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The Hazmat Chemistry Mini Review

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ISBN: 978-0-9651516-7-2 Library of Congress Control Number: 2005909317 Printed in the United States of America Second Printing

Important Message to My Readers

This book contains a very 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.

Acknowledgments

The following people provided valuable input for my *Hozmat Chemistry Study Guide*, which was the basis for this book: Dieter Heinz, Brian Heinz, Kevin Smith, Chris Waters, Robert Delaney, Todd Spellman, Richard C. Dufek, and Bryan Callowhill.

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.

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Dedication

To Robert Charles Innis, who sparked my imagination in junior high school and inspired in me a passion for writing. Little did we know we'd be soulmates later in life.



6



Terms and Definitions \bullet 7

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 whether vapors can "get to us."

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.

8 • Terms and Definitions

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).

760 mmHg = 14.7 psi = 1 atm

If the vapor pressure of a substance equals or exceeds 760 mmHg at sea level, the product is a gas in its normal state.



Terms and Definitions • 9

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).

10 • Terms and Definitions



Terms and Definitions • 11

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.



12 • Terms and Definitions

July a handful of		
	Gas	Vapor Density
chan air, and	Hydrogen	0.07
	Helium	0.138
nany of those	Natural Gas	0.550
the density of air	Methane	0.553
the difference	Ammonia	0.589
s negligible to	Hydrogen Fluoride	0.690
the emergener	Neon	0.696
responder	Acetylene	0.898
	Hydrogen Cyanide	0.932
	Diborane	0.954
	Nitrogen	0.966
	Ethylene	0.967
	Carbon Monoxide	0.967
-		

Terms and Definitions • 13

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. Atomic weight of each element is indicated on the periodic table of elements. (This will be explained in Chapter 2.)

14 • Terms and Definitions

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

- Because **temperature** affects vapor pressure, it affects the rate at which gases and vapors dispersed
- **Moisture** in the atmosphere can be absorbed by gases and vapors, causing them to be less buoyant.
- Lower **atmospheric pressures** at higher elevations will allow gases and vapors to disperse more readily.

Terms and Definitions • 15

- 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 will disperse more readily than higher concentrations.

16 • Terms and Definitions

Flash point is the minimum temperature at which a liquid produces enough vapor to form an ignitable mixture in air. (*Fire point*—where vapors will support combustion—is only a few degrees higher.) Flash point is generally considered the most important property in assessing flammable liquids. **The lower the flash point, the greater the hazard**.



Terms and Definitions • 17

Ignition (autoignition) temperature is the minimum temperature required to cause self-sustained combustion, independent of an ignition source. Put more simply, it's the minimum temperature to which a material must Cigarette be exposed before it will 975°F / 523.9°C ignite. The lower the ignition Ignition Temperature of Gasoline temperature, the 853°F / 456.1°C greater the risk of ignition.

18 • Terms and Definitions

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. Oily rags left lying in a pile are a fire hazard.



Terms and Definitions • 19

Boiling point 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. It is **the point of maximum vapor production**.



The lower the boiling point, the greater the hazard potential.

20 • Terms and Definitions

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

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

The wider the flammable range, the greater the span at which ignition is possible and the greater the risk.



Terms and Definitions • 21

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.



22 • Terms and Definitions

The terms *miscibility* and *solubility* are often used interchangeably. **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** or **soluble** (watersoluble), while those that don't are called **immiscible** or **insoluble**.

Terms and Definitions • 23

Specific gravity is the weight of a liquid compared to an equal volume of water.

An immiscible substance with a specific gravity less than one (<1) will float on water. It is a **floater**. 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**.



24 • Terms and Definitions

Polarity 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**.



Terms and Definitions • 25

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.

26 • Terms and Definitions

0

0



Terms and Definitions • 27

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*.

28 • Terms and Definitions

• **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 very rare reaction associated with nuclear blasts.

Terms and Definitions • 29

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.

30 • Terms and Definitions

Polymerization is a chemical reaction in which small compounds (monomers) react with themselves to form larger molecules (polymers).



Terms and Definitions • 31

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.



32 • Terms and Definitions

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.

Terms and Definitions • 33



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.

34 • Terms and Definitions


Elements and Compounds • 35

Matter can be organized as illustrated below.



36 • Elements and Compounds

A **pure substance** is a homogenous one—one in which 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.

Elements and Compounds • 37

A pure substance can be either a single **element** or a **compound** (molecule) comprised of two or more elements chemically bonded. Elements are represented by a single capital letter or by a capital letter followed by a lowercase letter. Compounds are represented by formulas showing multiple elements.



38 • Elements and Compounds

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). **Nonmetals** generally are not lustrous, are not good conductors, and are neither malleable nor ductile. **Metalloids** tend to have properties of each. (Metalloids are beyond the scope of this book.)



Elements and Compounds • 39

Metals and nonmetals are identified on the periodic table of elements (to be explained shortly). Metalloids are the elements immediately surrounding the dividing line between metals and nonmetals.



40 • Elements and Compounds

Compounds are further divided into salts and nonsalts. Most **salt compounds** are comprised of a metal element bonded to one or more nonmetal elements. **Nonsalt compounds** are comprised solely of nonmetal elements.



Elements and Compounds • 41

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.



 $42 \bullet$ Elements and Compounds

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.



Elements and Compounds • 43

The periodic table of elements displays elements according to their atomic structure. They're divided into metals and nonmetals (as illustrated on page 40). The vertical columns reflect the number of outer shell electrons (explained later), whereas the horizontal rows reflect weight and size. 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.

The periodic table on the next page shows each element by name, symbol, atomic number, and atomic weight.



44 • Elements and Compounds



Elements and Compounds • 45

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**.



46 • Elements and Compounds

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 outer shell electrons. This will be explained in the next chapter.



Elements and Compounds • 47

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.

48 • Elements and Compounds

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.



50 • Elements and Compounds

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*.



Elements and Compounds • 51

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.



52 • Elements and Compounds

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).

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.



Elements and Compounds • 53

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.)



54 • Elements and Compounds

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 and Compounds • 55

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 ... which leads us to Chapter 3.



56 • Elements and Compounds



Chemical Bonding • 57

All elements other than the noble gases (Group VIII on the periodic table) 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**.



58 • Chemical Bonding

Ionic bonds are formed from the **transfer of electrons** from a metal element to a nonmetal element. The result is a **salt compound**. Salts are covered in Chapter 4.



Metal elements donate electrons from their outermost shells, 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.

Chemical Bonding • 59

Covalent bonds are formed between two or more nonmetal elements that **share electrons**. Their outermost shells overlap so that electrons seem to belong to each atom at the same time. The result is a **nonsalt compound**.



60 • Chemical Bonding

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 Molecule of Oxygen (O₂)

Other diatomic molecules include hydrogen (H_2), nitrogen (N_2), fluorine (F_2), chlorine (Cl_2), bromine (Br_2), and iodine (I_2).

Chemical Bonding • 61

In **resonant bonds**, the electrons rotate very rapidly between the carbon atoms.



Compounds with resonant bonds are aromatic hydrocarbons, like benzene (above). These are also nonsalt compounds. Hydrocarbons are covered in Chapter 5.

62 • Chemical Bonding

The chart below summarizes the three types of bonds.

Bond	Composition	Electron Action	Result
lonic	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. Some compounds can release a tremendous amount of energy (in the form of heat and light) when their bonds are broken. This is one of the dangers we may face at a hazmat incident.

Chemical Bonding • 63

Let's now look at the relation between outer shell electrons, chemical bonding, and the behavior of the four families highlighted on the periodic table below. The number of outer shell electrons is indicated by the Roman numeral group numbers at the top of each column. Because the number of electrons in the outermost shell is the characteristic that

most influences chemical bonding (chemical reactivity), each element in the same family will behave similarly



64 • Chemical Bonding

Group I - Alkali metals are highly reactive. Elements with just one electron on the outer shell are so close to the ideal (stable) condition of having a filled outer shell that they'll react vigorously to donate that one outer shell electron.

When in contact with water, alkali metals produce flammable hydrogen gas, a strong caustic runoff, and excessive heat. These elements are also flammable. Sodium and potassium, the most common alkali metals, will ignite spontaneously if exposed to moist air. Sodium will even ignite on contact with dry air.



Chemical Bonding • 65

Group II - Alkaline earth metals are fairly reactive, but less so than the 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" to bond with others.

These elements are flammable and often water-reactive Magnesium, a common example of an alkaline earth metal, is very water-reactive when burning. It will rip apart the water molecules to get at oxygen atoms, causing great danger to anyone nearby.



66 • Chemical Bonding

Group VII - Halogens are also one electron away from having a filled outer shell, so they're highly reactive too. They'll readily grab one more electron from a metal element to form an ionic bond or share electrons with a nonmetal element to form a covalent bond.

Halogens are nonflammable, but they are powerful oxidizers that will support combustion. 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.



Chemical Bonding • 67

Group VIII - Noble gases have filled outer shells already. They have no reason to react (bond) with other elements. They are inert.

Inert doesn't mean harmless, however. These gases are simple asphyxiants often stored or transported as cryogenic liquids, making them also a thermal hazard with high expansion ratios. (Expansion ratio is the comparison between the volume of a product in a gaseous state versus in a compressed or liquefied state.)



68 • Chemical Bonding

Dash style illustrations are used in this book to represent the **structural formulas** of compounds.

Chemical formulas can take many forms. Ethyl alcohol (right) is most commonly written as C_2H_5OH . Its **condensed structural formula** (CH₃CH₂OH) identifies more precisely how the atoms are arranged, whereas the **molecular formula** (C₂H₆O) identifies only



how many atoms of each element are present. Molecular formulas don't help distinguish between multiple compounds with the same ratio of elements, for example, ethyl alcohol (C_2H_5OH) and dimethyl ether (CH_3OCH_3).

Chemical Bonding • 69

Some products can have the same molecular *formula* but different molecular *structures*. These products are known as **isomers** of each other.



Despite having the same formulas, isomers can have measurably different characteristics and hazards.

70 • Chemical Bonding


Salts • 71

Most **salt compounds** are formed through an ionic bond between a metal element and one or more nonmetal elements, just like the familiar table salt (sodium chloride).



72 • Salts

Notable Exceptions

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.

Salts • 73

Characteristics common to most salts:

- 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 cause severe environmental damage.



74 • Salts

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*).

Salt	Composition	Naming	Example
Binary Salt	metal + nonmetal (not otherwise listed below)	metal + nonmetal root (ends in "ide")	CaC ₂ calcium carbide
Metal Cyanide	metal + cyanide	metal + "cyanide"	KCN potassium cyanide
Metal Oxide (Binary Oxide)	metal + oxygen	metal + "oxide"	Na₂O sodium oxide
Metal Hydroxide	metal + hydroxide	metal + "hydroxide" (or alkali, caustic, or base)	NaOH sodium hydroxide
Metal Peroxide	metal (Group For II) + peroxide	metal + "peroxide"	Na ₂ O ₂ sodium peroxide
Metal Oxysalt	metal + element + oxygen	metal + oxyradical (ends in "ate" or "ite") (may include prefix "per" or "hypo")	NaNO ₃ sodium nitrate

Salts • 75

The **IUPAC** (International Union of Pure and Applied Chemists) **naming system** identifies salts according to the elements that comprise them, starting with the metal element and ending with the nonmetal element(s).

Again, five types of salts have names ending in *-ide*. Oxysalts 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_4). If so, it's a salt. If not, it's a



76 • Salts

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



The toxicity can vary from nontoxic (e.g., sodium chloride) to very toxic (e.g., sodium fluoride). The worst binary salts are water-reactive (e.g., 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.

Salts • 77

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



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. Metal oxides don't release a gas in contact with water. They are not oxidizers. Many are toxic.

78 • Salts

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

Examples of Metal Cyanide Salts Sodium Cyanide - NaCN Potassium Cyanide - KCN

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

Salts • 79

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

Examples of Metal Hydroxide Salts

Sodium Hydroxide (Caustic Soda, Lye) – NaOH Potassium Hydroxide (Caustic Potash, Potash Lye) – KOH Calcium Hydroxide (Caustic Lime, Slaked Lime) – Ca(OH)₂

The worst of the metal hydroxides are caustic (corrosive). Those made with alkali (Group I) metals are some of the most destructive chemicals. 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. The chart above includes some other very common names for these salts.

80 • Salts

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



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.

Salts • 81

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 (NaMnO₄) and potassium permanganate (KMnO₄) are examples of oxysalts with two metal elements.





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 (which is explained further on the next page).



Salts • 83

The two nonmetal elements in an oxysalt form an **oxyradical**. (Oxyradicals are also referred to as *polyatomic ions* or *complex ions*). The normal (most stable) state of an oxyradical is its **base state**. (For the oxyradical consisting of chlorine and oxygen, shown below, it is CIO_3 .) The addition or subtraction of oxygen atoms is reflected in the changing names of oxysalts.

Oxygen Content	Naming	Oxyradical	Example	Formula
1 extra atom	"perate"	Perchlorate	Sodium Perchlorate	NaClO ₄
base state	"ate"	Chlorate	Sodium Chlorate	NaClO ₃
1 less atom	"ite"	Chlorite	Sodium Chlorite	NaClO ₂
2 less atoms	"hypo ite"	Hypochlorite	Sodium Hypochlorite	NaClO

84 • Salts

The chart below shows the **base states** (most stable configurations) **of various oxyradicals**.



With **binary salts** and **oxide salts**, determining the ratio of metal and nonmetal elements is straightforward. When a metal element donates electrons, it becomes an ion with positive charge (protons outnumber electrons). When a nonmetal element accepts electrons, it becomes an ion with a negative charge (electrons outnumber protons). Ions must be paired in a ratio that results in an electrically neutral compound. The crisscross rule (illustrated below) is a technique for easily determining ratios. (Remember,

the number of electrons that elements can donate or accept is based on fulfilling the octet rule.)



86 • Salts

Peroxide salts, **cyanide salts**, and **hydroxide salts** contain polyatomic ions (complex ions) in which two or more atoms bonded together act as a single unit. The peroxide (O_2) radical has a charge of 2-. The cyanide (CN) and hydroxide (OH) radicals each have a charge of 1-. They pair with metal elements in ratios based on those charges.



Salts • 87

The **polyatomic ions in oxysalts** also have specific charges associated with them. Listed below are some examples.





Notable Exceptions

Most polyatomic ions have negative charges. However, the ammonium ion (NH_4^{\dagger}) 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 (NH_4CI) and ammonium nitrate (Na_4NO_3) , that don't contain a metal element.

Salts • 89

Many of the transition metals have more than one **oxidation state**; they can donate different numbers of electrons. For example, iron (Fe) can form either *ferrous* chloride (FeCl₂) or *ferric* chloride (FeCl₃). Below are examples of other ions with multiple oxidation states.

Element	Ion Name	Element
Chromium	Chromium (II) or Chromous	Cr ²⁺
	Chromium (III) or Chromic	Cr ³⁺
Manganese	Manganese (II) or Manganous	Mn ²⁺
	Manganese (III) or Manganic	Mn ³⁺
Copper	Copper (I) or Cuprous	Cu⁺
	Copper (II) or Cupric	Cu ²⁺
Mercury	Mercury (I) or Mercurous	Hg⁺
	Mercury (II) or Mercuric	Hg ²⁺

90 • Salts



Hydrocarbons • 91

The **four main types of hydrocarbons** (alkanes, alkenes, alkynes, and aromatics) are distinguished by the bonds between the carbon atoms.



92 • Hydrocarbons

All hydrocarbons have some common characteristics.



Hydrocarbons • 93

Additional characteristics are determined by the type of bond between carbon atoms. Single and resonant bonds are stable. Double and triple bonds are not.



94 • Hydrocarbons

Notable Exceptions



Styrene (C_gH_g) differs from other aromatic hydrocarbons in that it **has an unstable double carbon bond outside the resonant structure**. That makes it prone to polymerization.

Hydrocarbons • 95

Saturated hydrocarbons have every available bonding site filled with hydrogen. **Unsaturated hydrocarbons** do not. Only the alkanes, with single bonds between carbon atoms, can be saturated with hydrogen.



96 • Hydrocarbons

Common naming schemes help us identify hydrocarbons. The *-ane* ending signifies an **alkane**, and the *-yne* ending signifies an **alkyne**. The *-ene* ending may indicate either an **alkene** or an **aromatic**, so it's necessary to look at the prefixes to distinguish between the two types.



Hydrocarbons • 97



98 • Hydrocarbons



Hydrocarbons • 99



100 • Hydrocarbons

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



Hydrocarbons • 101

Hydrocarbons can also be recognized by formula. They contain only carbon and hydrogen, and 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.



pattern of other aromatics.

102 • Hydrocarbons

Straight-chain hydrocarbons have all the carbon atoms arranged in a row; **branched hydrocarbons** do not. The three compounds below are isomers of one another (same molecular formula, different molecular structure).



Hydrocarbons • 103

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 do their straight-chain cousins.



104 • Hydrocarbons

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



Hydrocarbons • 105

Molecular size affects physical and chemical properties,

many of which are directly or indirectly proportional to one another. The following are examples.



This assumes 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 does molecular size.

106 • Hydrocarbons
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.



Hydrocarbons • 107

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* Larger Molecules together in relation to each Ignition Temperature ŧ other. Larger compounds will Vapor Concentration **Boiling Point** Vapor Pressure output more heat because Flash Point they have more fuel. Heat Output

108 • Hydrocarbons

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.



Hydrocarbons • 109



110



Hydrocarbon Derivatives • 111

Hydrocarbon derivatives (next page) are comprised of one or more hydrocarbon radicals attached to a functional group. A **hydrocarbon radical** (below) is a hydrocarbon

molecule in which one or more hydrogen atoms have been removed. Hydrocarbon radicals cannot exist by themselves because they are not electrically balanced. The missing hydrogen atoms must be replaced by something else.



112 • Hydrocarbon Derivatives



Hydrocarbon Derivatives • 113

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



The **functional group** tells us the **category** (type) of hydrocarbon derivative. The **hydrocarbon radical** tells us the **specific compound**.

The OH functional group in the illustration (right) makes the compound an alcohol. The C_2H_5 hydrocarbon radical makes it ethyl alcohol (as opposed to methyl alcohol, propyl alcohol, etc.).



Hydrocarbon Derivatives • 115



116 • Hydrocarbon Derivatives



Hydrocarbon Derivatives • 117

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.



118 • Hydrocarbon Derivatives

The chart below shows various **hydrocarbon radicals** and the hydrocarbon compounds from which they come.



Hydrocarbon Derivatives • 119

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.



120 • Hydrocarbon Derivatives

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



Hydrocarbon Derivatives • 121

Aldehydes have the functional group **CHO**. They have names ending in aldehyde or -al. Aldehydes are watersoluble compounds frequently used as preservatives. They are toxic and flammable, exhibiting a yellow flame with a blue base when burning. Some have wide flammable ranges (e.g., formaldehyde at 7% to 73% and acetaldehyde at 4% to 60%). Some н aldehydes can eventually H-C form unstable, explosive H-C-H organic peroxides when exposed to air. Aldehydes are noted for their choking, Acetaldehyde Formaldehyde (Ethanal) suffocating odors. (Methanal) **HCHO** CH₂CHO

122 • Hydrocarbon Derivatives

Notable Exceptions

Most aldehydes are liquids. (However, **formaldehyde** (previous page) is a gas in its natural state.



It's usually dissolved in water (commonly called formalin in solution).

The aldehyde propenal is more commonly called **acrolein** (left). The double bond between carbon atoms makes this unstable compound subject to polymerization.

Hydrocarbon Derivatives • 123

Organic (carboxylic) acids have the functional group **COOH**. Their names end in *-ic acid* or *-oic acid*. Organic acids are toxic and corrosive. They are combustible burning with a blue and yellow flame and clean smoke. They are water-soluble.



124 • Hydrocarbon Derivatives

Esters have the functional group **COO** (or CO_2). They have names ending in *-ate* (often *acetate* or *acrylate*). Esters are flammable, exhibiting a yellow flame with a blue base when burning. Those with a double bond between carbon atoms, such as methyl acetate (below right), are subject to polymerization. Esters are described as being "slightly soluble."



Hydrocarbon Derivatives • 125

Alcohols have the functional group **OH**. Their names end in *alcohol* or *-ol*. 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.



126 • Hydrocarbon Derivatives

Glycols are part of the larger alcohol family, but have **two OH groups** instead of one. Glycols are toxic and combustible. Most are highly soluble in water and are relatively nonvolatile.



Hydrocarbon Derivatives • 127

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.



128 • Hydrocarbon Derivatives

Ethers have the functional group **O**. Most have names ending in *ether*, but some names end in *oxide*. Ethers are very volatile. They are flammable. Many have flash points below 0°F (17.8°C), and some have relatively wide flammable ranges. Ethers burn with invisible flames. They are insoluble floaters. Many have anesthetic properties. Ethers with double bonds between carbon atoms are unstable compounds subject to polymerization.



Hydrocarbon Derivatives • 129

Ethers have limited shelf lives; they **form explosive organic peroxides** over time, particularly when exposed to air. For example, methyl ethyl ether $(CH_3OC_2H_5)$ bonds with oxygen in the atmosphere to become methyl ethyl peroxide $(CH_3OOC_2H_5)$. Crystals developing on the container indicate extreme danger.



130 • Hydrocarbon Derivatives

Notable Exceptions

Ethylene oxide is unique in name and appearance, but its structure (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 (fuel and oxidizer in the same compound) allows ethylene oxide to burn inside its own container with no air present. It's also subject to polymerization.

Hydrocarbon Derivatives • 131

Organic peroxides have the functional group **OO** (or O_2). They normally have *peroxide* or *peroxy* in the name. Organic peroxides are extremely unstable. They are very sensitive to heat and friction and are prone to runaway polymerization if overheated. Many are also very sensitive to contamination. They're both flammable and oxidizing and are highly reactive with other chemicals. Many are toxic. Some are corrosive. They are insoluble floaters.



132 • Hydrocarbon Derivatives

Although organic peroxides are not explosive, per se—they are DOT Class 5.2—they are **similar to explosives** in that they contain a fuel component and an oxidizer component in the same formula. Their instability is a much greater concern than their oxidizing ability.



Hydrocarbon Derivatives • 133

Notable Exceptions

Many organic peroxides have names that are complex and difficult to pronounce. Not all have names containing *peroxide* or *peroxy*. Some have names with a *per*- prefix and an *-ate* ending (e.g., isopropyl percarbonate). Some 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.

134 • Hydrocarbon Derivatives



Hydrocarbon Derivatives • 135

The simplest **amines** are those containing the functional group \mathbf{NH}_2 bonded to a single hydrocarbon radical. Amines are often called ammonia derivatives, since the functional group begins as ammonia (\mathbf{NH}_3). The ammonia base and hydrocarbon radicals both 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.



136 • Hydrocarbon Derivatives

Secondary and tertiary amines can be created by substituting additional hydrocarbon radicals for hydrogen atoms.



Hydrocarbon Derivatives • 137

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*. The cyanide group makes these hydrocarbon derivatives toxic. 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.



138 • Hydrocarbon Derivatives

Carbamates have the functional group **NH**₂**COO**, but hydrogen atoms normally attached to the nitrogen atom can be replaced by additional hydrocarbon radicals, as in carbaryl (below right). These compounds often have names starting with the prefix carba-. Carbamates are used as pesticides, often in place of the more toxic organophosphate

compounds. Nevertheless. carbamates are still toxic and combustible



Hydrocarbon Derivatives • 139

Amides have the functional group **CONH**₂, but hydrogen atoms normally attached to the nitrogen atom can be replaced by additional hydrocarbon radicals (not shown). 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.



140 • Hydrocarbon Derivatives

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).



Hydrocarbon Derivatives • 141

Alkyl halides (halogenated hydrocarbons) have no specific functional group. Rather, what they have in common is the use of one or more **halogens** in place of hydrogen atoms. The most common are the chlorinated hydrocarbons. The six shown on these two facing pages are based on methane.



142 • Hydrocarbon Derivatives
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, giving off toxic decomposition products. Alkyl halides are insoluble sinkers.



Hydrocarbon Derivatives • 143

Not all alkyl halides are based on methane. For example, chloroethane (below left) is based on ethane (C_2H_0) and trichloroethylene (below right) is based on ethene (C_2H_0).



144 • Hydrocarbon Derivatives



Hydrocarbon Derivatives • 145

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



146 • Hydrocarbon Derivatives

The following salts and hydrocarbon derivatives share some **naming similarities**, evident in the name endings

Salts	Hydrocarbon Derivatives
Cyanide Salts	Cyanides (Nitriles)
Oxide Salts	Ethers with "Oxide" Names
Peroxide Salts	Organic Peroxides
Binary Salts (-ide endings)	Some Alkyl Halides and Amides (-ide endings)
Oxysalts (-ate endings)	Esters and Some Organic Peroxides (-ate 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).

Hydrocarbon Derivatives • 147

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.



148 • Hydrocarbon Derivatives



Fire Chemistry and Chemical Reactions • 149

We often use the **fire triangle** to identify the components necessary for fire to occur. However, the fire triangle fails to reflect the way products produced in the combustion process further propagate the fire.

The **fire tetrahedron** starts with the same three elements: a *reducing agent* (fuel), an *oxidizing agent* (oxygen or other oxidizer), and *temperature* (heat). The fourth element, the **chemical chain reaction**, is a complex process in which fuels are broken down by the heat of the fire. The free radicals formed from their components combine with other free radicals to form new compounds (products of combustion), many of which will also burn.

150 • Fire Chemistry and Chemical Reactions

The simple example of methane burning illustrates how combustion by-products can further propagate a fire. Methane (CH₄) breaks down to yield free radicals, such as methyl (CH_a) and atomic hydrogen (H), that are not electrically balanced and must combine with something else. Oxygen from the atmosphere is also broken down in the process, yielding free radicals (O) of its own. Ultimately, all of these free radicals combine to form the more stable compounds of diatomic hydrogen (H_a), carbon monoxide (CO), carbon dioxide (CO₃), and water (H_2O). The first two are flammable and will continue to burn in the presence of sufficient oxygen.

Introduction of Oxygen (0_{2})

Fire Chemistry and Chemical Reactions • 151

Products of combustion vary, depending on the fuel. Carbon dioxide (CO₂) and carbon monoxide (CO) are usually produced in large quantities at any fire. Carbon dioxide is a product of **complete combustion**, which requires sufficient oxygen to react with all the available fuel. When the oxygen content is insufficient to oxidize all of the fuel present, the resulting **incomplete combustion** produces carbon monoxide. Both gases are present at most fires because the fuel doesn't burn evenly throughout.

Even products that don't burn can give off **hazardous decomposition products** when broken down by heat. For example, the old extinguishing agent carbon tetrachloride (CCL) releases toxic phosgene gas (COCL₂).

152 • Fire Chemistry and Chemical Reactions

Other common toxic fire gases include:

- Hydrogen cyanide (HCN) from materials containing nitrogen (e.g., wool, silk, nylon, and polyurethane)
- Nitrogen oxides, particularly nitrogen dioxide (NO₂) and nitric oxide (NO) also from materials containing nitrogen
- Hydrogen chloride (HCl) from materials containing chlorine (e.g., PVC)
- Acrolein (CH₂:CHCHO) from cellulosic materials



Fire Chemistry and Chemical Reactions • 153

Oxygen content affects not just the fire gases produced but also the intensity of the fire and how quickly it spreads. An **oxygen-enriched atmosphere** will cause materials to ignite more readily and burn more fiercely. Fire may burn in an **oxygen-deficient atmosphere**, but it won't burn as well. As the oxygen drops, so does flame propagation.



154 • Fire Chemistry and Chemical Reactions

Backdraft occurs when oxygen (air) is suddenly introduced into an area where fire has been smoldering from lack of oxygen (e.g., when someone opens a door or window to the fire room). Fire goes from the smoldering stage to the freeburning stage with explosive force.

Flashover is the sudden simultaneous ignition of combustibles that have become heated to their ignition temperatures by radiated heat from the fire. In the moments before flashover, one can see heavy smoke developing at upper levels, followed by flame rolling across the ceiling.



Fire Chemistry and Chemical Reactions • 155

Fire (combustion) is a form of oxidation. **Oxidation** is the chemical combining of oxygen with any substance. Fire is rapid oxidation producing heat and light. However, oxidation takes other forms besides fire. The rusting of iron is an example of very slow oxidation. The formation of organic peroxides from ethers (first shown on page 130) is also an oxidation reaction.



156 • Fire Chemistry and Chemical Reactions

These reactions are also known as **redox reactions** (or **reduction-oxidation reactions**), because when one substance is oxidized, the other is reduced. Redox reactions are generally defined as ones in which electrons are exchanged. The electron exchange is seen most easily with ionic bonds, but is obviously not limited to them.



Fire Chemistry and Chemical Reactions • 157

The reaction on the previous page is also a **synthesis reaction** (sometimes called a *combination reaction*). In a synthesis reaction, two or more substances combine to form a new one. For instance, when hydrogen (H) and fluorine (F) combine, they create the highly toxic hydrogen fluoride (HF) gas, which in solution becomes the very corrosive hydrofluoric acid (also written as HF).



158 • Fire Chemistry and Chemical Reactions

Decomposition reactions are the reverse of synthesis reactions; a single compound is broken down into the elements or molecules that comprise them. For example, when ammonium nitrate (NH_4NO_3) thermally decomposes, the potentially explosive reaction produces nitrous oxide (N_2O) and water (H_2O).



Fire Chemistry and Chemical Reactions • 159

In **single replacement reactions**, one element or compound breaks away from its original "partner" and joins another. For instance, when sodium (Na) is exposed to water (H_2O), a hydroxyl (OH) group breaks away from the original water molecule and joins the sodium atoms, resulting in flammable hydrogen gas (H_2) and a caustic solution of sodium hydroxide (NaOH).



160 • Fire Chemistry and Chemical Reactions

In **double replacement reactions**, elements or compounds from each substance change "partners," forming two entirely new compounds. In the example below, when calcium carbide (CaC_2) reacts with water (H₂O), both molecules split. Their components change partners to form flammable acetylene gas (C_2H_2) and a caustic solution of calcium hydroxide $(Ca[OH]_2)$.



Fire Chemistry and Chemical Reactions • 161

Acid-base reactions (or neutralization reactions) are double replacement reactions between an acid and a base. The reaction below is a very dangerous one involving two strong corrosives. Sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) are on opposite ends of the pH scale. If mixed, the reaction will generate a tremendous amount of heat. That's why whenever hazmat technicians attempt to neutralize an acid or base, they must do so with a weak corrosive of the opposite pH.



162 • Fire Chemistry and Chemical Reactions



Toxicity and Risk • 163

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.
- 164 Toxicity and Risk

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.

Toxicity and Risk • 165

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 can



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.

166 • Toxicity and Risk

Several factors affect the risk to exposed individuals:

- 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.
- Sex (if chemicals affect the reproductive system).
- **Age**. Young children and the elderly are often more vulnerable to injury.
- Individual susceptibility and overall health.
- Promptness and quality of **decon** and **medical care**.



Toxicity and Risk • 167

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

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.

However, 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.

168 • Toxicity and Risk

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 on the next page shows the relation between contaminant concentration and oxygen concentration. However, 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. Nitrogen and Other Gases (79.1%)

Toxicity and Risk • 169

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



170 • Toxicity and Risk

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 equations below.



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

Toxicity and Risk • 171



172 • Toxicity and Risk





Toxicity and Risk • 173

At the bottom of the relative hazard ladder are **workplace environmental exposure limits (WEEL)** established for workers without any special protection. The first three 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.

- **Permissible Exposure Limit (PEL)** is a legal limit from OSHA.
- **Recommended Exposure Limit (REL)** is a recommended limit from NIOSH.
- Threshold Limit Value—Time-Weighted Average (TLV-TWA) is a recommended limit from the ACGIH.



174 • Toxicity and Risk

Workers can exceed the permitted or recommended exposure limits if they stay within the short-term and ceiling exposure limits below:

A Short-Term Exposure Limit (STEL) is the maximum concentration to which a worker may be exposed for short durations (usually 15 minutes). Exposures above the STEL should be at least 60 minutes apart and not repeated more than 4 times per day.

A Ceiling Exposure Limit is the concentration that may not be exceeded at any time.



Toxicity and Risk • 175

At the top of the relative hazard ladder are **Lethal Dose** (**LD**) and **Lethal Concentration (LC)**—the exposure required to kill a given percentage of the test population. LD_{50} and LC_{50} are the numbers most often cited. They indicate that 50% of the test population died from the specified exposure. LD_{10} and LC_{10} identify level that killed the first test subject.

Lethal dose is used for solids and liquids and is expressed in milligrams per kilogram (mg/kg) of body weight. Lethal concentration is used for gases and vapors and is usually expressed in parts per million (ppm) or milligrams per cubic meter (mg/m³). It is independent of body weight.

176 • Toxicity and Risk

An immediately dangerous to life and health (IDLH)

atmosphere is one 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 allows for an escape window of up to 30 minutes, but every effort should be made to exit immediately.

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

Toxicity and Risk • 177

Level of Concern (LOC) is one of the values used most often for protecting emergency workers in the cold zone and citizens in the surrounding area. It 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.

178 • Toxicity and Risk
Emergency Response Planning Guideline

(ERPG) levels from the AIHA provide an estimate of concentrations where one might anticipate adverse effects for exposures exceeding one hour.

- Level 1: no more than mild transient health effects or a clearly defined objectionable odor.
- **Level 2**: no irreversible or serious health effects or symptoms that could prevent taking protective actions.
- Level 3: no life-threatening health effects.

The DOE has a more extensive list of **Temporary Emergency Exposure Limits (TEEL)** to provide guidance until the AIHA publishes more ERPGs. TEELs are similar to ERPGs, but don't specify a one-hour time frame.

Toxicity and Risk • 179

Sometimes it's not possible to find all these exposure values in reference books. However, **IDLH and LOC can be estimated** if you know the TLV-TWA.



180 • Toxicity and Risk

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 produce olfactory fatigue. And people vary in their ability to detect odors. So odor threshold is nice to know, but not necessarily reliable in judging one's potential exposure.

Toxicity and Risk • 181



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Acronyms and Abbreviations

ACGIH	American Conference of Governmental Industrial Hygienists
AIHA	American Industrial Hygiene Association
atm	Atmospheres
CSTI	California Specialized Training Institute
DNA	Deoxyribonucleic Acid
DOE	Department of Energy
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
LOC	Level of Concern
mg/kg	Milligrams per Kilogram
mg/m ³	Milligrams per Cubic Meter
mmHg	Millimeters of Mercury

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Acronyms and Abbreviations (continued)

NIOSH	National Institute for Occupational Safety and Health
OSHA	Occupational Safety and Health Administration
PEL	Permissible Exposure Limit
ppb	Parts per Billion
ppm	Parts per Million
psi	Pounds per Square Inch
Redox	Reduction-Oxidation (Reactions)
REL	Recommended Exposure Limit
RNA	Ribonucleic Acid
STEL	Short-Term Exposure Limit
TEEL	Temporary Emergency Exposure Limit
TLV-TWA	Threshold Limit Value—Time-Weighted Average
UEL	Upper Explosive Limit
WEEL	Workplace Environmental Exposure Limit

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About the Author

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 has been a volunteer firefighter for the Santa Clara County Fire Department (CA) since 1980. In 1995 she became a CSTI-certified hazmat specialist and a first responder outreach instructor.

In her spare time, Jill helps build homes with Habitat for Humanity.

Other Books by Jill Meryl Levy

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

Hazmat Chemistry Study Guide

Take Command of Your Writing

Crimes Against the English Language

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