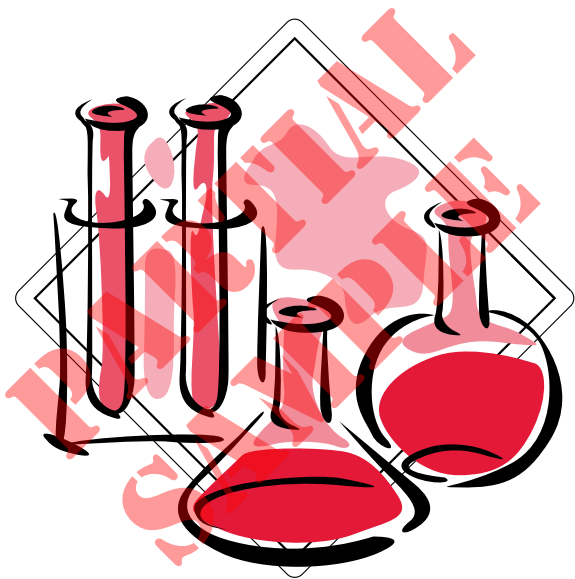


The Hazmat Chemistry Pocket Pal



Jill Meryl Levy
Firebelle Productions

Table of Contents

Ch.	Topic	Page
1	Terms and Definitions	7
2	Elements and Compounds	21
3	Chemical Bonding	37
4	Salts	45
5	Hydrocarbons	57
6	Hydrocarbon Derivatives	67
7	Toxicity and Risk	91
8	Comparing Three Primary Threats	107
9	Cheat Sheets	115
—	Acronyms and Abbreviations	125
—	Index	127
—	About the Author	133
—	Other Books by Jill Meryl Levy	134

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.

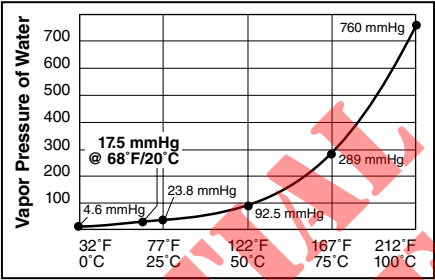
$$760 \text{ mmHg} = 14.7 \text{ psi} = 1 \text{ atm}$$

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.

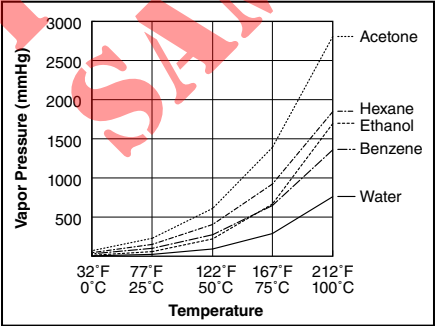
While there is no official dividing line between a “safe” vapor pressure and an “unsafe” vapor pressure, common sense tells us that a product whose vapor pressure is less than that of water probably isn’t going to “reach out and touch someone” who follows the basic principles of “isolate and deny entry.” 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:

<u>Gas</u>	<u>Vapor Density</u>
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

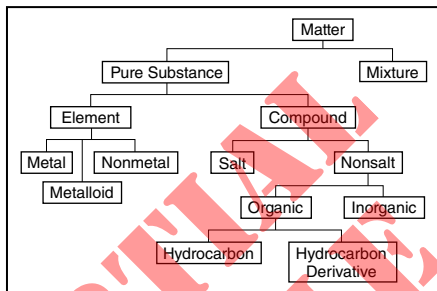
* Natural gas consists mostly of methane, with varying amounts of other gases and odorizers.

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

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_2O) 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 (CO_2), sodium cyanide (NaCN), calcium carbonate (CaCO_3), and carbon tetrachloride (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.

Symbol

1.008 H—

Hydrogen

Name

57	La	Lanthanum	58	Ce	Cerium	59	Pr	Praseodymium	60	Nd	Neodymium	61	Pm	Promethium	62	Sm	Samarium	63	Eu	Europium	64	Gd	Gadolinium	65	Tb	Terbium	66	Dy	Dysprosium	67	Ho	Holmium	68	Er	Erbium	69	Tm	Thulium	70	Yb	Ytterbium	71	Lu	Lutetium
89	Ac	Actinium	90	Th	Thorium	91	Pa	Protactinium	92	U	Uranium	93	Np	Neptunium	94	Pu	Plutonium	95	Am	Americium	96	Cm	Curium	97	Bk	Berkelium	98	Cf	Californium	99	Es	Einsteinium	100	Fm	Fermium	101	Md	Mendelevium	102	No	Nobelium	103	Lr	Lawrencium

Chemical Bonding

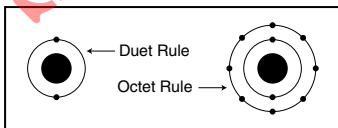
Why Elements Bond

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.)

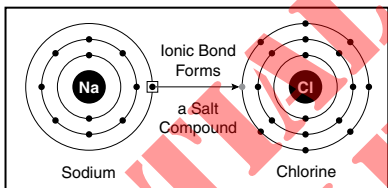
All elements other than the noble gases have outer shells that aren't filled with the maximum number of electrons, so they must bond with others to create a full outer shell.

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).

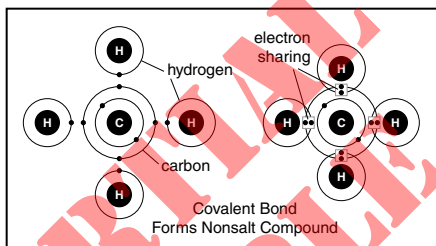


While the two elements are now stable, they're no longer electrically balanced. When the metal element donates electron(s), it's left with a net positive charge (protons outnumber electrons). Conversely, when the nonmetal element accepts electrons, it's left with a net negative charge (electrons outnumber 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

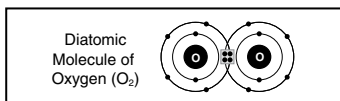
Oppositely charged ions attract each other, forming a strong bond that holds them together. Although there has been a transfer of electrons, the atoms involved cannot stray far because the ions can't exist by themselves. The union of a metal element and one or more nonmetal elements creates a **salt 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 (CH_4). (Hydrocarbons are covered in Chapter 5.)

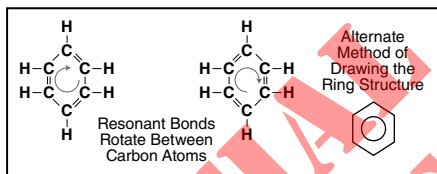


Covalent compounds are comprised of nonmetal elements only. Most of the ones hazmat technicians encounter consist solely of carbon, hydrogen, and oxygen in various combinations. The bulk of the covalent compounds that contain other elements are limited to nitrogen, phosphorus, sulfur, and the halogens (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 (O_2), hydrogen (H_2), nitrogen (N_2), fluorine (F_2), chlorine (Cl_2), bromine (Br_2), and iodine (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

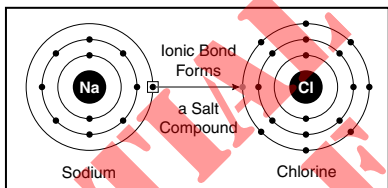
Now that you've seen the relation between outer shell electrons and chemical bonding, let's go back to the periodic table and to the four families of elements considered so important to your understanding of hazardous materials.

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

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 (NH_4Cl) and ammonium nitrate (NH_4NO_3). That's because the ammonium ion (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 ₂ O
hydroxide	sodium hydroxide	NaOH
peroxide	sodium peroxide	Na ₂ O ₂
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—NH₄). If so, it’s a salt. If not, it’s a nonsalt. (See also “Naming Similarities on page 89.)



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.

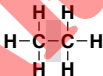
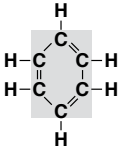
Hydrocarbon

alkane
alkene
alkyne
aromatic

Bond

single
double
triple
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)

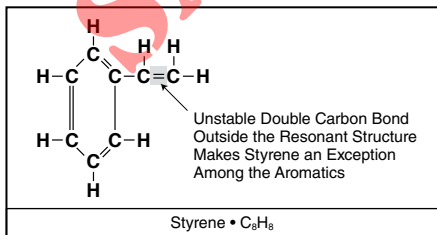
All hydrocarbons have common characteristics.

- 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_3H_8)	Propene (C_3H_6)

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	-ane	methane, ethane
alkene	-ene	ethene, propene *
alkyne	-yne	ethyne, propyne
aromatic	-ene	benzene, toluene

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

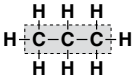
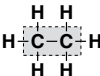
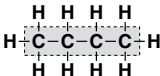


As with any other naming system, there are exceptions. For example, despite the *-ene* ending, acetylene (C_2H_2) is an alkyne with a highly unstable triple bond between carbon atoms. (Acetylene is also known as *ethyne*.)

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})

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*.

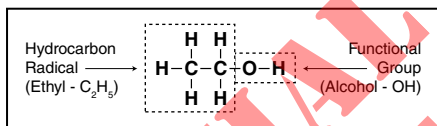
Hydrocarbon Radical	+	Functional Group	=	Hydrocarbon Derivative
$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}- \\ \\ \text{H} \end{array}$		$-\text{O}-\text{H}$		$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{O}-\text{H} \\ \\ \text{H} \end{array}$
Methyl (CH_3)		Hydroxyl (OH)		Methyl Alcohol (CH_3OH)
$\begin{array}{cc} \text{H} & \text{H} \\ & \\ \text{H}-\text{C} & -\text{C}- \\ & \\ \text{H} & \text{H} \end{array}$		$-\text{O}-\text{H}$		$\begin{array}{cc} \text{H} & \text{H} \\ & \\ \text{H}-\text{C} & -\text{C}-\text{O}-\text{H} \\ & \\ \text{H} & \text{H} \end{array}$
Ethyl (C_2H_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 (CH_3) comes from methane (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 (CH_4)	Methyl- (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 (C_2H_6)	Ethyl- (C_2H_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.

Original Hydrocarbon

Methane	CH_4
Methane	CH_4
Ethane	C_2H_6
Ethane	C_2H_6
Ethene	C_2H_4
Propane	C_3H_8
Propene	C_3H_6
Butane	C_4H_{10}
Benzene	C_6H_6

Hydrocarbon Radical

Methyl	CH_3-
Form-	$H(C)\equiv$
Ethyl	C_2H_5-
Acet-	$CH_3(C)\equiv$
Vinyl	C_2H_3-
Propyl	C_3H_7-
Allyl, Acryl	$C_2H_3(C)\equiv$
Butyl	C_4H_9-
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.)

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

$\text{R}-\text{S}-\text{H}$	$\text{R}-\text{P} \begin{array}{l} \diagup \\ \diagdown \end{array}$
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.

<u>Hydrocarbon Derivative</u>	<u>Functional Group</u>
ketones	CO
aldehydes	CHO
organic (carboxylic) acids	COOH
esters	COO or CO ₂
alcohols	OH
glycols	(OH) ₂
glycerols	(OH) ₃
ethers	O
organic peroxides	OO or O ₂
nitros	NO ₂
amines	NH ₂
nitriles (cyanides)	CN
carbarnates	NH ₂ COO
amides	CONH ₂
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 (CO) and carbon dioxide (CO_2). (The prefix *mono-* is rarely needed and is used only with the element oxygen.) Carbon tetrachloride (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 (CHCl_3), for instance, has three chlorine atoms joined to a hydrocarbon radical that started life as methane (CH_4). Conversely, dimethyl ketone (CH_3COCH_3) has two methyl radicals joined to a ketone (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 (NH_3) and water (H_2O).

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:

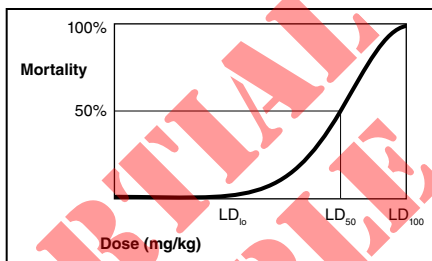
- **Carcinogens** cause cancer.
- **Mutagens** cause changes to the genetic material of cells (DNA and RNA) that can be inherited by offspring. The genetic changes can have numerous effects, including the failure of important biochemical processes. Some can also cause cancer.
- **Teratogens** cause malformations 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

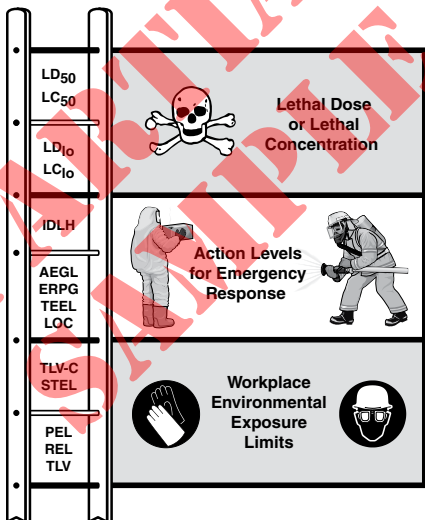
Toxicity is sometimes measured in **milligrams per cubic meter (mg/m³)**. There is no easy correlation between this and percent by volume or parts per million, because milligrams per cubic meter is based on the molecular weight of the material, which is different for every substance. However, it is possible 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 (mg/m^3) in air. It is independent of body weight.

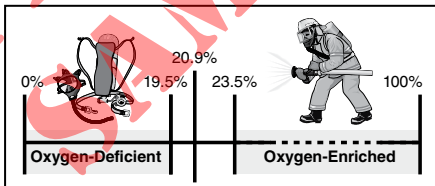
Comparing Three Primary Threats at a Hazmat Incident

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

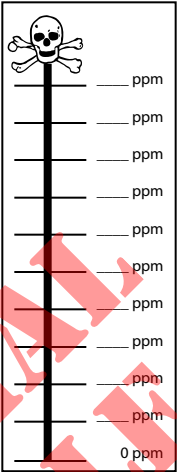
The chart below, repeated from Chapter 7, shows the relation between contaminant concentration and oxygen concentration. At the point where OSHA defines an atmosphere as being oxygen-deficient (19.5%), there can be as much as 70,000 ppm of a contaminant present. Many substances are deadly at far lower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

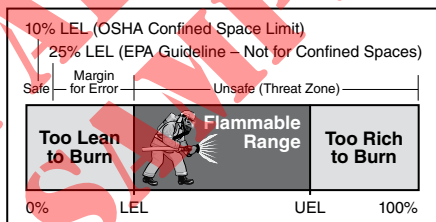


As with any tool, the trick is to make it work for you rather than twist yourself into knots trying to fit within the confines of the tool. If there isn't enough room on the hazard ladder to plot all of values identified in this chapter, don't worry about it. If your objective is emergency response, 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.

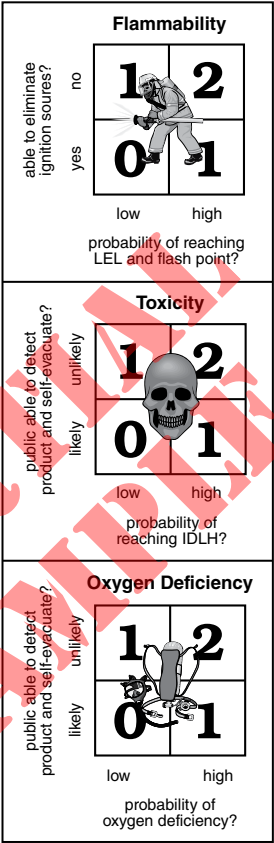
The **toxicity** hazard ladder below reflects IDLH (immediately dangerous to life and health), but it could be modified to reflect other values as needed.

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



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		Alkaline Earth Metals 2 • II		The Periodic Table of Elements																Halogens 17 • VII		Noble Gases 18 • VIII												
1 H Hydrogen	2 He Helium																			3 Li Lithium	4 Be Beryllium	5 B Boron	6 C Carbon	7 N Nitrogen	8 O Oxygen	9 F Fluorine	10 Ne Neon							
11 Na Sodium	12 Mg Magnesium	13 Al Aluminum	14 Si Silicon	15 P Phosphorus	16 S Sulfur	17 Cl Chlorine	18 Ar Argon	19 K Potassium	20 Ca Calcium	21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton									
37 Rb Rubidium	38 Sr Strontium	39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon	55 Cs Cesium	56 Ba Barium	57 La Lanthanum	58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium	61 Pm Promethium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolinium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu Lutetium
87 Fr Francium	88 Ra Radium	89 Ac Actinium	90 Th Thorium	91 Pa Protactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lr Lawrencium	104 Rf Rutherfordium	105 Db Dubnium	106 Sg Seaborgium	107 Bh Bohrium	108 Hs Hassium	109 Mt Meitnerium	110 Ds Darmstadtium	111 Rg Roentgenium	112 Cn Copernicium	113 Nh Nihonium	114 Fl Flerovium	115 Mc Moscovium	116 Lv Livermorium	117 Ts Tennessine	118 Og Oganesson			

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

alkane
alkene
alkyne
aromatic

Bond

single
double
triple
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	CH_4	Methyl	CH_3-
Methane	CH_4	Form-	$\text{H}(\text{C})\equiv$
Ethane	C_2H_6	Ethyl	C_2H_5-
Ethane	C_2H_6	Acet-	$\text{CH}_3(\text{C})\equiv$
Ethene	C_2H_4	Vinyl	C_2H_3-
Propane	C_3H_8	Propyl	C_3H_7-
Propene	C_3H_6	Allyl, Acryl	$\text{C}_2\text{H}_3(\text{C})\equiv$
Butane	C_4H_{10}	Butyl	C_4H_9-
Benzene	C_6H_6	Phenyl, Benzyl	C_6H_5-

Hydrocarbon Derivatives

<u>Hydrocarbon Derivative</u>	<u>Functional Group</u>
ketones	CO
aldehydes	CHO
organic (carboxylic) acids	COOH
esters	COO or CO_2
alcohols	OH
glycols	$(\text{OH})_2$
glycerols	$(\text{OH})_3$
ethers	O
organic peroxides	OO or O_2
nitros	NO_2
amines	NH_2
nitriles (cyanides)	CN
carbarnates	NH_2COO
amides	CONH_2
thiols (mercaptans)	SH
alkyl halides *	F, Cl, Br, or I
organophosphates	P
hi-tech compounds	$\text{B, Si, As, Be, Sn, or Ti}$

* 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%
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Index

- Abbreviations 125–126
- Acids 105–106
- Acronyms 125–126
- Action levels for emergency response 98–99
- Acute exposure guideline levels (AEGs) 95–96, 100
- Air reactivity 19
- Alcohols 69, 71, 77–78
- Aldehydes 69, 71, 73, 74–75
- Alkaline earth metals 27, 28, 41
- Alkali metals 27–28, 41
- Alkanes 57–61
- Alkenes 57–61
- Alkyl halides (halogenated hydrocarbons) 70–71, 86–88
- Alkynes 57–61
- Amides 70–71, 85
- Amines 70–71, 83–84
- Aromatic hydrocarbons 40, 57–61
- Atomic structure 32–35
- Atomic weight 33
- Bases 105–106
- Base state of oxyradicals 52–53
- Binary salts 49–50
- Boiling point 7, 17, 18
- Branched hydrocarbons 62
- Carbamates 70–71, 84–85
- Carbonyls 69, 73–77
- Catalysts 20
- Ceiling exposure limit (TLV-C) 95–96, 103
- Chemical bonding 37–44
 - Relation to four families of elements 40–41
 - Types of bonds 38–40
 - Why elements bond 37
- Chemical formulas and illustrations 42
- Chemical incompatibility 19
- Chemical name and formula recognition 120–121

Chemical reaction 18–19
Combustible liquids 14
Comparing three primary threats 107–114
Confined space atmospheres 13, 111
Contaminant concentration 94, 109, 119
Contamination versus exposure 93–94
Corrosives / corrosivity 105–106
Covalent bonds 39, 40
Crisscross rule 48–49
Cyanides (nitriles) 70–71, 84
Cyclo compounds 62
Decision matrix 113–114
Diatomic molecule 39
Dieter's top 13 nonmetals and metals 30–32
Dose-response curve 93
Effect of molecular size 63–65, 117
Electrical charge of electrons 33–34
Electrons 33–35
Element form 32
Elements and compounds 21–35
Emergency response planning guidelines (ERPGs) 95–96, 100, 101
Esters 69, 71, 73, 76–77
Ethers 69, 71, 79–80
Exothermic 19
Exposure limits and toxicity values
 Action levels for emergency response 98–99
 Lethal levels 96–98
 Protective action criteria 100–101
 Workplace environmental exposure limits 102–104
Exposure versus contamination 93–94
Fire point 11
Flammability 10–14, 111–114
Flammable (explosive) range 12–13, 111
Flammable (inflammable) 14
Flammable liquids 14
Flash point 10–11, 14, 64–65, 111
Floater 15

Functional group 67–68, 71
Glycerols 69, 71, 78
Glycols 69, 71, 78
Halogenated hydrocarbons (alkyl halides) 70–71, 86–88
Halogens 27, 29, 41
Hazard zones 104
Health effects 91–92
Hi-tech compounds 70–71, 88–89
Hydrocarbon derivatives 24, 67–89, 118
 Defined 67–68
 Naming similarities with salts 89
 Overview 69–72
 Part 1 - carbonyls 69, 73–77
 Part 1 - other 69, 77–82
 Part 2 - nitrogen-based 70, 82–85
 Part 2 - Other 70, 86–89
Hydrocarbon radicals 67–68, 118
Hydrocarbons 24, 57–65
 Effect of molecular size 63–65, 117
 Four types of hydrocarbons 57–59, 116–117
 Names and formulas 59–63, 117
Ignition temperature 11–12, 64–65
Immediately dangerous to life and health (IDLH) 95–96, 98–99, 112–113
Incompatible chemicals 19
Inflammable (flammable) 14
Inhibitors 20
Inorganic compounds 23
Ionic bonds 38, 40, 45
Isomers 43–44
Isotopes 34
Ketones 69, 71, 73, 74
Lethal concentration (LC) 95–98
Lethal dose (LD) 95–98
Lethal levels 96–98
Level of concern (LOC) 95–96, 99
Lower explosive limit (LEL) 12–13, 99, 111, 112–113

Matter 21–24
Maximum safe storage temperature (MSST) 82
Mercaptans (thiols) 70–71, 86
Metal cyanide salts 50–51
Metal hydroxide salts 51
Metalloids 23
Metal oxide salts 50
Metal oxysalts 52–55
Metal peroxide salts 51–52
Metals 22–23, 26–28, 31–32
Miscibility 15–16
Mixture 21
Molecular formula 42
Molecular weight 10
Multiple double bonds 63
Nitriles (cyanides) 70–71, 84
Nitros 70–71, 82–83
Noble gases 27, 29, 41
Nonmetals 22–23, 26, 30–31
Nonsalts 23, 39
Odor threshold 104
Organic (carboxylic) acids 69, 71, 76
Organic compounds 23–24, 73
Organic peroxides 69, 71, 80–82
Organophosphates 70–71, 88
Oxidation state 55
Oxygen-deficient atmospheres 107–108, 112–114
Oxygen-enriched atmospheres 107–108
Oxyradicals 52–54
Periodic table of elements 24–27, 115
Permissible exposure limits (PEL) 95–96, 102
Pesticide signal words 105
pH scale 105–106
Physical reaction 17–18
Poison inhalation zone (PIH) 104
Polarity 16
Polyatomic ions 48–49, 53–54
Polymerization 20
Protective action criteria 100–101

Pure substance 21–22
Pyrophoric 19
Rare earth elements 26
Recommended exposure limits (REL) 95–96, 102
Relative hazard ladder 95
Representative elements 26
Resonant bonds 40, 57–58
Routes of entry 91
Salts 23, 38, 45–55
 Names and formulas introduction 46–49
 Naming similarities with hydrocarbon derivatives 89
 Overview 45–46, 116
 Types of salts 49–55
Saturated hydrocarbons 59
Self-accelerating decomposition temperatures (SADT) 82
Semimetals 23
Short-term exposure limit (STEL) 95–96, 103
Signal words 105
Sinkers 15
Solubility 15–17
Specific gravity 15
Spill estimation chart 122–124
Spontaneous ignition 12
Straight-chain hydrocarbons 61
Structural formula 42
Swimmer 15
Temporary emergency exposure limits (TEEL) 95–96, 100, 101
Terms and definitions 7–20
Thiols (mercaptans) 70–71, 86
Threshold limit value-ceiling (TLV-C) 95–96
Threshold limit value–time-weighted average (TLV-TWA) 95–96, 99, 103
Toxic inhalation zone (TIH) 104
Toxicity and risk 91–106, 109–110, 112–114
 Factors affecting risk 92–93
Toxicity terminology 94–104

Transition metals 26
Unsaturated hydrocarbons 59
Upper explosive limit (UEL) 12–13, 111
Vapor density 9–10
Vapor pressure 7–9
Viscosity 18
Volatility 9
Water reactivity 19
Workplace environmental exposure limits (WEEL)
102–104

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