text{H} \end{array}$		$-\text{O}-\text{H}$		$\begin{array}{cc} \text{H} & \text{H} \\   &   \\ \text{H}-\text{C} & -\text{C}-\text{O}-\text{H} \\   &   \\ \text{H} & \text{H} \end{array}$
Ethyl ( $\text{C}_2\text{H}_5$ )		Hydroxyl (OH)		Ethyl Alcohol ( $\text{C}_2\text{H}_5\text{OH}$ )

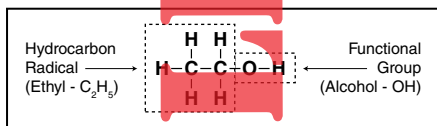
A **hydrocarbon radical** is a hydrocarbon from which one or more hydrogen atoms have been removed. For example, the methyl radical ( $\text{CH}_3$ ) comes from methane ( $\text{CH}_4$ ).

Original Hydrocarbon	Hydrocarbon Radical
$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{H} \\   \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}- \\   \\ \text{H} \end{array}$
Methane ( $\text{CH}_4$ )	Methyl- ( $\text{CH}_3$ )
$\begin{array}{cc} \text{H} & \text{H} \\   &   \\ \text{H}-\text{C} & -\text{C}-\text{H} \\   &   \\ \text{H} & \text{H} \end{array}$	$\begin{array}{cc} \text{H} & \text{H} \\   &   \\ \text{H}-\text{C} & -\text{C}- \\   &   \\ \text{H} & \text{H} \end{array}$
Ethane ( $\text{C}_2\text{H}_6$ )	Ethyl- ( $\text{C}_2\text{H}_5$ )



Hydrocarbon radicals cannot exist by themselves, because they are not electrically balanced. The missing hydrogen atoms must be replaced by something else—a functional group.

**Functional groups** are similar to hydrocarbon radicals in that they, too, are electrically unbalanced; not all of the available bonding sites are filled. Functional groups must bond with something else.



The functional group tells us the category (type) of hydrocarbon derivative (e.g., an alcohol). The hydrocarbon radical tells us the specific compound. The example above is ethyl alcohol ( $C_2H_5OH$ ).

The chart below shows the various hydrocarbon radicals (right) and the hydrocarbon compounds (left) from which they come.

<u>Original Hydrocarbon</u>		<u>Hydrocarbon Radical</u>	
Methane	$CH_4$	Methyl	$CH_3-$
Methane	$CH_4$	Form-	$H(C)\equiv$
Ethane	$C_2H_6$	Ethyl	$C_2H_5-$
Ethane	$C_2H_6$	Acet-	$CH_3(C)\equiv$
Ethene	$C_2H_4$	Vinyl	$C_2H_3-$
Propane	$C_3H_8$	Propyl	$C_3H_7-$
Propene	$C_3H_6$	Allyl, Acryl	$C_2H_3(C)\equiv$
Butane	$C_4H_{10}$	Butyl	$C_4H_9-$
Benzene	$C_6H_6$	Phenyl, Benzyl	$C_6H_5-$

# Overview of Hydrocarbon Derivatives

The hydrocarbon derivatives can be divided into groups based on the elements they contain.

**Part 1 hydrocarbon derivatives** contain only carbon, hydrogen, and oxygen. The group is further divided by general structure. The **carbonyls** all have a double bond between the carbon and oxygen atoms within their structures; the others do not.

Carbonyls	Others
ketones	alcohols
aldehydes	glycols
organic (carboxylic) acids	glycerols
esters	ethers
	organic peroxides

The following is a pictorial representation of these first nine hydrocarbon derivative types. (The "R" stands for hydrocarbon radical.) Each will be discussed in more detail shortly.

$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{R} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{H} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{O}-\text{H} \end{array}$
Ketones	Aldehydes	Organic Acids
$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{O}-\text{R} \end{array}$	$\text{R}-\text{O}-\text{H}$	$\text{R}-(\text{O}-\text{H})_2$
Esters	Alcohols	Glycols
$\text{R}-(\text{O}-\text{H})_3$	$\text{R}-\text{O}-\text{R}$	$\text{R}-\text{O}-\text{O}-\text{R}$
Glycerols	Ethers	Organic Peroxides

**Part 2 hydrocarbon derivatives** may contain carbon, hydrogen, or oxygen, but they also contain other elements.

Contain Nitrogen

nitros  
amines  
nitriles (cyanides)  
carbamates  
amides

Contain Other Elements

thiols (mercaptans)  
alkyl halides \*  
organophosphates  
hi-tech compounds

\* Alkyl halides may also be referred to as halogenated hydrocarbons.

The following is a pictorial representation of the five hydrocarbon derivatives that introduce nitrogen. (Again, “R” stands for hydrocarbon radical.)

$\text{R}-\text{N} \begin{array}{c} \diagup \text{O} \\ \diagdown \text{O} \end{array}$	$\text{R}-\text{N} \begin{array}{c} \diagup \text{H(R)} \\ \diagdown \text{H(R)} \end{array}$	$\text{R}-\text{C} \equiv \text{N}$
Nitros	Amines	Nitriles (Cyanides)
$\begin{array}{c} \text{(R)H} \\ \text{(R)H} \end{array} \text{N} \begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array} \text{O}-\text{R}$	$\text{R}-\text{C} \begin{array}{c} \text{O} \\ \parallel \\ \text{N} \end{array} \begin{array}{c} \diagup \text{H(R)} \\ \diagdown \text{H(R)} \end{array}$	
Carbamates	Amides	

Thiols (also known as mercaptans) introduce sulfur. Alkyl halides (also known as halogenated hydrocarbons) contain one or more halogens (indicted by “X” below). Organophosphates have phosphorus in their structures. Hi-tech compounds (not shown) can vary greatly.

$\text{R}-\text{S}-\text{H}$	$\text{R}-\text{P} \begin{array}{c} \diagup \\ \diagdown \end{array}$
Thiols (Mercaptans)	Organophosphates
$\text{R}-\text{X}$	
Alkyl Halides (Halogenated Hydrocarbons)	

It's generally easy to identify hydrocarbon derivatives if you isolate the hydrocarbon radicals and functional groups. This will become clearer over the next few pages. Meanwhile, the chart below shows the functional group for each type of hydrocarbon derivative. This is the thing to look for in chemical formulas.

Hydrocarbon Derivative	Functional Group
ketones	CO
aldehydes	CHO
organic (carboxylic) acids	COOH
esters	COO or CO <sub>2</sub>
alcohols	OH
glycols	(OH) <sub>2</sub>
glycerols	(OH) <sub>3</sub>
ethers	O
organic peroxides	OO or O <sub>2</sub>
nitros	NO <sub>2</sub>
amines	NH <sub>2</sub>
nitriles (cyanides)	CN
carbamates	NH <sub>2</sub> COO
amides	CONH <sub>2</sub>
thiols (mercaptans)	SH
alkyl halides	F, Cl, Br, or I
organophosphates	P
hi-tech compounds	B, Si, As, Be, Sn, or Ti

One additional naming system bears mentioning. The naming system isn't limited to hydrocarbon derivatives, but you'll see it more often over the next few pages. It's one used with *binary covalent compounds*, meaning those containing two nonmetal elements. It uses specific prefixes to indicate how many atoms of each element are present.

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

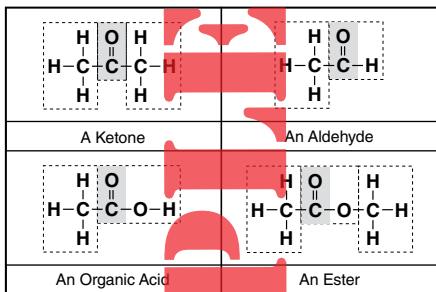
Two familiar examples are carbon monoxide ( $\text{CO}$ ) and carbon dioxide ( $\text{CO}_2$ ). (The prefix *mono-* is rarely needed and is used only with the element oxygen.) Carbon tetrachloride ( $\text{CCl}_4$ ) is another example, addressed later in this chapter.

Even though the naming system is designed for binary compounds, it is also used liberally with hydrocarbon derivatives containing more than two elements. Trichloromethane ( $\text{CHCl}_3$ ), for instance, has three chlorine atoms joined to a hydrocarbon radical that started life as methane ( $\text{CH}_4$ ). Conversely, dimethyl ketone ( $\text{CH}_3\text{COCH}_3$ ) has two methyl radicals joined to a ketone ( $\text{CO}$ ) functional group. You'll see illustrations of these compounds shortly.

A few very familiar compounds don't follow this naming system. The hydrocarbons identified earlier have their own system. Other significant examples include ammonia ( $\text{NH}_3$ ) and water ( $\text{H}_2\text{O}$ ).

## Part 1 Derivatives - Carbonyls

*Ketones, aldehydes, organic acids, and esters* are all **carbonyls**, with a double bond between carbon and oxygen. This is a very stable bond, unlike a double bond between two carbon atoms.



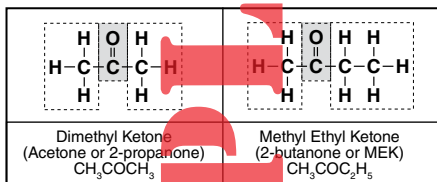
The four carbonyls illustrated above are also represented in the chart below. They were chosen for their *graphic* similarity. Notice that each has a methyl radical ( $\text{CH}_3$ ) on the left. The ketone and the ester both also have methyl radicals on the right. However, the aldehyde and the organic acid have nothing on the right because their particular functional groups leave no open bonding sites.

Type	Example	Name
ketone	$\text{CH}_3\text{COCH}_3$	dimethyl ketone
aldehyde	$\text{CH}_3\text{CHO}$	acetaldehyde
organic acid	$\text{CH}_3\text{COOH}$	acetic acid
ester	$\text{CH}_3\text{COOCH}_3$	methyl acetate

(Technically, carbamates and amides are carbonyls too, because they contain a double bond between carbon and oxygen. They are presented separately, however, because they introduce a new element—nitrogen.)

**Ketones** have the functional group **CO**. They have names ending in *ketone* or *-one*.


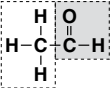
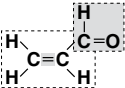
Dimethyl ketone ( $\text{CH}_3\text{COCH}_3$ ) was pictured on the previous page. If the second methyl radical is replaced by an ethyl radical, it creates methyl ethyl ketone ( $\text{CH}_3\text{COC}_2\text{H}_5$ ), often called MEK. There are other ketones, but two examples are sufficient to illustrate the structure of these compounds. These two are the most important in the ketone family.



Ketones are water-soluble solvents that are toxic and flammable, exhibiting a yellow flame with a blue base when burning. They can have a narcotic effect on the central nervous system.

**Aldehydes** have the functional group **CHO**. They have names ending in *aldehyde* or *-al*. (Don't confuse this with the *-ol* ending in alcohols. For example, *ethanal* is not *ethanol*.)

Acetaldehyde ( $\text{CH}_3\text{CHO}$ ) was pictured earlier, but the simplest of all aldehydes (formaldehyde) has a single hydrogen atom (H) bonded to the functional group (CHO). All of the others have hydrocarbon radicals.

		
Formaldehyde (Methanal) HCHO	Acetaldehyde (Ethanal) CH <sub>3</sub> CHO	Acrolein (Propenal) CH <sub>2</sub> :CHCHO

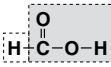
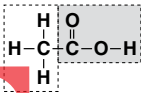
Aldehydes are water-soluble compounds frequently used as preservatives. Most are liquids. The exception is formaldehyde, which is a gas in its natural state, but which is usually transported dissolved in water. It's commonly called formalin in solution.

Like ketones, aldehydes are toxic and flammable, exhibiting a yellow flame with a blue base when burning. Aldehydes generally have wide flammable ranges, the most dramatic examples being formaldehyde (7% to 73%) and acetaldehyde (4% to 60%). Some aldehydes can form unstable, explosive organic peroxides over time, particularly when exposed to air. While many of the carbonyls are irritants, the aldehydes are particularly noted for choking, suffocating odors.

One aldehyde deserves special mention. *Propenal* (CH<sub>2</sub>:CHCHO) is more commonly called *acrolein*. Firefighters may recognize it as the major irritant in smoke given off by burning wood, wood products, and other Class A combustibles. The formula for acrolein is typically depicted with either a colon (:) or an equal (=) sign to signify a double bond between the carbon atoms. This double bond between carbon atoms makes acrolein prone to polymerization.



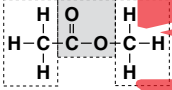
**Organic (carboxylic) acids** have the functional group **COOH**. Their names end in *-ic acid* or *-oic acid*.

	
Formic Acid (Methanoic Acid) <chem>HCOOH</chem>	Acetic Acid (Ethanoic Acid) <chem>CH3COOH</chem>

Organic acids are **toxic and corrosive**. They are combustible, burning with a blue and yellow flame and clean smoke. They are water-soluble.

**Esters** have the functional group **COO** (or **CO<sub>2</sub>**). They have names that end in *-ate*. Often they end in *acetate* or *acrylate*.

Esters and some of the organic peroxides are the only hydrocarbon derivatives with an *-ate* ending. (Some metal oxysalts also have names that end in *-ate*. But the metal element identifies them as salts rather than hydrocarbon derivatives.)

	
Methyl Acetate <chem>CH3COOCH3</chem>	Methyl Acrylate <chem>C2H3COOCH3</chem>

Esters are commonly used to synthesize resins and plastics. Those with a double bond between carbon atoms are particularly valuable in the plastics industry because of their tendency to polymerize. It's this same property that makes them so dangerous. Esters are also commonly used in the perfume industry because many of them have pleasant fruity or floral odors.

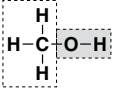
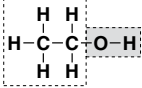
Esters are flammable, exhibiting a yellow flame with a blue base when burning. Esters are described as only slightly soluble.

## Part 1 Derivatives - Other

The next five hydrocarbon derivatives also contain carbon, hydrogen, and oxygen, but they do not have a double bond between carbon and oxygen.

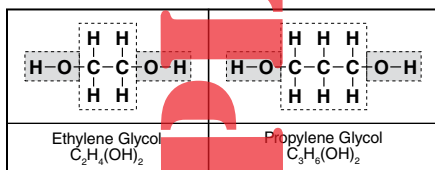
**Alcohols** have the functional group **OH**, called a *hydroxyl group*. Their names end in *alcohol* or *-ol*. (Don't confuse this with the *-al* ending used with aldehydes. For example, *ethanol* is not *ethanal*.)

Metal hydroxide salts also contain OH in the formula, but it's a negatively charged hydroxide ion ( $\text{OH}^-$ ). Hydroxyl groups, on the other hand, have no electrical charge. Further details are beyond the scope of this book. What is important to recognize is the difference between alcohols (with carbon-based hydrocarbon radicals) and hydroxide salts (containing a metal element instead).

	
Methyl Alcohol (Methanol) $\text{CH}_3\text{OH}$	Ethyl Alcohol (Ethanol) $\text{C}_2\text{H}_5\text{OH}$

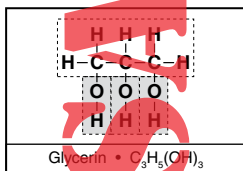
Alcohols are either flammable or combustible, burning with a clean blue flame. The smallest alcohols, methyl and ethyl, have relatively wide flammable ranges (6% to 36% and 3.3% to 19%, respectively). These water-soluble compounds are generally toxic, although toxicity varies from one alcohol to another.

**Glycols** are part of the larger alcohol family, but they have **two OH groups** instead of one. They have *glycol* in the name.



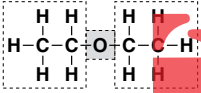
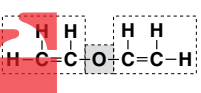
Glycols are toxic and combustible. Most are highly soluble in water and are relatively nonvolatile.

**Glycerols** are also part of the larger alcohol family, but they have **three OH groups** to set them apart.



Glycerols, in general, should be considered toxic and combustible. However, the most common one, glycerin, is relatively harmless in low concentrations. It is used to make a variety of products, from dynamite to candy and pharmaceuticals.

**Ethers** have the functional group **O**. Most have names ending in *ether*, but some have names that end in *oxide*. (Oxide salts also have names ending in *oxide*, but they have a metal element in the name and formula.)

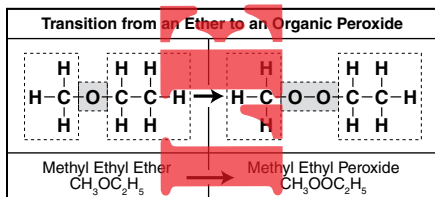
	
Diethyl Ether (Diethyl Oxide) $C_2H_5OC_2H_5$	Divinyl Ether $C_2H_3OC_2H_3$

Ethers are very volatile. They are flammable. Many have flash points below 0°F (17.8°C), and some have relatively wide flammable ranges, including diethyl ether (1.9% to 36%) and divinyl ether (1.7% to 27%). When ethers burn, they do so with invisible flames.

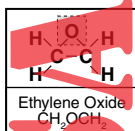
Ethers are insoluble in water; they are floaters. Most have anesthetic properties, which is one reason diethyl ether (commonly referred to simply as “ether”) was once widely used as a general anesthetic in hospitals before being replaced by safer products.

Ethers with double bonds between carbon atoms, such as divinyl ether, are unstable compounds subject to polymerization.

Ethers have limited shelf lives; they form explosive organic peroxides over time, particularly when exposed to air. For example, methyl ethyl ether ( $\text{CH}_3\text{OC}_2\text{H}_5$ ) bonds with oxygen to become methyl ethyl peroxide ( $\text{CH}_3\text{OOC}_2\text{H}_5$ ). Crystals developing on the container indicate extreme danger.



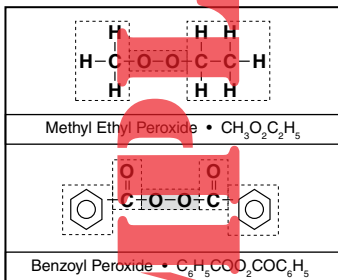
Ethylene oxide is unique in name and appearance, but its structure (an oxygen atom between two carbon atoms) makes it an ether. Ethylene oxide is an extremely hazardous gas with a flammable range of 3% to 100%. That plus its composition (a fuel and an oxidizer in the same compound) allows ethylene oxide to burn inside its own container with no air present. It's also subject to polymerization.



**Organic peroxides** have the functional group **OO** (or **O<sub>2</sub>**). They normally have *peroxide* or *peroxy* in the name. However, there are many exceptions. Some organic peroxides have names with a *per-* prefix and an *-ate* ending (e.g., isopropyl percarbonate).

(Peroxide salts also contain *peroxide* in the name. And some oxysalts also contain *per-* and *-ate*. However, salts contain metal elements, whereas organic peroxides contain hydrocarbon radicals instead.)

Some names are even more misleading (e.g., peracetic acid). It's a poignant reminder of how important it is to check reference sources at a hazmat incident rather than rely solely on name recognition and a limited knowledge of chemistry.



Organic peroxides are extremely unstable. Organic peroxides are not explosive, per se—they are DOT Class 5.2—but they are similar to explosives in that they contain a fuel component (the hydrocarbon radicals) and an oxidizer component (the peroxide) in the same formula. Two sides of the fire triangle are already present.

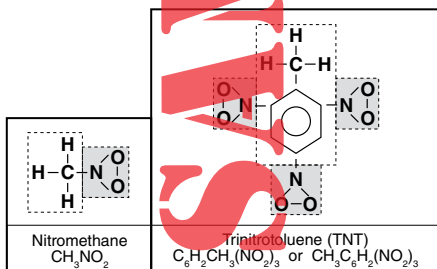
Although organic peroxides are oxidizers, their instability is a much greater concern than their oxidizing ability. They are very sensitive to heat and friction. Many are also very sensitive to contamination. They're flammable and highly reactive with other chemicals. Many are toxic. Some are corrosive. They are insoluble floaters.

Organic peroxides are often used as catalysts in the plastics industry to initiate the polymerization process. They are prone to runaway polymerization if exposed to elevated temperatures, so many reference sources list *self-accelerating decomposition temperatures* (SADT) for these compounds. The SADT is the temperature at which an organic peroxide begins to decompose. (As a rule of thumb, increasing the temperature by 10 degrees will cause the reaction rate to double.) Once the reaction begins, it can't be stopped. Organic peroxides should be kept below the *maximum safe storage temperature* (MSST)—a temperature far enough below the SADT to provide a margin of safety.

## Part 2 Derivatives - Nitrogen-Based

The next set of hydrocarbon derivatives introduce one new element—nitrogen.

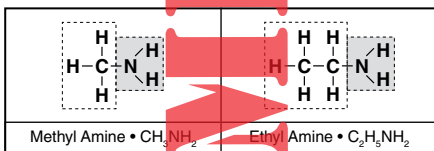
**Nitros** have one or more nitro ( $\text{NO}_2$ ) groups bonded to a hydrocarbon radical. Most nitro compounds have *nitro* in the name.



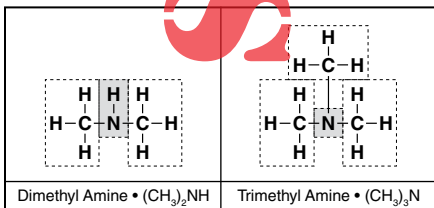
The bonded pair of oxygen atoms makes the nitro group a strong oxidizer. The hydrocarbon radical provides the fuel component. With both an oxidizer and a fuel component in the same structure, two sides of the fire triangle are complete. Consequently, these compounds are explosive and highly flammable. Many are sensitive to shock or heat.

Nitros are also toxic by inhalation, ingestion, and skin absorption. Many nitros are vasodilators, exposure to which can cause a sudden drop in blood pressure. They vary in solubility.

**Amines** are often called ammonia derivatives, since the functional group begins as ammonia ( $\text{NH}_3$ ). The simplest amines are those containing the functional group  $\text{NH}_2$  bonded to a single hydrocarbon radical. They contain *amine* in the name.



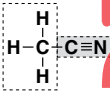
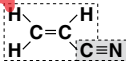
Secondary and tertiary amines can be created by substituting additional hydrocarbon radicals for hydrogen atoms. Notice, however, that these products no longer have the telltale  $\text{NH}_2$  in the formula.





Both the ammonia base and hydrocarbon radicals contribute to the toxicity and flammability of amines. Some amines are also corrosive. Amines exhibit a yellow flame when burning. They are water-soluble and have characteristically foul odors.

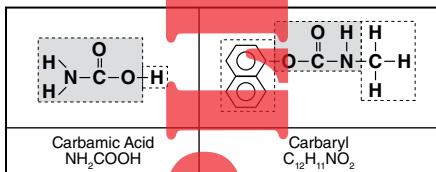
**Nitriles** (also called **cyanides**) contain the functional group **CN**, with a triple bond between the carbon atom and the nitrogen atom. These compounds have names containing *nitrile* or *cyanide*. (Cyanide salts also have *cyanide* in the name, but they have a metal element in the name and formula.)

	
Acetonitrile (Methyl Cyanide) $\text{CH}_3\text{CN}$	Acrylonitrile (Vinyl Cyanide) $\text{CH}_2=\text{CHCN}$

Nitriles are toxic due to the cyanide compounds in their structures. They are flammable, exhibiting a yellow flame with a blue base when burning. Those nitriles with a double bond between carbon atoms are subject to polymerization. Nitriles are water-soluble solvents.

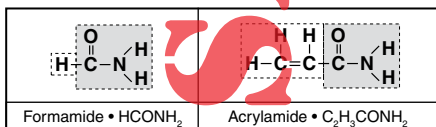
**Carbamates** are generally recognized by the functional group **NH<sub>2</sub>COO**—essentially a combination of the functional groups seen with amines (NH<sub>2</sub>) and esters (COO). These compounds often have names starting with the prefix *carba*-.

Carbamic acid ( $\text{NH}_2\text{COOH}$ ) is the simplest carbamate, with a hydrogen atom filling the one open bonding site. Carbaryl ( $\text{C}_{12}\text{H}_{11}\text{NO}_2$ ), below right, is a more complex example, where one of the hydrogen atoms normally attached to nitrogen has been replaced by another hydrocarbon radical. Thus it lacks the telltale  $\text{NH}_2\text{COO}$  in the formula. On the other side of the functional group are two benzene rings.



Carbamates are used as pesticides, often in place of the more toxic organophosphate compounds. Nevertheless, carbamates are still toxic and combustible.

**Amides** have the functional group  $\text{CONH}_2$ . However, hydrogen atoms normally attached to the nitrogen atom can be replaced by additional hydrocarbon radicals (not shown). Thus some amides lack the telltale  $\text{CONH}_2$  in the formula. These compounds often contain *amide* in the name.

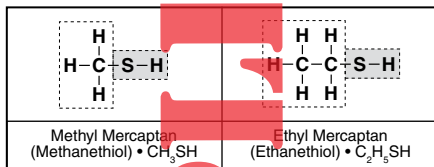


Amides have low to moderate toxicity. They are flammable. Those with a double bond between carbon atoms are subject to polymerization.

## Part 2 Derivatives - Other

This final section introduces other elements beyond just carbon, hydrogen, oxygen, and nitrogen.

**Thiols** (or **mercaptans**) contain the functional group **SH** (sulfur and hydrogen). They commonly have either *thiol* or *mercaptan* in the name.



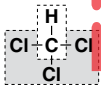
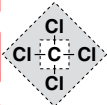
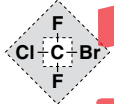
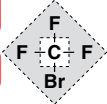
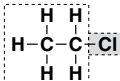
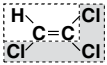


These compounds are flammable and toxic. They are also strong irritants. Many have skunk-like odors and are used as odorizers for hydrocarbon fuels (e.g., as a warning agent for natural gas).

**Alkyl halides (halogenated hydrocarbons)** have no specific functional group. Rather, what they have in common is that one or more hydrogen atoms in the original hydrocarbon is replaced by a halogen (fluorine, chlorine, bromine, or iodine). The most common are the chlorinated hydrocarbons. The first six shown on the next page are based on methane ( $\text{CH}_4$ ), the most simple hydrocarbon.

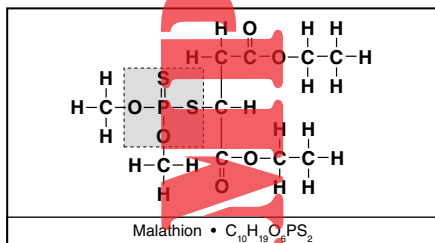
Not all alkyl halides are based on methane. For example, chloroethane ( $\text{C}_2\text{H}_5\text{Cl}$ ) is based on ethane ( $\text{C}_2\text{H}_6$ ) and trichloroethylene ( $\text{ClCH}:\text{CCl}_2$ ) is based on ethene ( $\text{C}_2\text{H}_4$ ). They are the bottom two alkyl halides illustrated on the next page.

The proper names of these compounds clearly identify the original molecule (methane, ethane, ethene, etc.) and the halogens used. The common or alternate names, such as methylene chloride, chloroform, and Halon, are the ones that don't necessarily give a clear indication as to chemical composition. (Note: Some of these names have *-ide* endings, similar to most of the salts. However, the absence of metal elements distinguishes these as alkyl halides.)

	
Chloromethane (Methyl or Methylene Chloride) $\text{CH}_3\text{Cl}$	Dichloromethane (Chloroform) $\text{CH}_2\text{Cl}_2$
	
Trichloromethane $\text{CHCl}_3$	Tetrachloromethane (Carbon Tetrachloride) $\text{CCl}_4$
	
Difluorochlorobromomethane (Halon 1211) $\text{CF}_2\text{ClBr}$	Trifluorobromomethane (Halon 1301) $\text{CF}_3\text{Br}$
	
Chloroethane (Ethyl Chloride) $\text{C}_2\text{H}_5\text{Cl}$	Trichloroethylene $\text{ClCH}:\text{CCl}_2$


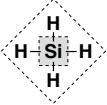
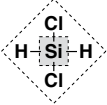

Alkyl halides are generally toxic, some more so than others. Some are flammable, but most do not burn. In fact, some are used as extinguishing agents. Most will break down at relatively low temperatures (as low as 325°F/162.8°C), giving off toxic decomposition products. For example, carbon tetrachloride, once used as an extinguishing agent, decomposes to toxic phosgene gas when heated. Alkyl halides are insoluble in water; they are sinkers.

**Organophosphates** are very large compounds containing **phosphorus double-bonded to sulfur or oxygen**. But functional groups vary. Malathion (below) has a functional group of  $\text{P}(\text{SO})_2$ . Parathion (not shown) has  $\text{PSO}_3$ .



These toxic compounds are used as insecticides. They are often mixed with flammable liquids for dissemination.

**Hi-tech compounds** are a variety of products that don't fit any other category. There is no pattern in the names, formulas, or structures, but many contain arsenic (As), beryllium (Be), boron (B), silicon (Si), tin (Sn), or titanium (Ti).

			
Arsine $\text{AsH}_3$	Silane $\text{SiH}_4$	Dichlorosilane $\text{H}_2\text{SiCl}_2$	Phosphine $\text{PH}_3$

Many hi-tech compounds are reactive, pyrophoric, and/or toxic. Some are flammable. Until proven otherwise, these compounds should all be treated as extremely dangerous.

## Naming Similarities with Salts

The salts and hydrocarbon derivatives below share some naming similarities, evident in the name endings. Remember the two clues for distinguishing between salts and hydrocarbon derivatives. Salts have names beginning with a metal element (except those containing the ammonium ion). Hydrocarbon derivatives generally have names identifying the hydrocarbon radical(s).

### Salts

cyanide salts

oxide salts

peroxide salts

binary salts (*-ide*)

oxysalts (*-ate*)

### Hydrocarbon Derivatives

cyanides (nitriles)

ethers with "oxide" names

organic peroxides

some alkyl halides and amides

esters, some organic peroxides

Keep in mind, however, that there are different naming schemes, not all of which are as simple as the IUPAC naming system emphasized in this book. This book provides a foundation to help you recognize hazardous materials and, in turn, begin predicting hazards and behavior. However, there is no substitute for checking multiple reference sources at a hazmat incident.

# SAMPLE

# Toxicity and Risk

## Routes of Entry / Health Effects

Hazardous materials can invade the body through several routes of entry/exposure:

- **Inhalation**—the most dangerous route. Lungs are very vulnerable to injury, and chemicals that enter the lungs can be rapidly absorbed into the bloodstream and transferred to other organs or body systems.
- **Absorption** through skin or eyes. Eyes and parts of the body rich in hair follicles are particularly susceptible.
- **Ingestion** due to poor hygiene (eating, drinking, or smoking before thoroughly washing one's hands).
- **Injection** through a cut, scratch, or puncture wound sustained at an incident.

Hazmat emergencies generally result in **acute** (one-time or short-term) exposures, with effects manifesting either immediately or within hours or days. Effects of **chronic** (repeated or long-term) exposures are often not detectable for years.

**Local** effects occur directly to the area exposed, while **systemic** effects affect the entire body.

The health effects of most chemicals are fairly predictable, but when two or more chemicals are involved, the **synergistic effect** can produce dramatically different signs and symptoms.



Some materials are particularly insidious in the damage they cause:

- **Carcinogens** cause cancer.
- **Mutagens** cause changes to the genetic material of cells (DNA and RNA) that can be inherited by offspring. The genetic changes can have numerous effects, including the failure of important biochemical processes. Some can also cause cancer.
- **Teratogens** cause malformations in an unborn child. Exposure during the embryonic stage (first eight weeks) can result in deformed or absent limbs. Later exposures can result in physiological and behavioral effects.

## Factors Affecting Risk

Several factors affect the risk to exposed persons:

- The toxicity of the material.
- The form of the material (gas, liquid, powder, solid).
- Dose (or concentration) to which someone is exposed.
- Duration and frequency of exposure.
- Gender. (Chemicals can have different effects on the male and female reproductive systems.)
- Age. (Young children and the elderly are often more vulnerable to injury.)
- Individual susceptibility and overall health.
- Promptness and quality of decontamination and medical care.

The relation between exposure and harm can be illustrated by the **Dose-Response Curve**. It's the old familiar saying: The dose makes the poison. Below a certain threshold, a substance won't cause detrimental effects in the test population being observed. However, as the dose increases, so do the health effects. The dose-response curve will look different for each substance, depending on its toxicity. The illustration below is a generic representation.



## Exposure Versus Contamination

The terms *exposure* and *contamination* are often used interchangeably, but they mean different things.

A person can be **exposed** without being contaminated. Examples include patients who have inhaled a gas or vapor and those who have received a dose of gamma radiation. They pose no risk of secondary contamination.

A **contaminated** person is one who has the hazardous material on his or her body, posing a risk of secondary contamination to others. Someone who is contaminated is also exposed.

The most commonly used units of measure are **parts per million (ppm)** and **parts per billion (ppb)**. These are straightforward representations of how much contaminant exists per million or billion units of the atmosphere. A concentration of 1% is equal to 10,000 parts per million.

The chart below shows the relation between contaminant concentration and oxygen concentration. Note that at the point where OSHA defines the atmosphere as being oxygen-deficient (19.5%), there can be 70,000 ppm of a contaminant present. Many substances are deadly at far lower concentrations.

<u>Contaminant Concentration</u>	<u>Oxygen Concentration</u>
1% (10,000 ppm)	20.7%
2% (20,000 ppm)	20.5%
3% (30,000 ppm)	20.3%
4% (40,000 ppm)	20.1%
5% (50,000 ppm)	19.9%
6% (60,000 ppm)	19.7%
7% (70,000 ppm)	19.5%

It's important to recognize that because oxygen represents roughly one fifth of the normal atmosphere, a 1% drop in the oxygen level is really a 5% displacement of the overall atmosphere.

## Toxicity Terminology

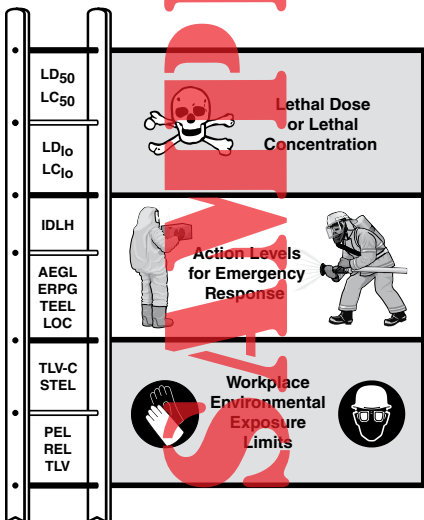
Toxicity is sometimes measured in **milligrams per cubic meter (mg/m<sup>3</sup>)**. There is no easy correlation between this and percent by volume or parts per million, because milligrams per cubic meter is based on the molecular weight of the material, which is different for every substance. However, it is possible to convert from one to the other with the following equations.

$$\text{ppm} = [(\text{mg}/\text{m}^3) / (\text{mw})] \times (24.44)$$

$$\text{mg}/\text{m}^3 = [(\text{mw})(\text{ppm})] / 24.44$$

Milligrams per kilogram (mg/kg) measures dose in relation to body weight. One kilogram equals 2.2 pounds.

A relative hazard ladder provides a quick visual representation (not to scale) of how common exposure limits and toxicity values stack up against one another. (The abbreviations and definitions are covered on the following pages.)



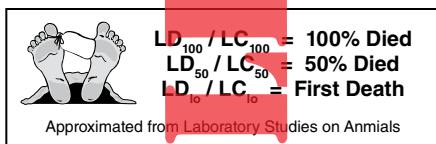
*A Relative Hazard Ladder (Not to Scale)*

LD	Lethal Dose ( $LD_{50}$ = 50% mortality rate, $LD_{10}$ = first death)
LC	Lethal Concentration ( $LC_{50}$ = 50% mortality rate, $LC_{10}$ = first death)
IDLH	Immediately Dangerous to Life and Health
AEGL	Acute Exposure Guideline Level (1, 2, or 3)
ERPG	Emergency Response Planning Guideline (1, 2, or 3)
TEEL	Temporary Emergency Exposure Limit (1, 2, or 3)
LOC	Level of Concern
TLV-C	Threshold Limit Value-Ceiling
STEL	Short-Term Exposure Limit
PEL	Permissible Exposure Limit (OSHA limits)
REL	Recommended Exposure Limit
TLV	Threshold Limit Value—Time-Weighted Average (TWA)

## Exposure Limits and Toxicity Values: Lethal Levels

**Lethal dose (LD)** and **lethal concentration (LC)** reflect the exposure required to kill a given percentage of a test population. Lethal dose is used for solids and liquids and is expressed in milligrams of chemical per kilogram (mg/kg) of body weight. Lethal concentration is used for gases and vapors and is usually expressed in parts per million (ppm), parts per billion (ppb), or milligrams per cubic meter ( $\text{mg}/\text{m}^3$ ) in air. It is independent of body weight.

The subscript notation refers to the percentage of test population affected.  $LD_{50}$  or  $LC_{50}$  is the number most often cited in reference sources. It means that 50% of the test population died from exposure to the specified dose or concentration of the material.  $LD_{100}$  or  $LC_{100}$  means that 100% died. ( $LD_{hi}$  and  $LC_{hi}$  mean the same thing.)  $LD_{lo}$  or  $LC_{lo}$  is the exposure that killed the first individual in a test study.



These numbers are derived from laboratory studies on animals, so they're only an approximation of how humans may be affected. And the information is very limited. If the number cited in reference sources is the  $LD_{50}$  or  $LC_{50}$ , there's no way to tell what exposure levels killed the first 49% of the test population. It's the first fatality (the  $LD_{lo}$  or  $LC_{lo}$ ) that matters most to emergency responders. Additionally, the data shows only fatalities, with no regard for debilitating health effects suffered by the survivors. It also shows only those fatalities that occurred within the test period (typically 14 days). So if test subjects die a month later as a direct result of the exposure, they're not factored into the statistic.

The distinction between toxic and highly toxic materials is based on  $LD_{50}$  and  $LC_{50}$  when albino rats are subjected to ingestion, absorption, and inhalation of the chemicals being studied. The precise definitions of *toxic* and *highly toxic* can be found in 29 CFR 1910.1200, Appendix A, but the down-and-dirty distinction is that highly toxic materials are deadly at far lower exposures.

Proper personal protective equipment (PPE) is required to protect against exposures in the lethal ranges. Self-contained breathing apparatus (SCBA) will be necessary to prevent airborne exposures. Structural firefighting clothing may not be adequate; chemical protective clothing may be required.

## **Exposure Limits and Toxicity Values: Action Levels for Emergency Response**

The values we use most often in emergency response are IDLH and LOC. **Immediately Dangerous to Life and Health (IDLH)** means an atmosphere that poses an immediate threat to life, would cause irreversible adverse health effects, or would impair an individual's ability to escape from a dangerous atmosphere.

IDLH values were initially developed as part of a joint project by NIOSH and OSHA as a tool for selecting respirators in the workplace. As a safety margin, IDLH values were based on effects that might occur from a 30-minute exposure, but it was not meant to imply that workers should stay in the environment without proper PPE any longer than necessary. Rather, every effort should be made to exit immediately. IDLH should be thought of like an SCBA low-air alarm. It's a window for escape, not a window for squeezing in additional mitigation measures in the time remaining.

IDLH is often used to distinguish between a rescue and a body recovery operation. If a victim has been exposed to the product at or above an IDLH concentration for more than 30 minutes, the chances of survival drop significantly. However, IDLH is only part of the risk-versus-gain analysis. It is generally not possible to make a positive determination of death from a distance.

IDLH is generally based on toxicological data. However, where flammability is a significantly greater risk than toxicity, IDLH may be set at 10% of the lower explosive limit (LEL).

**Level of Concern (LOC)** is the value used to determine the geographic area of risk in the event of a chemical release. This is generally the point at which evacuation or in-place protection measures are implemented. (LOC is a rough way of setting community exposure limits when one has no other information. The protective action criteria defined on the following pages are more definitive.)

LOC is generally defined as 10% of the IDLH. Unlike the other limits, LOC has no associated description of health effects that might be expected. It is simply a safety margin of 10%—just like 10% of a lower explosive limit (LEL) provides a safety margin to keep from entering the flammable range.

If you can't find IDLH or LOC in your reference books, you can estimate them based on the TLV-TWA. (TLV-TWA is defined on page 103.) LOC is generally defined as 10% of the IDLH or 3 times the TLV-TWA; thus IDLH is 10 times the LOC or 30 times the TLV-TWA. Remember, however, that these are approximations only.

General Definition	Alternate Definition	Rough Estimate
$\frac{\text{IDLH}}{\div 10}$ LOC	$\frac{\text{TLV-TWA} \times 3}{\text{LOC}}$	$\frac{\text{TLV-TWA} \times 30}{\text{IDLH}}$



## Exposure Limits and Toxicity Values: Protective Action Criteria

Whenever possible, emergency planning and community protection should be based on one of the Protective Action Criteria (PAC) below:

- Acute Exposure Guideline Levels (AEGLs)
- Emergency Response Planning Guidelines (ERPGs)
- Temporary Emergency Exposure Limits (TEEL)

Of the three Protective Action Criteria, AEGLs are the most comprehensive and should be your first choice if available. ERPGs are the second choice. TEELs can be used if no AEGL or ERPG exists.

There are three **Acute Exposure Guideline Levels (AEGLs)**, each representing the maximum airborne concentration *above which* it is predicted that the general population, including susceptible individuals, could experience ...

<u>Level</u>	<u>Description</u>
AEGL-1	notable discomfort, irritation, or certain asymptomatic nonsensory effects. However, the effects are not disabling and are transient and reversible upon cessation of exposure.
AEGL-2	irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape.
AEGL-3	life-threatening adverse health effects or death.

**Emergency Response Planning Guidelines (ERPGs)** provide an estimate of concentrations where one might reasonably anticipate adverse effects for exposures that exceed an hour in duration. ERPGs reflect only acute health effects, not long-term complications.

ERPG levels are the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour *without* experiencing or developing ...

<u>Level</u>	<u>Description</u>
ERPG-1	anything other than mild transient health effects or perceiving a clearly defined objectionable odor.
ERPG-2	irreversible or other serious health effects or symptoms that could impair an individual's ability to take protective action.
ERPG-3	life-threatening health effects.

**Temporary Emergency Exposure Limits (TEEL)** are temporary limits designed to facilitate the emergency planning process for chemicals that don't have AEGLs or ERPGs. TEELs are an approximation derived from other data; they don't undergo the extensive study and peer review associated with AEGLs or ERPGs.

TEELs have the same definitions as ERPGs, with two exceptions:

- TEELs do not specify a one-hour time frame.
- TEELs have a fourth level (TEEL-0), which is the threshold concentration below which most people will experience no appreciable risk of health effects.

## Exposure Limits and Toxicity Values: Workplace Environmental Exposure Limits

Workplace environmental exposure limits (WEEL) are established for workers without any special protective equipment. The first three below represent the maximum concentration to which an average person in average health may be exposed repeatedly on a day-to-day basis (40 hours per week, 8 to 10 hours per day) with no adverse health effects. Each is established by a different agency. Often the limits established by each agency are the same, but that's not always the case. Some of these published limits will have a "[skin]" notation, meaning that there's a potential for dermal absorption and that workers should protect against skin exposure.

- **Permissible Exposure Limits (PEL)** are established by the Occupational Safety and Health Administration (OSHA). These are time-weighted average (TWA) concentrations that, unless otherwise noted, must not be exceeded during any 8-hour shift of a 40-hour workweek. (*Time-weighted average* means that one can exceed the identified concentration, within limits, as long as the average exposure over an 8-hour shift does not exceed the PEL.) Because PELs are OSHA limits, compliance with PELs is mandated by law.
- **Recommended Exposure Limits (REL)** are similar to PELs in that they are also time-weighted averages for a 40-hour workweek. However, they allow for a 10-hour shift versus an 8-hour shift, and they are recommended limits established by the National Institute for Occupational Safety and Health (NIOSH), not regulatory limits from OSHA.

- **Threshold Limit Value—Time-Weighted Average (TLV-TWA)** is also a recommended limit, one from the American Conference of Governmental Industrial Hygienists (ACGIH). It's based on an 8-hour shift and 40-hour workweek.

Workers can exceed the permitted or recommended exposure limits if they stay within the short-term and ceiling exposure limits explained below. Short-term and ceiling exposure limits may be either regulatory limits or recommended limits, depending on whether they're established by OSHA or another agency. (If reference books don't cite the source, err on the side of safety and assume it's a regulatory limit.)

- A **Short-Term Exposure Limit (STEL)** is the maximum concentration to which a worker may be exposed for short durations (15 minutes, unless otherwise noted). Exposures above the STEL should be at least 60 minutes apart and not repeated more than 4 times per day. (Often this is written as TLV-STEL.)
- A **Ceiling Exposure Limit** is the concentration that may not be exceeded at any time. (Often this is written as TLV-C.)



## Odor Threshold

**Odor threshold** is the lowest concentration of a substance in air that can be smelled. It's helpful to know the odor threshold and where it stacks up against the toxicity values. Will people detect a substance before they can be harmed, or is it dangerous at concentrations well below the odor threshold?

*Caution:* Some substances have no odor. Others, like chlorine, produce olfactory fatigue. When people stop smelling chlorine, it's not necessarily because the chlorine has dissipated. It may be because olfactory fatigue has obstructed their ability to detect chlorine by smell alone.

Additionally, people vary in their ability to detect odors. For example, at least 25% of the population is genetically unable to smell the bitter almond odor of hydrogen cyanide. So odor threshold is nice to know, but it's far from reliable in judging one's potential exposure.

## Hazard Zones

Poisonous materials are sometimes identified by **poison inhalation zone (PIH)** or **toxic inhalation zone (TIH)**. They mean the same thing. Four zones are used for poisonous gases (DOT Class 2). Two are used for poisonous substances (DOT Class 6). In both cases, Hazard Zone A is the worst.

Zone	$LC_{50} >$	$LC_{50} \leq$	DOT Class
A	—	200 ppm	2 & 6
B	200 ppm	1000 ppm	2 & 6
C	1000 ppm	3000 ppm	2
D	3000 ppm	5000 ppm	2

## Pesticide Containers Signal Words

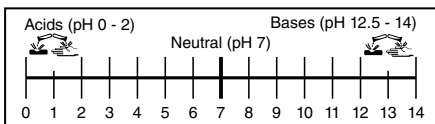
Pesticide container labels must include additional **signal words**: *danger* (meaning high toxicity), *warning* (moderate toxicity), or *caution* (relatively low toxicity). The words *extremely flammable* are also displayed on the label if the contents have a flash point below 80°F (26.7°C).

## Corrosivity and the pH Scale

**Corrosives** are materials that degrade metals and cause destruction to living tissue. **Corrosivity** is a measure of a material's ability to corrode—to dissolve or wear away by chemical action.

Corrosives are classified as either acids or bases. **Acids** are those compounds that release hydronium ions ( $\text{H}_3\text{O}^{+1}$ ) when dissolved in water. **Bases** (also called *caustics* or *alkalis*) release hydroxide ions ( $\text{OH}^{-1}$ ) when dissolved in water. (The superscript notations  $^{+1}$  and  $^{-1}$  refer to positive and negative charges, respectively.) We can't see the release of ions, but we can measure them with **pH** (which stands for *power of hydrogen*).

The **pH scale** goes from 0 to 14, with 7 being neutral. Chemicals with a pH of 0 to 6.9 are acidic, while those with a pH of 7.1 to 14 are basic (or caustic or alkaline). However, when it comes to actually classifying corrosives, the Code of Federal Regulations (40 C.F.R. § 261.22) defines acids as those materials with a pH of 2 or less and bases as those with a pH of 12.5 or more.



The pH scale is a logarithmic scale, meaning each number reflects a ten-fold difference in corrosivity. For example, a solution with a pH of 1 is ten times more acidic than one with a pH of 2 and a hundred times more acidic than one with a pH of 3. At the opposite end of the scale, a solution with a pH of 13 is ten times more alkaline than one with a pH of 12 and a hundred times more alkaline than one with a pH of 11.

One of the most significant differences between acids and bases is the way in which they damage human tissue:

- An acid in contact with the skin will cause the tissue to harden even as it eats away at that tissue, thereby limiting the damage to some degree.
- A base, on the other hand, will soften and dissolve the tissue, creating far more penetrating and severe injuries. (It will also create a slippery, soapy sensation on the skin.)

In both cases the damage will continue until the corrosive is thoroughly flushed from the body. And frequently the extent of the injury is not immediately obvious (something corrosive burns have in common with thermal burns).

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

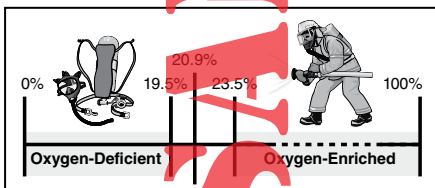
# Comparing Three Primary Threats at a Hazmat Incident

We often evaluate hazmat incidents in terms of three primary threats: oxygen deficiency, toxicity, and flammability. These three threats affect some of the decisions we have to make, for example, what PPE to wear or what protective actions to implement.

This section is designed to help you compare these three threats. However, it is not a substitute for the more thorough risk assessment generally needed at a hazmat incident.

## Evaluating Oxygen-Deficient (and Oxygen-Enriched) Atmospheres

The normal atmosphere contains roughly 78% nitrogen, 20.9% oxygen, and 1.1% argon and other gases. Although 20.9% oxygen is considered normal, we don't hit the "threat zones" until we drop below 19.5% or rise above 23.5%.



If the oxygen level is above 23.5%, the atmosphere is considered potentially explosive. An oxygen-enriched atmosphere will cause any flammable or combustible material to ignite more readily and burn more fiercely. It's unsafe to enter an oxygen-enriched atmosphere.



An oxygen concentration of 19.5% is considered by OSHA and NIOSH to be the minimum safe level. Below that, the atmosphere is oxygen-deficient and responders must wear self-contained breathing apparatus (SCBA) or supplied air respirators (SAR). Air purifying respirators (APR) are not acceptable, even if they are capable of filtering the specific contaminants in the atmosphere, because they don't provide responders with a source of oxygen.

## Evaluating Oxygen-Deficient Atmospheres

An atmosphere with less than 19.5% oxygen is not an immediate threat to life. There's still a margin of safety. However, oxygen deficiency does affect mental and physical abilities.

Oxygen	Effects of Oxygen Deficiency
20.9%	normal concentration
19.5%	minimum OSHA/NIOSH safe level, but doesn't address possible contaminant concentration
↓	increasing impairment to breathing, coordination, perception, and judgment
6%	difficulty breathing, convulsions, death in minutes

Any displacement in the oxygen concentration is an indication there may be a contaminant present in the atmosphere. Since oxygen comprises roughly one fifth (1/5) of the normal atmosphere, a 1% displacement (from 20.9% to 19.9% oxygen) means there is roughly a 5% concentration of a contaminant gas. In other words, although your oxygen meter shows a 1% displacement, that contaminant gas is really displacing one part oxygen and four parts everything else. Further monitoring is required.

Note: Some atmospheric monitors, such as combustible gas indicators, require at least 16% oxygen to function properly. If the oxygen level is less than 16%, meter readings may not be accurate.

## Evaluating Toxicity

**Contaminant concentration** is often cited in percent by volume in air (%) or in parts per million (ppm) or parts per billion (ppb). A concentration of 1% is equal to 10,000 parts per million (ppm) or 10,000,000 parts per billion (ppb).

<u>% by Volume</u>	<u>ppm</u>	<u>ppb</u>
0.1%	1,000	1,000,000
1%	10,000	10,000,000
10%	100,000	100,000,000

The chart below, repeated from Chapter 7, shows the relation between contaminant concentration and oxygen concentration. At the point where OSHA defines an atmosphere as being oxygen-deficient (19.5%), there can be as much as 70,000 ppm of a contaminant present. Many substances are deadly at far lower concentrations.

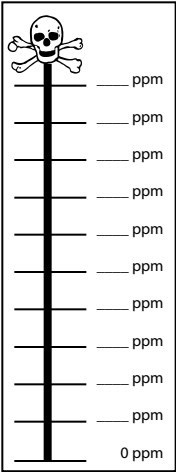
<u>Contaminant Concentration</u>	<u>Oxygen Concentration</u>
1% (10,000 ppm)	20.7%
2% (20,000 ppm)	20.5%
3% (30,000 ppm)	20.3%
4% (40,000 ppm)	20.1%
5% (50,000 ppm)	19.9%
6% (60,000 ppm)	19.7%
7% (70,000 ppm)	19.5%

Some people like using “hazard ladders” to plot important values. Hazard ladders can help you visualize exposure limits and toxicity values in comparison to contaminant concentrations.

This hazard ladder on this page can be customized with small numbers for highly toxic materials or large numbers for less toxic materials.

Determine a helpful scale from 0 ppm to the highest value you need to plot. Then plug in exposure limits, toxicity values, and meter readings as appropriate.

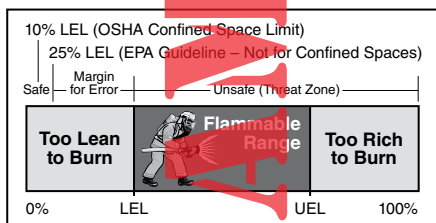
As with any tool, the trick is to make it work for you rather than twist yourself into knots trying to fit within the confines of the tool. If there isn’t enough room on the hazard ladder to plot all of values identified in this chapter, don’t worry about it. If your objective is emergency response, concentrate on IDLH and the protective action criteria. If you are evaluating workplace exposure levels instead, concentrate on those values.



## Evaluating Flammability

The concentration of a gas or vapor in air is also important when evaluating flammability. The most important value in this case is the **lower explosive limit (LEL)**, which was covered in Chapter 1. Below the LEL, vapors are too lean to burn. Above the upper explosive limit (UEL), vapors are too rich to burn. From the LEL to the UEL, ignition is possible. This is the flammable range.

Again, only atmospheres well below the LEL are safe to enter. OSHA prohibits working in confined space atmospheres with more than 10% of the LEL. The EPA's recommended limit for other environments is 25% of the LEL. Both limits (10% and 25%) leave a good margin of error to guard against everything from fluctuations in the chemical concentration to defective monitors or errors in interpreting the meter readings.



Also important is **flash point**—the minimum temperature at which a liquid produces enough vapors to form an ignitable mixture in air. Flash point is generally considered to be the most important temperature in assessing the hazards of flammable and combustible liquids. The lower the flash point, the greater the hazard.

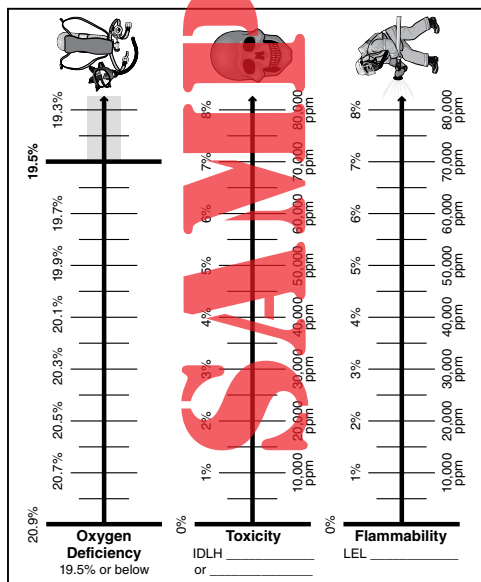
## Evaluating the Three Risks Together

For people who are visually oriented, plotting all three threats on parallel hazard ladders can help show which threat may be encountered first.

The **oxygen-deficiency** hazard ladder contains a shaded section that represents the threat zone.

The **toxicity** hazard ladder below reflects IDLH (immediately dangerous to life and health), but it could be modified to reflect other values as needed.

The **flammability** hazard ladder shows only LEL, not UEL, because it's vital to stay well below the LEL.



*Caution:* Looking only at numbers on a hazard ladder can be misleading. You must also consider other relevant factors, such as how much of an escape window you have if something goes wrong.

- An LEL atmosphere presents an immediate risk if vapors ignite.
- An IDLH atmosphere provides an escape window of up to 30 minutes, although immediate exit is encouraged.
- An oxygen-deficient atmosphere has an extended escape window with a good safety margin at the OSHA limit of 19.5%. (Remember, however, this gives no information about the hazards of any contaminants present.)

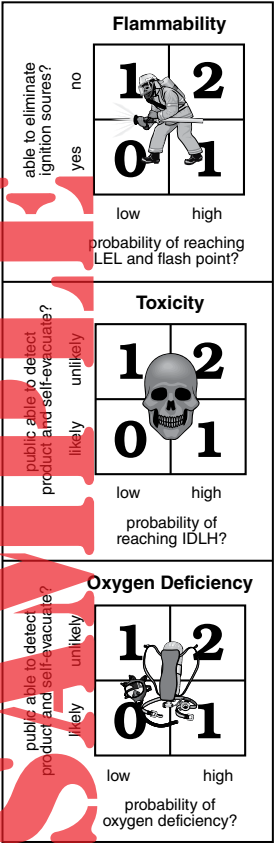
A simple **decision matrix** that weighs probability of risk against potential consequences is another good tool that can be easily adapted to evaluate the dangers associated with flammability, toxicity, and oxygen deficiency.

Consequences	Low	High
	0	1
Probability of Risk		
		Low
		High

This simple decision matrix can be used in many ways to evaluate the probability and consequence of risk. The examples on the next page were written to identify which threat would trigger protective actions, but it could be edited to reflect other concerns. The threat with the highest score is likely your first priority.

Each matrix looks at the probability of reaching the threat zone. The flammability matrix then looks at whether you can eliminate ignition sources. The other two matrices look at whether people are likely to detect the product and self-evacuate. (Or if people don't know the risks, are they likely to sense a chemical release and either evacuate on their own or call 911 and be directed to do so?)

Again, this tool is flexible enough to be edited to fit your needs.



# Cheat Sheets

This chapter puts several handy reference charts in one easy-to-find location.

Alkali Metals

1 • I

1

H

Hydrogen

Alkaline Earth Metals

2 • II

3

Li

Lithium

Alkaline Earth Metals

2 • II

4

Be

Beryllium

Alkaline Earth Metals

2 • II

11

Na

Sodium

Alkaline Earth Metals

2 • II

12

Mg

Magnesium

Alkaline Earth Metals

2 • II

19

K

Potassium

Alkaline Earth Metals

2 • II

20

Ca

Calcium

Alkaline Earth Metals

2 • II

37

Rb

Rubidium

Alkaline Earth Metals

2 • II

38

Sr

Strontium

Alkaline Earth Metals

2 • II

55

Cs

Cesium

Alkaline Earth Metals

2 • II

56

Ba

Barium

Alkaline Earth Metals

2 • II

87

Fr

Francium

Alkaline Earth Metals

2 • II

88

Ra

Radium

Alkaline Earth Metals

2 • II

107

Nh

Nihonium

Alkaline Earth Metals

2 • II

108

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## Salts Overview

Salt	Composition	Naming
Binary Salt	metal + nonmetal (not otherwise listed)	metal + nonmetal root (ends in <i>ide</i> )
Metal Cyanide	metal + cyanide	metal + <i>cyanide</i>
Metal Oxide (Binary Oxide)	metal + oxygen	metal + <i>oxide</i>
Metal Hydroxide	metal + hydroxide	metal + <i>hydroxide</i>
Metal Peroxide	metal (Group I or II) + peroxide	metal + <i>peroxide</i>
Metal Oxy salt	metal + element + oxygen	metal + oxyradical (ends in <i>ate</i> or <i>ite</i> ) (may include prefix <i>per</i> or <i>hypo</i> )

## Common Naming Scheme for Oxy salts

Metal	+	"per (nonmetal) ate"
Metal	+	"(nonmetal) ate"
Metal	+	"(nonmetal) ite"
Metal	+	"hypo (nonmetal) ite"

## The Four Types of Hydrocarbons

Hydrocarbon	Bond
alkane	single
alkene	double
alkyne	triple
aromatic	resonant

## Common Prefixes

# Atoms	Prefix	Prefix
1	meth-	mono-
2	eth-	di-
3	prop-	tri-
4	but-	tetra-
5	pent-	penta-
6	hex-	hexa-
7	hept-	hepta-
8	oct-	octa-
9	non-	nona-
10	dec-	deca-

## Hydrocarbon Formulas

Type	Formula	Example
Alkane	$C_n H_{2n+2}$	$C_2 H_6$ (Ethane)
Alkene	$C_n H_{2n}$	$C_2 H_4$ (Ethene)
Alkyne	$C_n H_{2n-2}$	$C_2 H_2$ (Ethyne)
Aromatic *	$C_n H_{2n-6} (n \geq 6)$	$C_6 H_6$ (Benzene)

\* Styrene ( $C_8 H_8$ ) is an exception. It doesn't follow the pattern of other aromatics.

## Effect of Molecular Size

Property	Smaller Molecules	Larger Molecules
Boiling Point	lower	higher
Flash Point	lower	higher
Heat Output	lower	higher
Ignition Temperature	higher	lower
Vapor Concentration	higher	lower
Vapor Pressure	higher	lower

## Hydrocarbon Radicals

<u>Original Hydrocarbon</u>		<u>Hydrocarbon Radical</u>	
Methane	$\text{CH}_4$	Methyl	$\text{CH}_3-$
Methane	$\text{CH}_4$	Form-	$\text{H}(\text{C})\equiv$
Ethane	$\text{C}_2\text{H}_6$	Ethyl	$\text{C}_2\text{H}_5-$
Ethane	$\text{C}_2\text{H}_6$	Acet-	$\text{CH}_3(\text{C})\equiv$
Ethene	$\text{C}_2\text{H}_4$	Vinyl	$\text{C}_2\text{H}_3-$
Propane	$\text{C}_3\text{H}_8$	Propyl	$\text{C}_3\text{H}_7-$
Propene	$\text{C}_3\text{H}_6$	Allyl, Acryl	$\text{C}_2\text{H}_3(\text{C})\equiv$
Butane	$\text{C}_4\text{H}_{10}$	Butyl	$\text{C}_4\text{H}_9-$
Benzene	$\text{C}_6\text{H}_6$	Phenyl, Benzyl	$\text{C}_6\text{H}_5-$

## Hydrocarbon Derivatives

<u>Hydrocarbon Derivative</u>	<u>Functional Group</u>
ketones	$\text{CO}$
aldehydes	$\text{CHO}$
organic (carboxylic) acids	$\text{COOH}$
esters	$\text{COO}$ or $\text{CO}_2$
alcohols	$\text{OH}$
glycols	$(\text{OH})_2$
glycerols	$(\text{OH})_3$
ethers	$\text{O}$
organic peroxides	$\text{OO}$ or $\text{O}_2$
nitros	$\text{NO}_2$
amines	$\text{NH}_2$
nitriles (cyanides)	$\text{CN}$
carbamates	$\text{NH}_2\text{COO}$
amides	$\text{CONH}_2$
thiols (mercaptans)	$\text{SH}$
alkyl halides *	$\text{F}$ , $\text{Cl}$ , $\text{Br}$ , or $\text{I}$
organophosphates	$\text{P}$
hi-tech compounds	$\text{B}$ , $\text{Si}$ , $\text{As}$ , $\text{Be}$ , $\text{Sn}$ , or $\text{Ti}$

\* Alkyl halides may also be referred to as halogenated hydrocarbons.

## Concentration Comparisons

<u>% by Volume</u>	<u>ppm</u>	<u>ppb</u>
0.1%	1,000	1,000,000
1%	10,000	10,000,000
10%	100,000	100,000,000

## Contaminant & Oxygen Concentration

<u>Contaminant Concentration</u>	<u>Oxygen Concentration</u>
1% (10,000 ppm)	20.7%
2% (20,000 ppm)	20.5%
3% (30,000 ppm)	20.3%
4% (40,000 ppm)	20.1%
5% (50,000 ppm)	19.9%
6% (60,000 ppm)	19.7%
7% (70,000 ppm)	19.5%

# Chemical Name and Formula Recognition

Based on a Chart Developed by Kevin Smith  
Deputy Fire Marshal – Hazardous Materials  
Chino Valley Independent Fire District

Note: These are general guidelines only. There are sometimes variations within a particular group, and there may be exceptions in each category. *Do not rely solely on this chart.*

<u>Prefix</u>	<u>Suffix</u>	<u>Family</u>	<u>Formula Contains *</u>
—	—	Organophosphate	R + P
—	acetate	Ester	R + COO
—	acid	Organic Acid	R + COOH
—	acrylate	Ester	R + COO
—	al	Aldehyde	R + CHO
—	alcohol	Alcohol	R + OH
—	aldehyde	Aldehyde	R + CHO
—	amide	Amide	R + CONH <sub>2</sub>
—	amine	Amine	R + NH <sub>2</sub>
—	ane	Alkane	H & C only
iso	ane	Alkane (branched)	H & C only
**	ane	Alkyl Halide	C + F, Cl, Br, I
—	ate	Ester	R + COO
—	ate	Oxysalt	metal + ***
per	ate	Oxysalt	metal + ***
—	cyanide	Cyanide Salt	metal + CN
—	cyanide	Cyanide/Nitrile	R + CN
—	ene	Alkene	H & C only
iso	ene	Alkene (branched)	H & C only
—	ene	Aromatic	H & C only
**	ane	Alkyl Halide	C + F, Cl, Br, I
—	ether	Ether	R + O
—	glycerine	Glycerol	R + (OH) <sub>3</sub>
—	glycol	Glycol	R + (OH) <sub>2</sub>

—	hydroxide	Hydroxide Salt	metal + OH
—	ic acid	Organic Acid	R + COOH
—	ide	Salt	metal + ***
—	ide	Alkyl Halide	R + F, Cl, Br, I
—	ite	Oxysalt	metal + ***
hypo	ite	Oxysalt	metal + ***
—	ketone	Ketone	R + CO
—	mercaptan	Mercaptan/Thiol	R + SH
—	nitrile	Nitrile/Cyanide	R + CN
—	oic acid	Organic Acid	R + COOH
—	ol	Alcohol	R + OH
—	one	Ketone	R + CO
—	oxide	Ether	R + O
—	oxide	Oxide Salt	metal + O
—	peroxide	Organic Peroxide	R + O <sub>2</sub>
—	peroxide	Peroxide Salt	metal + O <sub>2</sub>
—	sulfide	Metal Sulfide	metal + S
—	thiol	Thiol/Mercaptan	R + SH
—	yne	Alkyne	H & C only
iso	yne	Alkyne (branched)	H & C only
carba	—	Carbamate	R + NH <sub>2</sub> COO
nitro	—	Nitro	R + NO <sub>2</sub>

\* R stands for a hydrocarbon radical

\*\* a halogen prefix (e.g., chloro, fluoro, bromo)

\*\*\* one or more nonmetals

# Spill Estimation Chart

Developed by Kevin Smith  
Deputy Fire Marshal - Hazardous Materials  
Chino Valley Independent Fire District

The table on the next page was constructed based on assumptions used by FEMA and the U.S. EPA for emergency planning purposes. The data and formulations are specifically from Appendix G, "Equations Used for the Estimation of Vulnerable Zones," Technical Guidance for Hazard Analysis (1987), and from the Unit Equivalency Table, page A-4, of the *Handbook of Chemical Hazard Analysis Procedures*.

Note: Weight assumes a specific gravity of 1. For true weight, multiply the weight shown by the specific gravity of the product. (Specific gravity data is available on MSDSs and in various reference sources.)

## Using the Chart with Circular Spills

This chart assumes that the spill is a circular one and that the spill is 0.033 feet (1 centimeter) deep. (Note: These same calculations can be used for spills contained within circular dikes.)

1. Determine either the radius or the diameter.
2. Read the "Gallons" and "Weight" columns in that row.
3. If the spill depth is either more or less than one centimeter, multiply or divide the numbers as appropriate. (If measuring in inches, convert inches to centimeters by multiplying by 2.54.)

Radius (feet)	Diameter (feet)	Area (sq. ft.)	Gallons	Weight (pounds)
1	2	3	0.8	6.5
2	4	13	3.1	25.9
3	6	28	7.0	58.2
4	8	50	12.4	103.5
5	10	79	19.4	161.7
6	12	113	28	233
7	14	154	38	317
8	16	201	50	414
9	18	254	63	524
10	20	314	78	647
11	22	380	94	783
12	24	452	112	931
13	26	531	131	1093
14	28	616	152	1268
15	30	707	174	1455
16	32	804	199	1656
17	34	908	224	1869
18	36	1018	251	2095
19	38	1134	280	2335
20	40	1257	310	2587
21	42	1385	342	2852
22	44	1521	375	3130
23	46	1662	410	3421
24	48	1810	447	3725
25	50	1963	485	4042
26	52	2124	524	4372
27	54	2290	565	4715
28	56	2463	608	5070
29	58	2642	652	5439
30	60	2827	698	5821
31	62	3019	745	6215
32	64	3217	794	6623
33	66	3421	844	7043
34	68	3632	896	7476
35	70	3848	950	7923
36	72	4072	1005	8382
37	74	4301	1062	8854
38	76	4536	1120	9339
39	78	4778	1179	9837
40	80	5027	1241	10,348



## Using the Chart with Rectangular Spills

If the spill is rectangular rather than circular, you must first calculate the area of the spill to determine gallons and pounds. (Note: These same calculations can be used for spills contained within rectangular dikes.)

1. Figure the area by multiplying length times width.
2. Find the closest match in the "Area" column.
3. Read the "Gallons" and "Weight" columns in that row.
4. If the spill depth is either more or less than one centimeter, multiply or divide the numbers as appropriate. (If measuring in inches, convert inches to centimeters by multiplying by 2.54.)

## Conversion Factors

1 cubic foot = 7.48 gallons

1 cubic foot = 30.30 square feet at 1 cm deep

1 gallon spill = 4.05 square feet at 1 cm deep

1 gallon of water = 8.34 pounds

1 inch = 2.54 centimeters

Diameter = Radius x 2

Area =  $\text{Pi} \times \text{R}^2$  ( $3.14 \times \text{R}^2$ )

# Acronyms and Abbreviations

ACGIH	American Conference of Governmental Industrial Hygienists
AEGL	Acute Exposure Guideline Level
AIHA	American Industrial Hygiene Association
atm	Atmospheres
CFR	Code of Federal Regulations
CSTI	California Specialized Training Institute
DNA	Deoxyribonucleic Acid
DOE	Department of Energy
DOT	Department of Transportation
EPA	Environmental Protection Agency
ERPG	Emergency Response Planning Guideline
IDLH	Immediately Dangerous to Life and Health
IUPAC	International Union of Pure and Applied Chemists
LC	Lethal Concentration
LD	Lethal Dose
LEL	Lower Explosive Limit
LFL	Lower Flammable Limit
LOC	Level of Concern
mg/kg	Milligrams per Kilogram
mg/m <sup>3</sup>	Milligrams per Cubic Meter
mmHg	Millimeters of Mercury
MSDS	Material Safety Data Sheet
MSST	Maximum Safe Storage Temperature
mw	Molecular Weight
NFPA	National Fire Protection Association
NIOSH	National Institute for Occupational Safety and Health
OSHA	Occupational Safety and Health Administration
PAC	Protective Action Criteria
PEL	Permissible Exposure Limit
pH	Power of Hydrogen
PIH	Poison Inhalation Zone

ppb	Parts per Billion
PPE	Personal Protective Equipment
ppm	Parts per Million
psi	Pounds per Square Inch
REL	Recommended Exposure Limit
RNA	Ribonucleic Acid
SADT	Self-Accelerating Decomposition Temperature
SCBA	Self-Contained Breathing Apparatus
STEL	Short-Term Exposure Limit
TEEL	Temporary Emergency Exposure Limit
TIH	Toxic Inhalation Zone
TLV-C	Threshold Limit Value—Ceiling
TLV-TWA	Threshold Limit Value—Time-Weighted Average
UEL	Upper Explosive Limit
UFL	Upper Flammable Limit
WEEL	Workplace Environmental Exposure Limit

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Jill Meryl Levy owns her own business called Firebelle Productions. She is an author and publisher, specializing in books on hazardous materials and more effective writing. She also produces brochures, booklets, and newsletters for fire departments and industry. Jill is now expanding her horizons by studying to become a paralegal.

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## Other Books by Jill Meryl Levy

The First Responder's Field Guide to Hazmat & Terrorism Emergency Response

Hazardous Materials and WMDs: A Field Guide for Awareness Level Personnel

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