

Chapter 2 Understanding Chemical Hazards

Many chemicals present multiple physical and/or health hazards.

Potentially hazardous chemicals can be found everywhere. There are an estimated 575,000 existing chemical products, hundreds of new ones are introduced annually. Almost 32,000,000 workers are potentially exposed to one or more hazardous substance in the workplace. Many of these materials have properties that make them hazardous; they can create physical (fire, explosion) and/or health (toxicity, chemical burns) hazards. Depending upon magnitude, chemical exposure may cause or contribute to serious health effects including cancer, heart disease, burns, rashes, kidney and lung damage. There are many ways to work with chemicals which can both reduce the probability of an accident to a negligible level and reduce the consequences of minimum levels should an accident occur. The fact that these same chemicals are available at your local hardware store does not mean they are without hazard. Risk minimization depends on safe practices, appropriate engineering controls for chemical containment, the proper use of personnel protective equipment, the use of the least quantity of material necessary, and substitution of a less hazardous chemical for the more hazardous one.

OSHA defines a hazardous chemical as any chemical that is a health hazard or a physical hazard.

To be classified as *hazardous*, a substance must be capable of producing adverse effects on humans or the environment. Before using any chemical, even if it is something that you have worked with at home or elsewhere, it is important to understand what the potential exposure hazards may be and how to use the chemical safely. In order to assess the hazards of a particular chemical, both the physical and health hazards of the chemical must be considered. Generally, more accurate information is available about a chemical's physical hazards than about its health hazards.

This chapter will help you identify chemical hazards and understand the Material Safety Data Sheets that accompany all purchased chemicals. Later chapters will describe appropriate control measures to work safely and reduce the hazards of laboratory chemicals.

2.1 Physical Hazards of Chemicals

Before beginning an operation, ask, "What would happen if ...?"

The physical hazards of a chemical are those hazards inherent to a chemical's physical characteristics. Types of chemical physical hazards are:

- ◆ flammable
- ◆ combustible
- ◆ compressed gas
- ◆ explosive
- ◆ organic peroxide
- ◆ oxidizer
- ◆ pyrophoric
- ◆ unstable
- ◆ water reactive

2.1.a Flammable or Combustible Chemicals

Flammable chemicals are classified according to flash point, boiling point and ignition temperature.

Flammability is the tendency of a chemical to burn. Flammable and combustible chemicals are those chemicals that evaporate rapidly and generate enough vapor to ignite in the presence of an ignition source (i.e., catches fire easily and burns readily). Flammable substances can be solid, liquid, or gaseous, but the most common type encountered in a laboratory setting is a flammable liquid or the vapor produced from such a liquid. Flammable chemicals are classified according to their flash point, boiling point and ignition temperature.

✓ **Flash point (FP)** is the lowest temperature at which a flammable liquid gives off sufficient vapor to ignite.

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Different agencies use different temperatures to define flammable liquids:

DOT $\leq 60.5\text{ }^{\circ}\text{C}$
 $\leq (141\text{ }^{\circ}\text{F})$
 EPA $< 60\text{ }^{\circ}\text{C}$
 $< (140\text{ }^{\circ}\text{F})$
 (*ignitable*)
 NFPA $\leq 37.8\text{ }^{\circ}\text{C}$
 $\leq (100\text{ }^{\circ}\text{F})$

- ✓ **Boiling point (BP)** is the temperature at which the vapor pressure of a liquid is equal to the atmospheric pressure under which the liquid vaporizes. Flammable liquids with low boiling points generally present special fire hazards.
- ✓ **Ignition (or auto-ignition) temperature** is the lowest temperature at which a chemical will ignite and burn independently of its heat source. The lower the ignition temperature, the greater the fire potential. When the flammable vapor reaches its auto-ignition temperature, a spark is not needed for ignition.

Additionally, flammable and combustible chemicals are those that can react with oxidizers to cause a fire or explosion (i.e., a compound may burn so rapidly that it produces an explosion). **Combustible materials** will generate sufficient vapors at or above $38\text{ }^{\circ}\text{C}$ ($100\text{ }^{\circ}\text{F}$). **Flammable chemicals** will generate sufficient vapors at temperatures below $38\text{ }^{\circ}\text{C}$ ($100\text{ }^{\circ}\text{F}$). The table illustrates flammable and combustible class characteristics.

	Flammable			Combustible	
	I-A	I-B	I-C	II	III
Flash Point	$< 23\text{ }^{\circ}\text{C}$ ($73\text{ }^{\circ}\text{F}$)	$< 23\text{ }^{\circ}\text{C}$ ($73\text{ }^{\circ}\text{F}$)	$\geq 23\text{ }^{\circ}\text{C}$ ($73\text{ }^{\circ}\text{F}$) $< 38\text{ }^{\circ}\text{C}$ ($100\text{ }^{\circ}\text{F}$)	$\geq 38\text{ }^{\circ}\text{C}$ ($100\text{ }^{\circ}\text{F}$) $< 60\text{ }^{\circ}\text{C}$ ($140\text{ }^{\circ}\text{F}$)	$\geq 60\text{ }^{\circ}\text{C}$ ($140\text{ }^{\circ}\text{F}$) $< 93\text{ }^{\circ}\text{C}$ ($200\text{ }^{\circ}\text{F}$)
Boiling Point	$< 38\text{ }^{\circ}\text{C}$ ($100\text{ }^{\circ}\text{F}$)	$\geq 38\text{ }^{\circ}\text{C}$ ($100\text{ }^{\circ}\text{F}$)	---	---	---

If appropriate, the Material Safety Data Sheet (see 2.3.b) may include a chemical's ignition temperature. Commercially produced chemicals are usually labeled as to flammability and flash point.

Flammable and combustible chemicals are also characterized by their explosive limits. The **lower explosive limit (LEL)** or lower flammable limit is the lowest vapor concentration of the substance that will produce a flash of fire (i.e., blast) when an ignition source is present. The **upper explosive limit (UEL)** or upper flammable limit is the highest vapor concentration of the substance that will produce a flash of fire when an ignition source is present. A substance's flammable range consists of all concentrations between the LEL and the UEL. The range may be dependent upon temperature and oxygen concentration. At higher concentrations than the UEL, the mixture is too rich to burn and at concentrations lower than the LEL, the mixture is too lean to burn. Note that, for flammable chemicals that are also toxic, concentrations at which the flammability is a hazard are usually well above the toxicity hazard concentrations.

The flammable liquids of most concern in laboratories are those that have flash points below room temperature, about $27\text{ }^{\circ}\text{C}$ ($80.6\text{ }^{\circ}\text{F}$). Flash points and flammability classifications of a few common laboratory liquids are:

Substance	$^{\circ}\text{C}$	$^{\circ}\text{F}$	Class	Substance	$^{\circ}\text{C}$	$^{\circ}\text{F}$	Class
Acetaldehyde	-39	-38	I-A	Gasoline	-46	-50	I-A
Acetone	-18	0	I-B	Glacial acetic acid	40	104	II
Benzene	-11	12	I-B	Heptane	-4	25	I-B
Carbon disulfide	-29	-20	I-B	Hexane	-18	0	I-B
Cyclohexane	-17	1	I-B	Methanol	12	54	I-B
Cyclohexanol	68	154	III	Pentane	-40	-40	I-A
Ethanol	13	55	I-B	Petroleum ether	-40	-40	I-A
Ethyl acetate	-4	24	I-B	Styrene monomer	32	90	I-C
Ethyl chloride	-50	-58	I-A	Toluene	4	40	I-B
Ethyl ether	-45	-49	I-A	Xylene	29	84	I-C

Flammables are more hazardous at high temperatures because they vaporize faster.

Check the flash point of each organic solvent you use.

Solvent flash points that are below room temperature can form an invisible vapor cloud that can be ignited by any spark and cause a fire or explosion.

Thus, xylene, with a flash point of 29 °C, or just above room temperature, is often used as a less toxic and safer substitute for benzene, with a flash point of -11 °C.

Organic solvents are one of the most hazardous chemicals in the lab. Solvents such as ether, alcohols and toluene, are highly volatile or flammable. Chlorinated solvents such as chloroform are nonflammable, but when exposed to heat or flame, they produce carbon monoxide, chlorine, phosgene, or other highly toxic gases. Always use volatile and flammable solvents in an area with good ventilation or in a fume hood. Never use ether or other highly flammable solvents in a room with open flames or other ignition sources present.

Remember, chemical flames of hydrogen and methanol are invisible, the vapors of flammable chemicals are invisible and a vapor trail to an ignition source can result in a flashback. However, for a fire to occur three conditions must occur simultaneously and in close proximity:

- ✓ an oxidizing atmosphere (e.g., air)
- ✓ a concentration of a flammable gas or vapor
- ✓ an ignition source.

The key to reducing fire risk is to control one or more of these three factors. Control the ignition source first, vapor production second, and oxygen third.

2.1.b Oxidizers

An **oxidizer** is a chemical that initiates or promotes combustion in other materials, thereby causing fire either of itself or through the release of oxygen or other gases.

Oxidation is related to electron levels. An **oxidizer** is an electronegative element or compound of electronegative elements and certain high valence state elements that can accept the transfer of electrons from another chemical into electron orbitals that are lower in potential energy than the donating orbitals of the chemical being oxidized, called the **reducer**, an electropositive element or compound of certain low valence state elements. The electrons are either transferred from one species to the other, are shared between the two species in a bond, or an electron deficient species (atom) is transferred from oxidizer to reducer. The difference in potential energy that the electrons experience is balanced by a difference in kinetic or heat energy (i.e., conservation of energy) experienced by the products. If the energy produced is retained in the products of the reaction, a temperature increase of a few hundred degrees could cause damage to the surroundings as it is transferred out. For example, gasoline reacting with oxygen in air can produce a 2000 °C increase in temperature which in the right circumstances produces a pressure increase that can be put to useful work and in the wrong circumstances can produce a fire or explosion.

An **oxidizer** is a substance such as chlorate, permanganate, inorganic peroxide, or a nitrate, that yields oxygen readily to stimulate the combustion of organic matter (49 CFR 173.151).

Simplistically, oxidizers are chemicals which react with other substances, fuels or reducing agents, leaving them fewer electrons with which to maintain their atoms' required electron octets. More electron sharing by additional bond formation internally or with oxide from the oxidizer must then occur. The reaction may result in fire or explosion depending upon the nature of the fuel. Most oxidizers supply oxygen to common fires, but oxygen is not the only oxidizer supplied, fluorine and chlorine from oxidizers based on these electronegative elements will do as well. Chlorine based bleaches spilled on paper or wood may combust also. Some common oxidizers are:

- ◆ fluorine
- ◆ chlorine
- ◆ chlorite
- ◆ bromate
- ◆ ozone
- ◆ permanganate
- ◆ nitric acid
- ◆ chromic acid
- ◆ hydrogen peroxide

Reactive

substances undergo chemical change with the release of large amounts of energy.

Reactive chemicals are sensitive to either friction or shock or they react in the presence of air, water, light or heat.

A **water-reactive** is a chemical that reacts with water to release a gas that either is flammable or presents a health hazard.

2.1.c Reactive Chemicals

Any chemical, with the exception of helium and neon, can react with something (e.g., fluorine or platinum hexafluoride). Chemicals that readily react with ordinary unreactive chemicals such as air, water, cellulose, protein and steel, especially if the reaction is vigorous, are called **reactive**. We also need to distinguish between reactivity and stability. In the above reactive examples, fluorine is stable by itself but platinum hexafluoride is not; it decomposes to its tetrafluoride and fluorine.

Oxidation is a form of reaction. Some chemicals, called self-reactive, even undergo change without any chemical input. Self reactivity can have three forms of change; fragmentation, polymerization and rearrangement of bonding, either inter- or intra- molecularly. Kinetically this could be gradually or suddenly, thermally it can be with varying amount of energy. The sudden and energetic ones need to be known if you are to work safely with them. Sensitivity to a stimulus such as heat, light, percussion, friction or chemical contact (usually acid) is the issue with those that rapidly produce energy. The reaction rate will increase with higher temperature, pressure or concentration.

Examining molecular structures, unobstructed double or triple bonds and strained rings can indicate potential polymerizability. An easy, logical electronic rearrangement to produce something simple and stable like nitrogen, oxygen or carbon dioxide, leaving the rest of the molecule stable, may indicate fragmentability. The presence of oxidizing functionality with electron rich functional groups that are easily rearranged to neutralize each other, can be a warning in an unfamiliar compound. The "bottom line" question: Is there a higher heat of formation arrangement of the atoms in a molecule and is there an easy way for them to get there?

Because reactive chemicals have a propensity to undergo vigorous, sometimes spontaneous, reactions and, under certain conditions, may spontaneously generate large quantities of heat, light, gases or toxic chemicals, work with reactive chemicals such as explosives, acid sensitives, oxidizers, reducers, water sensitives, and pyrophorics should be done only after understanding the possible reactions and potential energy release per mole.

Water-reactive Chemicals

Water-reactive chemicals react violently with water, water vapor or moist air to produce heat and flammable hydrogen gas which can ignite. Alternately, the reaction can produce a toxic gas or other hazardous condition. It makes a big difference whether the moisture enters slowly, if water is thrown on the substance or if the substance is thrown into water. Usually water splashed or poured onto the material is the greatest hazard since fire or explosion may result from the reaction. Examples of water-reactives include: alkali metals (e.g., lithium, sodium and potassium and their hydrides), calcium oxide, sulfur trioxide, silicon tetrachloride, anhydrous aluminum chloride, phosphorus pentoxide, trifluoromethanesulfonic anhydride, and chlorosulfonic acid.

In a world of where water can be a solid, liquid, or vapor (i.e., air humidity), chemical water reactivity is an important safety consideration. When water reacts with some chemicals, unfortunate results are possible. These can range from:

- ✓ spontaneous ignition
- ✓ violent heat production
- ✓ toxic gas release
- ✓ pressure building in a container
- ✓ oxidation or reduction by water reaction
- ✓ chemical effectiveness lost by hydrolysis or hydration

There are eight basic physical and / or chemical reactions that water can initiate:

1. Reduce ionic charge density by either protonation of a small anion, including hydrogen bonding with hydroxide from a strong base, or becoming a ligand on a positive ion, including being protonated by a strong acid.
2. Coordination expansion of an atom by adding across a double bond (e.g., sulfur trioxide hydration to sulfuric acid).
3. Replacing a weaker ligand, such as hydrolysis of an acid chloride.
4. Oxidation of a metal or a lower valence state transition metal compound, producing hydrogen gas in the process.
5. Reduction of a strongly oxidizing compound (e.g., cobalt(III) fluoride), producing oxygen gas.
6. Hydration of a non-ionic compound by hydrogen bonding or hydration cage structure.
7. Deliquescence, that is, hydration to the point of forming an aqueous solution of the chemical from airborne humidity.
8. Solution in water, by ionic dissociation or hydrogen bonding.

The first five can be rather energetic and fast reactions, while the latter three are less exothermic and may even be endothermic, being entropically driven. With the energetic reactions, adding the compound **to** water can be safer than adding limited water to the compound, simply because when you add it to water, the surrounding water will absorb the heat produced.

The water need not be liquid for the reaction. Water in air (i.e., humidity) can enter into a poorly closed container and react as well. Here the reaction is controlled by the diffusion rate of the air. Examples of unwanted reaction by air include:

- ♦ Calcium phosphide reacts slowly with humidity to produce phosphine and calcium hydroxide.
- ♦ Calcium carbide reacts to produce acetylene with enough heat to ignite the acetylene in air.
- ♦ Reaction with a non-alkaline metal halide or non-metal halide to produce hydrogen halide gas that, in the case of a small leak, diffuses out slower than the lighter air and water molecules can diffuse in so pressure builds up in the container.
- ♦ The infamous reaction of aluminum and arsenic oxide (e.g., a ladder placed in a pit containing arsenic) which builds deadly arsine gas in a confined space, will not occur without a proton donor, which can be water from humid air.

A **pyrophoric** is a chemical that will ignite spontaneously in air at a temperature of 130 °F (54.4 °C) or below.

Pyrophoric Chemicals

Chemicals that ignite on exposure to air at temperatures of 54 °C (130 °F) or lower temperature are considered to be **pyrophoric**. Such chemicals can be gases, solid or liquid, volatile or non-volatile. What occurs is that oxygen, in its ordinary form, reacts with the chemical in the gas phase or on the surface in a way that leads to sustained combustion for as long as oxygen is present. This requires that the reaction is rapid enough and delivers enough energy to propagate a flame in the gas phase or release underlying atoms / molecules in condensed phase for the air to contact. Pyrophoric chemicals can be elements or compounds. Some examples are boranes, triethylaluminum, and white or yellow phosphorus. Many metallic powders are pyrophoric. The degree of reactivity is primarily related to particle size. Solids are more susceptible if finely divided or somewhat volatile. Three distinct initiating events are possible:

- ✓ Oxygen binds to a metal atom, whether a lower valence transition metal compound (titanium(II) chloride), a covalent metal alkyl or hydride (triethylaluminum) or a transition metal finely divided.
- ✓ Oxygen binds to an unshared electron pair on an alkyl or hydro derivative of phosphorus, arsenic or antimony and
- ✓ Water in air combines with an alkaline metal ion that is in combination with hydride or alkylide (butyllithium), generating heat from creating a metal - oxide bond and protonation of the hydride or alkyl, which ignites the hydrogen or alkane in air.

Otherwise, an active metal binds water producing the metal oxide or hydroxide and hydrogen, which then ignites in the heat produced. Many active metals will react directly with oxygen and oxidize completely without igniting. Some pyrophoric reactions include:

- ◆ Some lower valence transition metal oxides and catalyst metal powders (palladium) can combine with oxygen in air producing a plume of hot nitrogen, but no other species that would glow to make the combustion visible, (i.e., a flame).
- ◆ White phosphorus, which will spontaneously ignite if warm, finely divided or damp in air will otherwise glow on air exposure from a slow reaction with oxygen that releases an intermediate's energy as phosphorescence.
- ◆ Unsaturated oils like linseed oil and hydrazine derivatives, methyl hydrazine, will react with oxygen if absorbed on cloth that allows enough air movement to supply oxygen but not so rapid as to carry away the heat of reaction, producing delayed spontaneous combustion.
- ◆ Phosphine at low concentrations in air will also glow (i.e., marsh gas).
- ◆ Hydrosulfite (dithionite) salts, if damp, but not dissolved in water will ignite due to the low level presence of sulfur dioxide radical anion from sulfur to sulfur bond disassociation.

Peroxide-forming Chemicals

There are many compounds that have "peroxide" in their name, some are hazardous and some are relatively safe at ambient pressure and temperature. Some chemicals become peroxides when exposed to air while in storage and in use. Commercially available reagent peroxides are prepared and contained so they can be used safely.

It is the organic peroxides that form unintentionally that are of great concern because of their unpredictability, explosivity, and often grave consequences. Peroxides form primarily in liquids but can also form in solids and even bottled gases that are liquified under pressure.

Explosion Hazard. The molecular arrangement of an oxygen to oxygen bond is common to all peroxides. Upon initiation, the molecule can rearrange its structure, losing the oxygen to oxygen and carbon to carbon (or hydrogen) bonds and forming carbon to oxygen bonds in the process (more stable bonds). A violent reaction or explosion can be initiated fairly easily; for example, mechanical shock, excessive or rapid heating, or surface to surface friction by removing a cap or lid from a bottle.

Peroxide Formation. When a substance slowly reacts with oxygen from the atmosphere (i.e., *autooxidation*), there are a number of different reactions possible. Many peroxide-formers will slowly rearrange to non-peroxide oxidized forms and cause no trouble beyond their eventual lack of usefulness. Examples of these are: benzaldehyde and other aldehydes, amines, mercaptans, sulfides, N-alkyl amides and

Oxygen-oxygen bonds are inherently unstable.

Sunlight can accelerate the formation of peroxides.

alkyl iodides. Other peroxide-formers will slowly polymerize and eventually become solid plastic. Examples of these substances include styrene, vinyl acetate and ethyl acrylate. Since these chemicals may be packaged in air, inhibitors of radical polymerization are added (hydroquinone, usually). But peroxides can form and polymerization eventually occurs even if the container has not been opened. Most common in peroxide formation is that of soluble (i.e., they remain dissolved) hydroperoxides and ketone peroxides from secondary alcohols, ethers, tertiary carbons (as in decalin), and allylic and benzylic carbons (as in alkenes and alkyl benzenes). See Chapter 4 for a more extensive list of peroxide-forming chemicals and safe storage and use practices.

Reactive and explosive chemicals produce large amounts of heat and gas; they are extremely dangerous.

Shock-Sensitive and Friction-Sensitive Explosives

Shock-sensitive explosives can spontaneously release large amounts of energy not only when struck, vibrated, dropped, heated, or otherwise agitated but also under normal conditions. Some chemicals become increasingly shock-sensitive with age. Of great concern in the laboratory is the inadvertent formation of shock-sensitive explosives such as peroxides in solvents and other materials that can be shock-sensitive explosives including:

Nitrate salts of metals, the oxides of which are water insoluble, if mixed and heated with nitric acid and ethanol can oxidize the ethanol to acetaldehyde and acetic acid, then nitrate it, decarboxylate and dehydrate it to fulminic acid, H-C=N-O, and finally form the fulminate salt.

- ◆ azides of hydrogen, ammonium, alkaline earth metals, copper, silver, mercury, thallium and lead
- ◆ carbides and acetylides of copper, silver, gold and mercury
- ◆ nitrides of sulfur, selenium, tellurium, copper (Cu₃N), "fulminating" silver (Tollin's test and silvering solutions) and gold, and mercury (Millon's base, HgN-Hg-OH)
- ◆ alkyl azides from sodium azide in DMSO (or similar) and alkyl halides (CH₂Cl₂, dichloroethane)
- ◆ fulminates (:C=N-O) of hydrogen, ammonium, and metals (in general)
- ◆ fulminates of silver, mercury, thallium and lead formed from nitrates dissolved and heated in ethanol
- ◆ mercuric oxide - mercuric cyanide, silver cyanate, mercury(II) cyanate, (light sensitive) silver cyanamide (Ag₂N=C=N), (light sensitive) mercury(I) cyanamide
- ◆ oxalate and tartrate of silver and mercury
- ◆ hypophosphite (phosphinate, H₂P(O)O⁻) acid, aluminum, magnesium (heating disproportionates them to phosphine which can ignite), dipotassium phosphinate, KHP(O)OK (ignites in air if wet), and shock and temperature sensitive:
 - copper(II) - silver - iron(III) - manganese(II) - lead(II)
- ◆ RedOx salts like basic stannous nitrate [Sn₃(OH)₄(NO₃)₂], ferrous perchlorate, guanidinium, hydrazinium, hydroxyl amine salts with:
 - nitrates - perchlorates - chromates
- ◆ ammonium salts mixed with salts of:
 - nitrite - chlorate - bromate - permanganate
- ◆ hydroxylamine free base disproportionates when heated
- ◆ hydroxylammonium iodide and phosphinate
- ◆ metal salts of picric acid, dinitrophenol, dinitroresorcinol and nitromethane (aci-nitro anions)
- ◆ chlorite salts of

- lithium (heat)	- nickel (heat / shock)	- copper (shock)
- sodium (heat / shock)	- lead (heat)	- silver (heat/shock)
- barium (heat)	- thallium(I) (shock)	- mercury(I) & (II) (unstable)

Every lab should have a copy of Bretherick's *Handbook of Reactive Chemical Hazards*.

This list is not inclusive. If you are in doubt as to the reactive or explosive potential of your chemical procedures, consult an authoritative reference such as Bretherick's *Handbook of Reactive Chemical Hazards*. The American Chemical Society has compiled an index of reported incidents of laboratory explosions that have appeared in *Chemical and Engineering News*. Call (800) 227-5558, for the ACS Health and Safety Referral Service for information.

Other laboratory shock-sensitives which may be encountered are perchlorates in fume hood ducts and azides in drain lines. It is important to distinguish between shock-sensitive and friction-sensitive compounds. Picric acid and ether peroxides are not especially shock-sensitive, however, opening a tight cap produces major frictional forces which can cause an explosion. If spilled on a concrete floor and not cleaned, picric acid will form calcium picrate, which is easily detonated by footsteps when dry.

2.1.d Compressed Gases

Compressed gases in the laboratory present chemical and physical hazards. If compressed gases are accidentally released, they may cause:

- ✓ depleted oxygen atmosphere
- ✓ fire
- ✓ adverse health effects

Some gases (e.g., arsine, phosphine, phosgene, nitric oxide, chlorine, sulfur tetrafluoride, etc.), are potentially lethal if the cylinder leaks and the leakage of a flammable gas can create an explosive atmosphere. In a laboratory fire, the heat may cause the cylinder's internal pressure to increase and the cylinder may rupture.

Cylinders that are knocked over or dropped can also be very dangerous and can cause serious injuries. A cylinder may contain a gas at a maximum pressure of 150 atmospheres. If all the gas were released from a 50 kg cylinder through the 2-cm diameter opening, the cylinder could be launched at a velocity of about 75 mph. Thus, a broken cylinder valve may cause the cylinder to act like a missile, passing through walls and possibly causing structural damage, severe injury, and death. See Chapter 4 for compressed gas cylinder requirements.

2.1.e Cryogenic Liquids

A *cryogenic liquid* is a liquid with a boiling point that is less than or equal to $-90\text{ }^{\circ}\text{C}$ at one atmosphere pressure. Cryogenic fluids, such as liquid air, liquid nitrogen, or liquid oxygen, are used to obtain extremely cold temperatures. Most cryogenic liquids are odorless, colorless, and tasteless. Cryogenic liquids are hazardous because of the physical and chemical characteristics of their super-cooled state.

Cryogenic Hazard Source	Hazard
Hydrogen, methane, acetylene	Gases are flammable
Oxygen	Increases the flammability of combustibles
Liquefied inert gases	Air oxygen condensation and concentration
Extremely cold surfaces	Materials made brittle

Liquefied gas is more concentrated than its vapor and may rapidly evaporate. Liquid nitrogen experiences a 700-fold increase in volume going from the condensed phase to the vapor phase. Five gallons could displace half the air in a 15' x 15' room, leaving only 10% oxygen (e.g., like the top of the Himalayas).

Compressed gas cylinders can become lethal projectiles.

Liquid nitrogen and other liquefied gases can displace breathable air and should be used only in well-ventilated areas.

Cryogenic liquids can cause fires (e.g., liquid oxygen or liquid hydrogen) or explosions, embrittlement of structural materials, asphyxiation and tissue destruction. Materials that are normally noncombustible (e.g., carbon steel) may ignite if coated with an oxygen-rich condensate. Liquefied inert gases (e.g., liquid nitrogen, liquid helium) are capable of condensing atmospheric oxygen and causing oxygen entrapment or enrichment in unsuspected areas. Extremely cold metal surfaces are also capable of entrapping atmospheric oxygen.

The gases in a solution of liquefied gases (e.g., liquid air) may evaporate at different rates leaving a concentration of a flammable gas. A cryogenic liquid spill (e.g., liquid nitrogen) on a person could be injurious almost immediately and it could be made worse by being spilled onto clothing that could trap larger amounts of cold liquid than would contact the otherwise unprotected skin. Because pressures may build up rapidly in a closed system, adequate venting is required.

2.2 Health Hazards of Chemicals

A chemical is called a *health hazard* if there is statistically significant evidence based on at least one study that indicates that acute or chronic health effects may occur in exposed employees.

When discussing the health effects of chemicals, two terms, *toxicity* and *hazard*, are often used. *Toxicity* is the ability of a chemical substance to produce injury once it reaches a susceptible site in or on the body. *Hazard* is the probability that a substance will produce injury *under the conditions / manner of use*. Risk of injury is the probability that a chemical will cause harm. With proper handling, even highly toxic chemicals can be used safely. Conversely, *less toxic chemicals can be extremely hazardous if handled improperly*.

Toxicity is a property of each chemical. Any substance can be harmful to living things. But, just as there are degrees of being harmful, there are also degrees of being safe. For every chemical, there are conditions in which it can cause harm and conditions in which it does not. The biological effects (beneficial, indifferent or toxic) of all chemicals are dependent on a number of factors: the route of exposure, rate, duration, frequency, total dose and the type of hazard.

2.2.a Routes of Entry

The actual health risk of a chemical depends on its toxicity and its exposure route. No matter how toxic a material is, there is little risk involved unless it enters the body. An assessment of the toxicity of the chemicals and the possible routes of entry will help determine what protective measures should be taken by workers.

Inhalation

The most common route of entry for chemical substances is through inhalation (i.e., breathing). When breathed in, gases, vapors and particles can pass into the bloodstream along with oxygen or they may also harm the tissues of the respiratory system (e.g., asbestos, silica, etc.).

Most chemicals have an odor which can be smelled at a certain concentration, called the *odor threshold*. Olfactory fatigue, which may occur when a worker has been exposed to high concentrations or after prolonged lower level exposure to some substances, may make an odor seem to diminish or disappear, while the danger of overexposure still remains.

Inhalation is the most common route of chemical exposure.

Overexposure symptoms may include headache, increased mucus production, and eye, nose and throat irritation. Narcotic effects, such as confusion, dizziness, drowsiness, or collapse, may result from exposure to some substances, including many common hydrocarbon solvents (e.g., toluene). In the event of overexposure, close containers, open windows or otherwise increase ventilation, and move to fresh air. If symptoms persist, seek medical attention.

Adequate ventilation is crucial when working with chemicals toxic by inhalation.

Chemicals that produce vapors should only be used in a well ventilated area or in a fume hood. Ventilation can be increased by local exhausts or fans but, occasionally, ventilation may not be adequate and a fume hood not practical, making it necessary to use a *respirator*. OSHA has strict requirements for respirator use which include a medical examination and a respirator fit test. The medical exam is necessary because wearing respirators increases the work of breathing which may cause health problems for some people. Also, the work environment must be evaluated to identify the concentration of the hazard and to help select the appropriate mask and filter system.

Respirator use requires a medical exam, fit test, and workplace evaluation.

Skin and Eye Contact

The second most common route of entry is absorption of chemical solids, liquids, vapors, and gases through the skin and eyes. Skin contact with a chemical may produce a local reaction (e.g., burn or rash) but can result in absorption into the bloodstream with no skin reaction. Absorption into the blood may then allow the chemical to cause toxic effects on other parts of the body.

Absorption through skin and eyes is the second most common route of entry.

The absorption of a chemical through intact skin is influenced by the health of the skin and the properties of the chemical. Skin that is dry or cracked or has small cuts or lacerations offers less resistance. Wear gloves and other protective clothing to minimize skin exposure. Symptoms of skin exposure may include dry, whitened skin, redness and swelling, rashes or blisters, and itching. In the event of chemical contact on skin, rinse the affected area with water for at least 15 minutes, removing clothing while rinsing, if necessary. Seek medical attention if symptoms persist.

If chemicals are spilled on the skin or in the eyes, immediately wash the area for at least 15 minutes and seek medical attention if symptoms persist.

Chemical contact with eyes can be particularly dangerous, producing a painful injury or even blindness. Wearing safety goggles or a face shield can reduce the risk of eye contact. Eyes which have been in contact with chemicals should be rinsed immediately with water continuously for at least 15 minutes (see Section 5.3.a). Contact lenses should be removed while rinsing, however, do NOT delay rinsing to remove the lenses, seconds count. Get medical attention if symptoms persist.

Ingestion

The third most common route of entry for chemicals into the body is ingestion (i.e., swallowing). Ingestion can occur by failing to wash hands before eating or drinking, eating or drinking contaminated food or beverages in the work area, or touching the mouth with contaminated hands. Workers can easily reduce the risk of ingestion by not eating, drinking, smoking (smoking is not allowed in any UW building), or storing food in the areas where chemicals are used or stored. Additionally, washing hands thoroughly after working with chemicals, even when gloves are worn, reduces the risk of cross contamination.

Do not bring food or drink into your lab.

In the event of accidental ingestion, immediately go to the emergency room or contact the UW Hospital Poison Control Center, 262-3702, for instructions. Use the MSDS to know the exact chemical involved. Do not induce vomiting unless directed to do so by a health care professional or by instructions in the MSDS.

Be careful when working with sharps.

Injection

Another possible route of exposure to chemicals is by accidental injection which can occur by needle sticks or through accidents with broken glassware or other sharp objects that have been contaminated with chemicals. If accidental injection has occurred, wash the area with soap and water and seek medical attention, if necessary. To reduce this risk, always use caution when handling sharp objects.

2.2.b Toxic Exposure Factors

While the daily use of many chemicals can be perfectly safe, the body normally reacts to exposure from harmful chemicals. Toxic effects of chemicals can range from mild and reversible (e.g., a headache from a single episode of inhaling the vapors of petroleum naphtha that disappears when the victim gets fresh air) to serious and irreversible (liver or kidney damage from excessive exposures to chlorinated solvents). A goal of chemical safety is to make workers aware of health hazards of the chemicals they are using.

The way a toxic exposure affects a person depends on many factors including: the amount of chemical involved, whether the exposure is acute or chronic, and the specific toxicity of the chemical.

The dose-time relationship is central to evaluating risk.

Type and Magnitude of Exposure

The toxic effects of a chemical may be local or systemic. **Local** injuries only involve the area of the body in contact with the chemical. For example, if you spill an acid on your arm, the effect will be on your arm. **Systemic** injuries involve tissues or organs away from the contact site where the toxic substance has been transported through the bloodstream. For example, methanol that has been swallowed may cause blindness. Certain chemicals may only affect a **target organ**. Lead primarily affects the brain, kidney and red blood cells while some organic solvents may harm the liver and kidneys. It is also important to distinguish between acute and chronic exposure / toxicity.

The magnitude and duration of exposure are factors affecting response.

Acute: rapid absorption from sudden and severe exposure.

✓ **Acute toxicity** results from a single, short intense exposure to a chemical where the acute effects usually appear quickly and are often reversible. Hydrogen cyanide, hydrogen sulfide, nitrogen dioxide, ricin, organophosphate pesticides and arsenic are examples of acute toxins. Do not work alone when handling acute toxins. Use a fume hood to ensure proper ventilation.

Chronic: prolonged/repeated exposure, duration of days, months, or years.

✓ **Chronic toxicity** results from repeated exposure to lower levels over a long period of time. The effects are usually delayed and gradual, and may even be irreversible. Mercury, lead, and formaldehyde are examples of chronic toxins.

Individual Susceptibility

People react differently in their sensitivity to chemical exposure. This variability in sensitivity to chemicals depends on factors such as: age, sex, eating habits, physical condition, obesity, medical conditions, drinking and smoking, pregnancy, etc.

Over time, regular exposure to some substances can lead to the development of an allergic rash, breathing difficulty, or other reactions. This physical response is referred to as **sensitization**. Continuing exposure past this point and the effects may occur with exposure to smaller and smaller amounts of the chemical. With sensitization, the effects usually disappear soon after the exposure stops. For reasons not fully understood, not everyone exposed to a sensitizer will experience this reaction. Examples of sensitizers include epoxy resins, nickel salts, isocyanates and

formaldehyde. Some workers even become sensitized to the rubber used in protective gloves where their hands may begin to itch. Some workers have even experienced life-threatening shock reaction from gloves made from natural latex.

Physical Class of Agent

The physical class of the substance (i.e., solubility) is also a key factor. Highly soluble materials like ammonia irritate the upper respiratory tract while relatively insoluble materials like nitrogen dioxide penetrate deep into the lung. Fat soluble materials like pesticides tend to have longer residence times in the body.

An aerosol is composed of solid or liquid particles of microscopic size dispersed in a gaseous medium. The toxic potential of an aerosol is only partly described by its concentration (mg/m^3). It is also necessary to know the particles size. Particles above 1 micrometer ($1\ \mu\text{m}$) tend to deposit in the upper respiratory tract. Particles less than $1\ \mu\text{m}$ in diameter enter the lung. Very small particles ($< 0.2\ \mu\text{m}$) are generally not deposited.

2.2.c Types of Health Hazards

Toxic chemicals used in labs can produce physical effects. The physiological classification of toxic materials include: allergens and sensitizers, irritants, corrosives, asphyxiants, anesthetics, hepatotoxic agents, nephrotoxic agents, neurotoxic agents, agents which affect the hematopoietic system, fibrosis-producing dusts, carcinogens, mutagens, or teratogens. Many chemicals have multiple toxic and/or hazardous characteristics.

Prior to working with a chemical you need to determine the answers to questions like: Is the chemical toxic? How toxic is it? Are you exposed to it? Does that exposure represent a risk to your health? What kind of risk? Find out all the information that you can concerning the health risks of the chemicals that you work with. Read the Material Safety Data Sheets and research the characteristics of the chemicals you plan to use. This chapter will help you ask the right questions and help you to understand some of the terms used in toxicology. With this information and the guidance in Chapter 4 you can then take the appropriate steps to reduce your exposure to those chemicals that represent a health risk.

Not all chemical health hazard information has been researched. The American Chemical Society's Chemical Abstracts Service (CAS) lists over ten million known chemicals. The National Institute of Occupational Safety and Health's (NIOSH's) *Registry of Toxic Effects of Chemical Substances*, a compendium of toxicity tests, lists fewer than 200,000 chemicals. Thus, millions of chemicals have not been tested for toxicity. Additionally, most toxicity tests are for acute toxicity and toxicity information is from animal studies where the species may react differently and often unpredictably to various chemicals. Thus, some of the information is not directly applicable to humans. So, there is still much to learn about the chemical toxicity.

Fortunately, Material Safety Data Sheets (see 2.3.b) contain adequate safety information for most commonly used chemicals. Some research laboratories may encounter the exotic, rare and newly synthesized chemicals for which toxicity data is sparse or nonexistent. This emphasizes the importance of handling all laboratory chemicals with the utmost care. Whenever you handle laboratory chemicals, minimize your exposure by using fume hoods and personal protective equipment (e.g., gloves) and the safety procedures described in Chapter 4.

Read and understand the Material Safety Data Sheets for the chemicals that you use.

There is a shortage of chemical toxicity information.

Handle all laboratory chemicals with care.

Material Safety Data Sheets (MSDS), when available, are a good source of information about chemicals.

Allergens and Sensitizers

An allergic reaction is an adverse immune response following repeat contact with otherwise harmless substance. A **chemical allergen** is a chemical substance that produces an allergic reaction.

Sensitizers may cause little or no reaction upon first exposure; but repeated exposures may result in severe allergic reactions.

A **sensitizer** causes a substantial portion of exposed people to develop an allergic reaction in normal tissue after repeated exposure to a chemical substance. A person may be exposed to an allergen by inhalation, ingestion, or penetration of the skin. The reaction may be as mild as a rash (contact dermatitis) or as serious as anaphylactic shock. Reactions can be delayed, taking hours or even days to develop. The skin is usually the site of such delayed reactions, becoming red, swollen and itchy. A delayed reaction can even occur some time after the chemical has been removed. Once sensitized, repeated exposures to even the most minute levels of sensitizers can result in life-threatening allergic reactions.

Allergens and sensitizers include a variety of substances capable of producing skin and lung hypersensitivity. Examples of common substances include: epoxides, nickel compounds, poison ivy, toluene diisocyanate and other isocyanates, chlorinated hydrocarbons, chromium compounds (i.e., chromates), formaldehyde, amines and certain phenols.

Primary Anesthetics

Primary anesthetics have a depressant effect upon the central nervous system, particularly the brain. Examples include: diethyl ether, alcohols and halogenated hydrocarbons (chloroform, trichloroethylene, carbon tetrachloride).

Asphyxiants

Asphyxiants have the ability to deprive tissue of oxygen.

Asphyxiants are substances that interfere with the transport of oxygen either in the lungs or in the red blood cells, depriving tissues and organs of oxygen. The brain is the system most easily affected by lack of oxygen and exposure to asphyxiants can be deadly.

- ✓ **Simple asphyxiants** are inert gases that displace oxygen in the air and include such substances as: nitrogen, carbon dioxide, helium, nitrous oxide and argon. Under certain conditions, even chemically inert and benign substances may be dangerous.
- ✓ **Chemical asphyxiants** combine with hemoglobin and render the body incapable of using an adequate oxygen supply. These chemical asphyxiants are toxic even at very low concentrations (e.g., a few ppm) in air and include substances such as carbon monoxide, hydrogen cyanide, and hydrogen sulfide.

Blood (Hematopoietic) Toxins

Some toxic agents can damage blood cells or hematopoietic system (e.g., bone marrow). Examples include: nitrites, benzene, toluidine, aniline and nitrobenzene.

Carcinogens

A **carcinogen** is any substance that contains an agent that can initiate or speed the development of malignant or potentially malignant neoplastic proliferations of cells (i.e., causes cancer). Many chemicals have been evaluated for their ability to cause cancer. It is believed that these carcinogens directly or indirectly interact with cellular DNA causing permanent alterations. Carcinogens are chronically toxic substances because they cause damage after repeated or long-duration exposure and the effects may not become evident for many years after exposure has stopped. The **latent period**, the length of time from exposure to cancer formation, for many cancers

ranges from twenty to forty or more years. The risk of developing cancer from exposure to a chemical increases with the length of exposure and with the chemical's exposure concentration.

There are very few chemicals known to cause cancer in humans, but there are many suspected carcinogens and many substances with properties similar to known carcinogens.

There is a distinction between human carcinogens and suspected human carcinogens. The term **human carcinogen** is used when there is clear evidence of a chemical's ability to cause cancer in humans. **Suspected human carcinogen** refers to chemicals that have been shown to cause cancer in two or more animal species and are therefore suspected of also causing cancer in humans. Examples of known carcinogens include: asbestos, benzene, tobacco smoke, aflatoxins.

Zero exposure should be the goal when working with known or suspected carcinogens. Persons working with or planning to work with carcinogens or suspected carcinogens must follow strict guidelines to minimize exposure. For a specific substance, the *Toxicity Data* section of the MSDS will state whether or not the substance is considered a carcinogen by OSHA, the National Toxicology Program (NTP), or the International Agency for Research on Cancer (IARC). Appendix D provides a more detailed discussion of carcinogens and other Particularly Hazardous Substances and includes procedures which should be implemented when working with these materials.

Corrosives

A corrosive chemical destroys or damages living tissue by direct contact.

A **corrosive** is a chemical that can cause visible destruction of or irreversible alterations in living tissue by chemical action at the site of contact. Corrosives can also react (e.g., oxidation) with metals causing deterioration of the metal surface. Acids and bases are corrosives. Aqueous solutions of acids with a pH less than 2, and bases with a pH greater than 12 are especially dangerous and require special precautions. Examples of common corrosives are:

acidic corrosives:	♦ hydrochloric acid	♦ sulfuric acid
alkaline corrosives:	♦ sodium hydroxide (lye)	♦ potassium hydroxide
corrosive dehydrating agents:	♦ phosphorous pentoxide	♦ calcium oxide
corrosive oxidizing agents:	♦ chromic acid	♦ perchloric acid
organic corrosives:	♦ phenol	♦ acetic acid

Because chemical corrosion actually covers a broad range of reactions that degrade structural materials, when working with chemicals, you must understand the reactions that are possible. Common reactions include: rusting steel, thinning glass-walled containers, softening hard plastic, disintegrating fabrics and living tissue cell destruction. These reactions can result from different types of chemical attacks: oxygen in moist air, aqueous hydrofluoric acid, solvents on plastics, acids on cellulose, bases on wool or leather, and a variety of lipid soluble chemicals on tissue. Some common material reactions include:

- ✓ Non-polar volatile liquids (e.g., alkylphosphines, amines and chlorinated solvents) can affect the structural integrity of containers and stoppers by being absorbed into rubber stoppers, septums and plastic containers causing swelling, softening or embrittlement.
- ✓ Ground glass stoppers can be frozen in due to welding of glass by action of dilute hydroxide from strong or weak bases and by fluoride ion, as acid or salt.
- ✓ Ethylene glycol, more so than any alcohol, has an enhanced tendency to promote rusting of the iron of its steel container (e.g., drum or five gallon can).

While pH describes the hydrogen ion concentration, it is not an absolute measurement of potential hazard. Sometimes, weak acids at high concentration can be more destructive to tissue than strong acids at lower concentrations. For example, 13 M acetic acid (i.e., 1:1 $\text{CH}_3\text{CO}_2\text{H}-\text{H}_2\text{O}$) with a pH of 1.25 (0.42% dissociated) is a greater danger to skin than sulfuric acid at the same pH (i.e., 0.056 M) because it is more able to penetrate skin. Hydroxide ion at pH 13 is a greater danger to skin than aqueous strong acid at pH 1 because proteins and lipids are more sensitive to bases. Phenol is not a strong acid but will readily penetrate skin and cause destruction by coagulation of proteins in cells and then enter the blood capillaries.

Environmental Toxins

Some chemicals are or may be very toxic to wildlife or can otherwise harm ecosystems but pose less risk to humans. Some factors contributing to environmental toxicity are persistency (resistance to degradation) and bioaccumulation as the chemical moves up the food chain. For some environmental toxins the degree of human toxicity is uncertain or controversial. DDT and polychlorinated biphenyls (PCBs) are examples of chemicals that have been shown to cause reproductive failure in certain species but appear to be less hazardous to humans. Despite these species differences, careful use and disposal of environmental toxins is required.

Hepatotoxic Agents

Hepatotoxic agents cause damage to the liver. Examples include carbon tetrachloride, nitrosamines, and 1,1,2,2-Tetrachloroethane.

Irritants

Irritants cause reversible inflammation or irritation to the eyes, respiratory tract, skin and mucous membranes.

Irritants are substances that inflame mucous membranes when they come in contact with these membranes. The inflammation occurs at concentrations far below those needed to cause tissue destruction. Chronic exposure to irritants can cause increased mucous secretions and result in chronic bronchitis. Commonly encountered irritants include:

- ◆ ammonia
- ◆ halogens (F_2 , Cl_2 , I_2)
- ◆ nitrogen dioxide
- ◆ hydrogen fluoride
- ◆ diethyl/dimethyl sulfate
- ◆ alkaline dusts and mists (hydroxides, carbonates, etc.)
- ◆ hydrogen chloride
- ◆ phosgene
- ◆ arsenic trichloride
- ◆ ozone
- ◆ phosphorus chlorides

Irritants that can also produce chemical asthma by causing changes in the mechanics of respiration and lung function include:

- ◆ sulfur dioxide
- ◆ sulfuric acid mist
- ◆ acetic acid
- ◆ acrolein
- ◆ iodine vapor
- ◆ formaldehyde
- ◆ formic acid

A **primary irritant** (e.g., hydrogen chloride) exerts no systemic toxic action because the products formed on the tissue of the respiratory tract are nontoxic or because the irritant action is far in excess of any systemic toxic action. A **secondary irritant's** effect on mucous membranes is overshadowed by a systemic effect resulting from absorption. Examples of secondary irritants include hydrogen sulfide and aromatic hydrocarbons. Exposure to a secondary irritant can result in pulmonary edema, hemorrhage and tissue necrosis.

Lung (Pulmonary) Toxic Agents

Some agents cause damage to the pulmonary tissue (lungs) by means other than immediate irritant action. Fibrotic changes can be caused by free crystalline silica and asbestos. Other dusts (e.g., coal dust, cotton dust, wood dust and talc) can cause a restrictive disease called pneumoconiosis.

Nephrotoxic Agents

Nephrotoxic agents damage the kidneys. Examples include halogenated hydrocarbons and uranium compounds.

Neurotoxic Agents

Neurotoxic agents can damage the central or peripheral nervous system. The nervous system is especially sensitive to organometallic compounds and certain sulfide compounds. The damage produced may be permanent or reversible. In many instances, detection of neurotoxic effects may require special exams, but effects can sometimes be inferred from behavior such as slurred speech or staggered gait. Many of these neurotoxic agents may be chronically toxic substances whose effects are not immediately apparent. Examples of neurotoxic agents include:

- ◆ trialkyl tin compounds
- ◆ tetraethyl lead
- ◆ thallium
- ◆ organophosphate insecticides (malathion, parathion, Vapona)
- ◆ methyl mercury
- ◆ carbon disulfide
- ◆ manganese

Personal Risk Analysis

A personal risk analysis (see Annex 2-2) may help you better understand your risk when working with hazardous chemicals. First, review the Material Safety Data Sheets (MSDSs) for each of your chemicals to determine the consequences of an accident or exposure. Are the chemicals you use corrosives, carcinogens, etc.? Second, consider the likelihood of an accident or exposure. This depends on the quantities of the chemicals used, the manner in which they are used, and the properties of the chemicals. Do you use five gallon cans of a flammable solvent? What is its flash point? Are toxic powders and volatile chemicals used in a fume hood? How much is used? What is the degree of their toxicity? A third indicator of risk is accident history. Ask your principal investigator and other researchers who do similar work about accidents and exposure incidents that have occurred with chemicals you will use.

This analysis will not precisely rank your chemical risks, but it can help you assess the relative risks of the chemicals you use. Most importantly, you'll know which chemicals require extra care, and where you should focus your safety efforts.

Annex 2-2 also contains an excellent Chemical Hazard Risk Assessment Form developed by the University of Arizona's Department of Risk Management and Safety.

2.2.d Reproductive Health Hazards

Some chemicals can cause damage to the reproductive systems of men or women leading to infertility, impotence, menstrual irregularities, spontaneous abortion or damage to offspring. Chemicals include heavy metals, some aromatic solvents (benzene, toluene, xylenes, etc.), and some therapeutic drugs.

Reproductive toxins are substances that cause chromosomal damage (*mutagens*) and substances with lethal or teratogenic (malformation) effects on fetuses. **Embryotoxins** or **fetotoxins** are substances that may be lethal to the fertilized egg, embryo or fetus, may be teratogenic (i.e., cause fetal malformations), may retard growth or may cause postnatal functional deficits. Male reproductive toxins can in some cases lead

Reproductive toxins can produce adverse effects in parents and developing embryos.

to sterility. Two well known male reproductive toxins are ethylene dibromide and dibromochloropropane.

Teratogens

When a pregnant woman is exposed to a chemical, some chemicals can cross the placental barrier affecting the fetus. A developing fetus may be more sensitive to some chemicals than the pregnant mother, especially during the first twelve weeks of pregnancy when the mother may be unaware she is pregnant.

Teratogenic chemicals are those substances that cause fetal death or malformation from maternal exposure during pregnancy. These **teratogens** are agents which interfere with normal embryonic and fetal development without apparent damage to the mother or lethal effects on the fetus. Because cellular genetic effects are not produced, these effects are not hereditary. Known human teratogens include organic mercury compounds, lead compounds, 1,2-dibromo-3-chloropropane, ionizing radiation, some drugs, alcohol ingestion, and cigarette smoking. Some substances which may cause adverse reproductive effects in males include 1,2-dibromo-3-chloropropane, cadmium, mercury, boron, lead, some pesticides, and some drugs. More than 800 chemicals have been shown to be teratogenic in animal models; many of these are suspected human teratogens.

Embryotoxins are substances that act during pregnancy to cause adverse effects on the fetus. These effects include death of the fertilized egg, the embryo, or the fetus, malformation, retarded growth and postnatal functional deficits. Examples of embryotoxins include organomercurials, lead compounds, and formamide.

Mutagens

A **mutagen** affects the genetic material of exposed cells. Mutations can occur on the gene level (gene mutations) as when one nucleotide base-pair is change to another. Mutations can also occur on the chromosomal level (chromosomal mutations) when the number of chromosomal units or their morphological structure is altered. The effect is inherited by daughter cells and, if it occurs in the gonads or reproductive organs, can become part of the genetic pool that is passed on to future generations. Examples of mutagens commonly found in biomedical research laboratories include: ethidium bromide, barium permanganate, methyl isocyanate and radioisotopes.

Known Reproductive Health Hazards

No recognized comprehensive list of known human reproductive toxins exists. The Occupational Safety and Health Administration (OSHA) only regulates four agents based on their reproductive toxicity: lead, ionizing radiation, 1,2-dibromo-3-chloropropane (DBCP), and ethylene oxide. Appendix D lists those substances considered to be reproductive toxins by the National Institute for Occupational Safety and Health (NIOSH), the State of California, and the U.S. Air Force.

Remember, toxicological data is lacking for a large number of chemicals. This is especially true for data on the human reproductive health effects. Most commercial chemicals and physical factors have not been thoroughly evaluated for their possible toxic effects on reproduction and development. Information on suspected reproductive health hazards is derived primarily from animal studies, which present problems of interpretation in extrapolating to effects in humans. Individuals also vary widely in susceptibility and extent of exposure to reproductive hazards. Proper handling of chemicals and use of protective equipment is effective in reducing fetal exposure to chemicals (see Chapter 4).

Appendix D discusses select carcinogens, reproductive toxins and substances with a high degree of acute toxicity.

Persons working with teratogens and other reproductive health hazards and those who are contemplating pregnancy or are already pregnant should review the toxicity of the chemicals in their workplace and, if concerned, should consult with the Safety Department to determine whether any of the materials pose additional risk during pregnancy and possible means to reduce those risks.

2.2.e Particularly Hazardous Substances

A group of chemicals have been evaluated and determined to have the potential to be particularly hazardous. These include acutely toxic substances, selected carcinogens and reproductive toxins. Labs with these substances must take the additional precautions described in Appendix D when working with these agents.

2.3 Sources of Chemical Safety Information

Safety is each worker's responsibility. A worker should be deeply involved in performing hazard evaluations and risk assessments for the procedures and compounds which will be used. As the worker grows in experience, this assessment / evaluation may become more cursory, particularly if the worker has performed similar procedures with similar compounds.

While this assessment effort may at first seem extreme, one must remember that chemical safety is inherently linked to other safety issues including laboratory procedures, personal protective equipment, electrical safety, fire safety, and hazardous waste disposal. The following equation summarizes reality:

$$\text{Chemical Safety} = \text{Knowledge} + \text{Common Sense} + \text{Caution}$$

A goal of this chapter is to provide information to enable you to obtain knowledge. There are many sources of information a worker can use to help in knowing the toxicity and hazard of a substance and how to work safely with each chemical.

2.3.a Chemical Hygiene Plan

Workers are provided with a relatively safe work place. Even if their work is considered to be *research*, there are standard procedures to insure the work can be done safely. Federal and state rules require that these procedures be made available to workers by requiring that every workplace in which hazardous chemicals are used have a written **Chemical Hygiene Plan (CHP)** which includes these procedures.

Your lab's CHP will include provisions capable of protecting workers from the physical and health hazards associated with the chemicals present in the laboratory. All laboratory workers should be familiar with the information in their lab's CHP.

Appendix C provides a template for completing a CHP. The information in this *Laboratory Safety Guide* can be referenced so your CHP need only provide procedures for handling specific laboratory chemicals (e.g., particularly hazardous substances). In these instances other references may be needed to better evaluate potential hazards.

2.3.b Material Safety Data Sheet

OSHA requires chemical manufacturers and suppliers provide users with **Material Safety Data Sheets (MSDS)**. These are designed to provide the information needed to protect workers from hazards associated with the chemical. Labs are required to have MSDSs for all chemicals and make them readily available to workers.



SIGMA-ALDRICH

Material Safety Data Sheet
 Date Printed: 07/27/2001
 Date Updated: 03/01/2001
 Version 1.70

Section 1 - Product and Company Information

Product Name	ACETONE		
Product Number	00585		
Brand	Fluka Chemical		
Company	Sigma-Aldrich		
Street Address	3050 Spruce Street		
City, State, Zip, Country	St. Louis, MO 63103 US		
Technical Phone:	3147715765	Emergency Phone:	414 273 3850 Ext.5996
Fax:	8003255052		

Section 2 - Composition/Information on Ingredient

<u>Substance Name</u>	<u>CAS #</u>	<u>SARA 313</u>
ACETONE	67-64-1	No
Formula	C3H6O	
Synonyms	Aceton (German, Dutch, Polish), Acetone (ACGIH:OSHA), Chevron acetone, Dimethylformaldehyde, Dimethylketal, Dimethyl ketone, Ketone, dimethyl, Ketone propane, beta-Ketopropane, Methyl ketone, Propanone, 2-Propanone, Pyroacetic acid, Pyroacetic ether, RCRA waste number U002	

Section 3 - Hazards Identification

Emergency Overview
 Flammable (USA) Highly Flammable (EU). Irritant.
 Irritating to eyes and skin. Repeated exposure may cause skin dryness or cracking. Vapors may cause drowsiness and dizziness.
 Target organ(s): Liver, Kidneys.

HMSIS Rating
 Health: 2* Flammability: 3 Reactivity: 0

NFPA Rating
 Health: 2 Flammability: 3 Reactivity: 0

*additional chronic hazards present.
 For additional information on toxicity, please refer to Section 11.

Section 4 - First Aid Measures

Oral Exposure
 If swallowed, wash out mouth with water provided person is conscious. Call a physician.

Inhalation Exposure
 If inhaled, remove to fresh air. If not breathing give artificial respiration. If breathing is difficult, give oxygen.

Dermal Exposure
 In case of contact, immediately wash skin with soap and copious amounts of water.

The MSDS provides a variety of fundamental health and safety information related to the chemical. This information will allow the user of the chemical to recognize and prepare for potential hazards associated with the chemical and prepare for and react to emergency situations

Risk assessment begins when the laboratory worker examines their experimental plan in order to identify the chemicals with toxicological properties with which they are not familiar. The worker should then review the MSDS for each of the unfamiliar chemical they will use.

Although federal rules do not mandate a format for the MSDS, manufacturers normally publish their MSDS following one of two generic formats (see table):

- ✓ OSHA Form 174 with 8 major sections
- ✓ American National Standards Institute (ANSI) has a 16-section format.

Annex 2-3 contains a thorough discussion of the ANSI format and content, the basic information found in both forms include:

OSHA Form 174	ANSI
Chemical Identity	1. Product and company identification
Section I. Manufacturer's Name and Contact Information	2. Hazards identification
Section II. Hazardous Ingredients / Identity Information	3. Composition / information on ingredients
Section III. Physical / Chemical Characteristics	4. First aid measures
Section IV. Fire and Explosion Hazard Data	5. Fire-fighting measures
Section V. Reactivity Data	6. Accidental release measures
Section VI. Health Hazard Data	7. Handling and storage
Section VII. Precautions for Safe Handling and Use	8. Exposure controls / personal protection
Section VIII. Control Measures	9. Physical and chemical properties
	10. Stability and reactivity
	11. Toxicological information
	12. Ecological information
	13. Disposal considerations
	14. Transport information
	15. Regulatory Information
	16. Other information

Name of supplier (with address and phone number) and date MSDS was prepared or revised -- because toxicity data and exposure limits may be revised, the MSDS

should be reviewed to insure information is still correct. The phone number provides a point-of-contact for additional information on hazards and emergency response.

Name of the chemical -- The identity of the substance as it appears on the label, for mixtures, this may include the identity of most, but not every ingredient.

Common synonyms are often listed.

Physical and chemical properties -- boiling point, molecular weight, vapor pressure, vapor density, specific gravity, melting point, evaporation rate, solubility in water, physical appearance and odor.

Physical hazards - related to flammability, reactivity, and explosibility. Flammability information may include flash point (and method used to determine it), flammability limits, extinguishing media, special fire fighting procedures, unusual fire and explosion hazards. Reactivity includes stability, conditions to avoid, incompatibility (materials to avoid), hazardous decomposition or byproducts, hazardous polymerization (and conditions to avoid).

Toxicity data -- OSHA and American Conference of Governmental Industrial Hygienist (ACGIH) exposure limits are listed. Lists the hazardous components by chemical identity and other common names. Includes OSHA Permissible Exposure Limit (PEL), ACGIH Threshold Limit Value (TLV) and other recommended exposure limits. May also include the percentage listings of the hazardous components.

Health hazards -- Acute (immediate) and chronic (build up over time) health hazards, routes of entry (inhalation, skin, ingestion), carcinogenicity (NTP, IARC monographs, OSHA regulated), signs and symptoms of exposure, medical conditions generally aggravated by exposure, emergency and first aid procedures.

Storage and handling procedures -- precautions for handling or storage and listing appropriate control measures including respiratory protection, ventilation (local, mechanical exhaust, special or other), protective gloves, eye protection, other protective clothing or equipment, work/hygienic practices, first aid treatment, steps to take if the material is released or spilled, and guidelines for the proper disposal of waste material. Because the MSDS is written to address the widest conceivable use of the material, the recommended procedures may be more stringent than necessary for laboratory use.

	METHYL ALCOHOL CAS:67-56-1 DOT-ID:NA 1230
	Protective Equipment OSHA Table Z-1-A air contaminant. Approved canister mask for high vapor concentrations; safety goggles; rubber gloves.
MaxiSoft, Inc.	

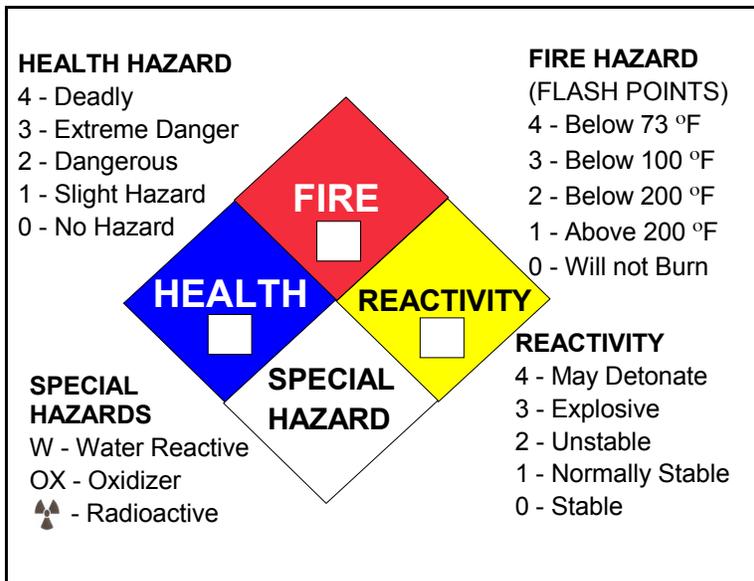
2.3.c Labeling Systems

Labels on containers can also be a source of safety information. There are several standardized labeling systems which workers may see in the work place. The most commonly types of labeling system encountered are the Department of Transportation (DOT), the National Fire Protection Association (NFPA), and the Hazardous Materials Information Systems (HMIS) (see Annex 2-4).



DOT Labels

When chemicals are shipped or transported in the public sector, there must be labels to satisfy DOT rules. Many larger containers (e.g., 5-gallon cans) are also individually labeled with the standard DOT labels. These labels are designed to identify DOT classes of hazardous materials (see Annex 4-1). These DOT labels are diamond-shaped and color-coded by hazard. The hazard class or division number appears in the lower corner. If you are



involved in the shipment or receipt of hazardous materials, you must be trained to assess the hazard and be capable of responding in an emergency. The Safety Department conducts training classes which will allow you to comply with DOT requirements, call 262-8769 and schedule a training session.

NFPA Labels

The popular NFPA diamond was developed by the *National Fire Protection Association* to aid emergency responders in recognizing potentially hazardous situations. The label contains 4 colored diamond shapes. Each colored diamond is

associated with a different type of physical or health hazard. However, because this system refers to the hazards associated with the material under fire-type conditions, the information is of limited value for routine laboratory use of the chemical.

HMIS Labels

Another popular system was developed by the *National Paint and Coatings Association*. It contains 4 different colored rectangular shapes that are related to different hazards. As opposed to the NFPA label, the Hazard Materials Information System (HMIS) rates the material risks under normal use conditions.



NFPA and HMIS Labeling Systems

Workers will probably see both types of labels used on containers. At first glance, these labeling systems appear quite similar. On both the NFPA and HMIS label, each color represents a specific type of hazard:

- ✓ **Blue** stands for health hazard
- ✓ **Red** means flammability hazard
- ✓ **Yellow** is reactivity hazard (NFPA) or **Orange** is physical hazard (HMIS)
- ✓ **White** stands for special hazard information or special notice

The blue, red, and yellow/orange sections also contain a number from 0 to 4 that tells the degree of hazard. The number 4 is for the most serious hazard, 0 the least serious. Annex 2-4 thoroughly explains each of these rating. The white section of the label uses no numbers. If a material presents a special hazard, then a symbol or phrase may be placed in the white section giving special attention. The HMIS label will sometimes note personal protective equipment using specially designated icons.

However, there are significant differences between the two systems. The HMIS system attempts to convey full health warning information to all employees while the NFPA diamond conveys hazard information to fire fighters and other emergency responders. HMIS is not intended for emergency circumstances.



The current version of the HMIS, called HMIS[®] III replaced an earlier system. The revision replaced a yellow Reactivity section (similar to the NFPA reactivity section) with the orange Physical Hazard section. While both types of labels may be seen, the label with the yellow Reactivity type label will ultimately vanish.

The HMIS label attempts to convey full health warning information to the user just as it is listed on an MSDS. Lets look at the information each of the sections of the label provide.

Health -- This conveys the health hazards of the material. The blue Health bar has two spaces, one for an asterisk and one for a numeric hazard rating. The asterisk, if present, indicates the substance is a *chronic health hazard*, meaning that long-term exposure to the material could cause a health problem such as emphysema or kidney damage. The NFPA diamond lacks this "chronic" information because NFPA is meant only for emergency or acute (short-term) exposures. The numbering system uses a 0 to 4 scale where 0 indicates minimal hazard and 4 indicates an extreme hazard.

Flammability -- Initially the NFPA and HMIS used the same criteria to assign numeric values (0 = low hazard to 4 = high hazard). In HMIS III, the flammability criteria are defined according to OSHA standards (see Annex B-1). OSHA defines a flammable liquid as "any liquid having a flash point below 100 °F (37.8 °C), except any mixture having components with flash points of 100 °F (37.8 °C) or higher, the total of which make up 99 percent or more of the total volume of the mixture. Flammable liquids shall be known as Class I liquids."

Physical Hazard -- HMIS III replaced the Reactivity (yellow) rating of HMIS II with an orange section using the OSHA criterion of physical hazard. Seven such hazard classes are recognized:

- ◆ water reactives
- ◆ organic peroxides
- ◆ explosives
- ◆ compressed gases
- ◆ pyrophoric materials
- ◆ oxidizers
- ◆ unstable reactives

The numerical rating values of 0 = low hazard / stable to 4 = high hazard / may detonate, are used to describe the magnitude of hazard from the substance.

Personal Protection -- This is by far the largest area of difference between the NFPA and HMIS systems. As described in Annex 2-4, the white diamond in the NFPA system is used to convey special hazards (e.g., water reactive, oxidizer, radioactive, etc.). The white section in the HMIS label indicates the personal protective

equipment that should be worn when working with the material. One drawback of the HMIS Personal Protection coding system is that it uses a letter coding system to prescribe the required protective equipment. The reason this is a drawback is that some of the letters / symbols used are used by other hazard communication systems and have completely different meanings and applications. Listed here, for your reference are the HMIS Personal Protection codes and corresponding equipment needs:

PROTECTIVE EQUIPMENT GUIDE	
A	
B	
C	
D	
E	
F	
G	
H	
I	
J	
K	

- A Safety Glasses
- B Safety Glasses, Gloves
- C Safety Glasses, Gloves, Apron
- D Face Shield, Gloves, Apron
- E Safety Glasses, Gloves, Dust Respirator
- F Safety Glasses, Gloves, Apron, Dust Respirator
- G Safety Glasses, Gloves, Vapor Respirator
- H Splash Goggles, Gloves, Apron, Vapor Respirator
- I Safety Glasses, Gloves, Dust and Vapor Respirator
- J Splash Goggles, Gloves, Apron, Dust and Vapor Respirator
- K Air Line Hood or Mask, Gloves, Full Suit, Boots
- X Ask supervisor or safety specialist for handling instructions

CAS # 67-64-1 **Warning!**

Flammable

Isopropyl Alcohol
dimethyl carbinol; 2-hydroxypropane; IPA; isopropanol; rubbing alcohol

Colorless liquid; slight odor. Irritating to the eyes/skin/respiratory tract. Eye exposure may cause corneal burns. Also Causes: drowsiness, dizziness, and incoordination. Chronic: dermatitis. Flammable!

PPE

Goggles Gloves Apron Check the use is respirator required?

Target Organs

Eye Skin Respiratory System Nervous System Kidneys

Emergency Procedures

First Aid
 Inhalation: Remove to fresh air and support breathing as needed. Eyes/Skin: Remove contaminated clothing. Flush with plenty of water for at least 15 min. Ingestion: Do not induce vomiting! Consult physician.

Fire
 Highly flammable. Can form explosive mixtures in the air. Use water as fog, dry chemical, carbon dioxide, or alcohol-resistant foam. Solid streams of water may spread fire.

Spills & Leaks
 Notify safety personnel, isolate and ventilate area, deny entry, stay upwind. Shut off heat and ignition sources. Take up with inert material such as sand or vermiculite. Cleanup personnel should protect against exposure.

Consult MSDS 0324 for more information H-2

For example, consider the NFPA labeling for a container of methanol. A hazard degree rating of 1 has been assigned to the health hazard which means the material is a slight hazard. The flammability rating is 3 which means it has a flash point below 100 °F and will readily ignite at normal temperatures. The reactivity rating of 0 means that the material is stable. Personal protective equipment includes safety goggles, rubber gloves and apron. Other symbols which might be used include no smoking, no open flames, no matches. Since it is poisonous, the "skull & crossbones" symbol or the word "poison" would appear on the NFPA label. The target organs affected from a hazardous exposure are blood, eyes, intestines, and stomach.

Other Labeling Systems

While the NFPA and HMIS systems are relatively common, some vendors have created their own label system which incorporates information from one or both of these labels. When looking at containers, look for the common elements rather than the differences (e.g., are the hazard ratings high or low, special equipment, etc.).

Labeling Secondary Containers

Sometimes workers need only a small amount of material for a specific task and may transfer the amount of chemical they need from

METHANOL

CAS #67561

CAUTION

HEALTH HAZARDS: Combustible, Do not sewer, Flammable, Poison, Store below 212 F.
 ORGANS HAZARDS : Blood, Eyes, Intestines, Stomach.

FLAMMABLE! No smoking, matches or open flames!
 FIRST AID: Immediately flush eyes w/ water for 15 minutes. Ingestion: Do not induce vomiting - give warm milk or water - call 911.



HAZARD RATINGS

4	Severe
3	Serious
2	Moderate
1	Slight
0	Minimal

HEALTH HAZARD: 3
 FIRE HAZARD: 3
 REACTIVITY: 0
 SPECIFIC HAZARD: --

CONSULT MATERIAL SAFETY DATA SHEET FOR FURTHER INFORMATION ON HAZARDS

the original container to a smaller, more portable, *secondary container*. If all of the material is to be used immediately by the employee who transferred the material, the secondary container need not have a label. However, the chemical can **only** be used by the worker who transferred it and it must be only used on that shift. It is better to label any secondary container with all the necessary information.

2.4 Toxicology Overview

"All substances are toxic. There is no substance without toxicity. It is solely the dose which determines toxicity."

--Paracelcus, 16th century alchemist

Examples of exposure to multiple chemicals:

- 1) **Additive effect** - combined toxicity is equal to the sum of toxicity of individual chemicals.
- 2) **Antagonistic effect** - combined toxicity is less than the sum of toxicity of individual chemicals.
- 3) **Independent effect** - chemical toxicities are independent of each other.
- 4) **Potentiating effect** - a chemical with a lower toxicity causes another chemical to have a higher toxicity than if the first chemical wasn't present.
- 5) **Synergistic effect** - combined toxicity is greater than the sum of toxicity of individual chemicals.

This assertion is the foundation of toxicology. It is important to determine your degree of exposure to a toxic agent, not merely that a particular chemical is present in the laboratory.

The chemicals used in research labs have a broad spectrum of physical, chemical, and toxicological properties and potential physiological effects. Understanding the risks associated with the use of laboratory chemicals is complicated because the risk of toxic effects is related to both the extent of exposure and the toxicity of a chemical. Factors included in exposure include the dose, duration and frequency of exposure and route of exposure.

Exposure to large doses of chemicals with little toxicity normally poses little risk. However, small quantities of chemicals with high toxicity or corrosivity may produce significant adverse effects. Duration and frequency of exposure also determine whether a chemical will produce harmful effects. In some instances, a single exposure to a chemical may produce poisoning. For others, repeated exposures are required to produce a toxic effect. The route of exposure (e.g., via the skin, eyes, gastrointestinal tract or respiratory tract) is crucial in assessing risk. For some chemicals, the effect on a single "*target*" organ may be the overriding concern.

Cumulative effects may occur if exposure is from materials that tend to build up in the body as a result of numerous chronic exposures. The effects are not seen until a critical body burden is reached (e.g., heavy metals).

Combinations of substances may result in toxic effects which are significantly greater than the toxic effect of either substance alone. For this reason, it is prudent to assume the product of a chemical reaction may be more toxic than the most toxic ingredient.

Thus, while previous sections described the various physical, chemical, and toxicological properties of chemicals, this section discusses some of the terminology encountered in toxicology as they relate to routes of exposure, sites of action, and acute and chronic toxicity. These terms are important to understanding the toxicity information published in safety documents (e.g., Material Safety Data Sheets, labels) and for assessing potential chemical exposure.

2.4.a Routes of Exposure to Chemicals

Remember, the presence or use of a hazardous chemical in the laboratory is not sufficient for it to present a risk to your health. **Risk involves exposure to a chemical.** That is, the chemical must come in contact with or enter the body and reach a site where the chemical exerts its effect. The paths a chemical uses to enter into the body are called **routes of entry**. Inhalation, skin absorption and ingestion are all routes of entry for toxic chemicals. A chemical may be severely toxic by inhalation but pose only moderate toxicity by other routes. Thus, it is extremely important to know the chemical's toxicity by each route of entry.

On the Material Safety Data Sheet (MSDS), toxicity by route of entry is shown. Abbreviations describing the route of administration used in the toxicity studies are:

SKN applied to the skin, to test for irritation or for systemic toxicity through dermal absorption.

ORL oral route, intragastric administration, or mixed with food or water.

IPR administration into the peritoneal (stomach / intestine) cavity.

SCU subcutaneous administration of the chemical.

IVN intravenous administration of the chemical.

IHL administration of the chemical through inhalation.

Inhalation (via the lungs) is usually the most critical route of exposure because the surface area of the lining of the lungs is as large as a tennis court, the lungs transfer chemicals directly into the bloodstream and we breathe large volumes of air. Most exposure standards are based on the inhalation route of exposure and are expressed in terms of parts per million (ppm), as μmole substance to mole total air (0.21 mole O_2 + 0.79 mole N_2), or as milligrams per cubic meter (mg/m^3) concentration in air.

2.4.b Sites of Action

The effects of chemicals on the body are classified as local or systemic depending upon the site of action. For a chemical to express its toxic characteristics it must come in contact with a target organ. If the effect is produced directly at the point of surface contact, without first being absorbed into the circulatory system, the lesions produced are considered to be **local effects**. Areas commonly damaged by local effects include the eyes, skin, lung and intestinal tract surfaces. If the effects are produced in tissues as a consequence of absorption and dissemination through the circulatory system, or are produced in tissues or organs away from the site of original contact, the lesions or effects are considered to be **systemic effects**. Chemicals can, of course, produce both types of effects.

Local: effect takes place at the point of contact.

Systemic: effect occurs at site other than the point of contact.

2.4.c Acute Toxicity

All chemicals are toxic under some condition of exposure. In order to compare the toxicity characteristics of chemicals, it is necessary to define these exposure conditions as well as the quantity involved in the exposure. **Acute toxicity** is the ability of a chemical to cause a harmful effect after a single exposure to the substance by any route for a short (i.e., acute) period of time (e.g., less than one day). Acute toxicity information consists of (1) lethality data, the levels of exposure (LC_{50}) or dose (LD_{50}) estimated to kill 50 percent of a specific population of animals under controlled

conditions and (2) dose-response (mortality) relationships. On MSDSs, the degree of acute toxicity is expressed by these acronyms:

LD_{Lo} The lowest dose of a material introduced by any route, other than inhalation, over any given period of time in one or more divided portions and reported to have caused death in humans or animals.

LC_{Lo} The lowest concentration of a material in air, which has been reported to have caused death in humans or animals.

LD₅₀ Lethal Dose to 50 percent of a population (of lab animals). The amount of dose, in mg/kg of body weight, to kill one-half of the animals to which it is administered. This is widely used as an index of toxicity. The lower the *LD₅₀*, the more toxic the substance.

LC₅₀ Lethal Concentration to 50 percent of a population (of lab animals). Refers to an airborne concentration of a contaminant that will kill one-half of the population of study organisms. Used as an index of toxicity. The lower the *LC₅₀*, the more toxic the substance.

Categories of acute lethal toxicity have been developed by toxicologists. An example of such a classification is given in the Classes of Acute Toxicity table.

Classes of Acute Toxicity

Toxicity Class	Dose (amount of substance per kg of body weight)	Probable Oral Lethal Dose (for a 70 kg Adult Human)	Examples	Rat Oral LD ₅₀ of Example
Practically nontoxic	> 15 g/kg	More than 1 quart	Sucrose	29.7 g/kg
Slightly toxic	5 - 15 g/kg	Between a pint and a quart	Ethanol	14 g/kg
Moderately toxic	0.5 - 5 g/kg	Between an ounce and a pint	Sodium Chloride	3 g/kg
Very toxic	50 - 500 mg/kg	Between a teaspoonful and an ounce	Caffeine	192 mg/kg
Extremely toxic	5 - 50 mg/kg	Between 7 drops and a teaspoon	Sodium Cyanide	6.4 mg/kg
Supertoxic	< 5 mg/kg	A taste (less than 7 drops)	Strychnine	2.5 mg/kg

If any of the following criteria are satisfied for a particular chemical, then it is considered **very toxic**:

- ✓ A chemical that has a median lethal dose (*LD₅₀*) of more than 50 mg per kilogram, but not more than 500 mg per kilogram of body weight when administered orally to rats.
- ✓ A chemical that has a median lethal dose (*LD₅₀*) of more than 200 mg per kilogram but not more than 1000 mg per kilogram of body weight when administered by continuous contact for 24 hours (or less if death occurs within 24 hours) with the bare skin of rabbits.

- ✓ A chemical that has a median lethal concentration (LC_{50}) in air of more than 200 ppm but not more than 2000 ppm by volume or less of gas or vapor, or more than 2 mg per liter but not more than 20 mg per liter of mist, fume, or dust, when administered by continuous inhalation for one hour (or less if death occurs within one hour) to rats.

Additionally, if any of the following criteria are satisfied for a particular chemical, then it is considered **extremely toxic**:

- ✓ A chemical that has a median lethal dose (LD_{50}) of 50 mg or less per kilogram of body weight when administered orally to rats.
- ✓ A chemical that has a median lethal dose (LD_{50}) of 200 mg or less per kilogram of body weight when administered by continuous contact for 24 hours (or less if death occurs within 24 hours) with the bare skin of rabbits.
- ✓ A chemical that has a median lethal concentration (LC_{50}) in air of 200 ppm by volume or less of gas or vapor, or 2 mg per liter or less of mist, fume, or dust, when administered by continuous inhalation for one hour (or less if death occurs within one hour) to rats.

2.4.d Chronic Toxicity

Chronic toxicity is the toxic effect resulting from repeated, low-level daily doses over a person's or animal's lifetime. These chronic effects can result from cumulative damage to tissues sustained from each small dose, or they can result from accumulation of the toxic chemical in the body over a long period of low-level exposure (e.g., mercury, lead). Latent effects, such as carcinogenicity or mutagenicity, are examples of long term or chronic effects. The damage done from one large or multiple low-level exposures to a carcinogen is often delayed. Thus, a cancer may not show up until after a 10 to 20 year latent period has elapsed. Likewise, the effect of exposure to a mutagen may not manifest itself until the birth of offspring with malformations resulting from the mutation.

2.4.e Hazard Exposure Guidelines

While higher exposures are generally more worrisome than lower ones, for a specific agent there may be a threshold exposure below which toxic effects do not occur. However, determining this threshold is often difficult. We know, for instance, that heavy alcohol consumption by a pregnant female can result in Fetal Alcohol Syndrome in her child. The unknown is whether there is some lesser amount of alcohol consumption which poses no risk to the fetus. For other agents there may be no safe dose; ingestion of as little as a single 50 mg capsule of thalidomide by a pregnant female can cause malformations in her child.

Individuals respond differently when exposed to chemicals.

Individual biology can also make a difference. Each person has a different degree of susceptibility or sensitivity to the effects of chemical exposure. Additionally, most people are exposed to more than one, often many chemicals at once. Data is available on the toxic effects of individual chemicals, but simultaneous chemical exposure can result in complex interactions which we do not yet fully understand.

There is no such thing as zero exposure to a chemical. If the chemical is present in the laboratory, and you are working with it, then you are probably exposed to it at some level.

Several sets of exposure standards have been established.

The American Conference of Governmental Industrial Hygienists (ACGIH) and the Occupational Safety and Health Administration (OSHA) have established limits for workplace exposures. The ACGIH's Threshold Limit Values (TLVs) are guidelines for use by industrial hygienists. TLVs represent an average level of exposure that a healthy worker can be exposed to over an 8-hour work day, 40-hour work week, essentially forever, without suffering significant adverse effects. The Permissible Exposure Limits (PELs) established by OSHA are more than just guidelines, they have the force of law and employers are responsible for assuring that their employees are not exposed to levels above the PEL. In many instances, the PEL and TLV are the same number. In stances where one is lower than the other, it is prudent to maintain exposures at the lowest level achievable.

On MSDSs, you will see acronyms for standards and regulations governing workplace chemical exposure:

- IDLH* Immediately Dangerous to Life or Health: Maximum concentration from which one could escape within 30 minutes without any escape-impairing symptoms or any irreversible health effects.
- ACGIH* American Conference of Governmental Industrial Hygienists
- TLV* Threshold Limit Value: refers to airborne concentrations of substances to which it is believed that nearly all workers may be repeatedly exposed day after day without adverse health effects. Established by the ACGIH as guidelines for use by professional industrial hygienists.
- SKIN* If a significant route of exposure for a substance is through the skin, mucous membranes and eyes, either by air or direct contact, the TLV or PEL will have a "skin" notation. Examples include pesticides, carbon tetrachloride, cyanides, ethylenediamine and thallium. This additional exposure route must be considered part of the total exposure to avoid exceeding the TLV for that substance.
- TWA* Time-Weighted Average: An average airborne concentration over an eight-hour work shift. Exposures may be somewhat higher or lower than the average at various times of the day as is normally the case in a work environment.
- STEL* Short-term Exposure Limit: Establishes a safe exposure limit of no more than four 15-minute periods a day. Limits established to avoid: 1) irritation, 2) chronic or irreversible tissue damage, or 3) narcosis of sufficient degree to increase the likelihood of accidental injury. Limits are published only for compounds where toxic effects have been reported from high, short duration exposures and are typically no more than 25 - 200% higher than the TLV.
- C* If a "C" precedes the TLV, this is a **ceiling** exposure limit; the concentration that should not be exceeded even instantaneously.
- PEL* Permissible Exposure Limit: Similar to a TLV, but established by OSHA as the legal limit for employee exposure. Employers have the legal responsibility to ensure that their employees' exposures do not exceed the PELs.

- OSHA* Occupational Safety and Health Administration: Federal Government agency, part of the Department of Labor, charged with ensuring the health and safety of private sector workplaces in the U.S. Establishes and enforces safety and health regulations.
- NIOSH* National Institute for Occupational Safety and Health: Part of the Centers for Disease Control of the Public Health Service of the U.S. Department of Health and Human Services. It conducts research and development in Occupational Safety and Health. Advises OSHA in rulemaking and standard-setting. Does respirator testing and approvals. Supports the training of industrial hygienists and occupational health nurses and physicians.
- REL* Recommended Exposure Limit: Similar to a TLV, but established by NIOSH, not ACGIH.
- Action Level* This is an OSHA term which pertains to a few substance-specific regulations. It is an airborne concentration (lower than the PEL) that, when exceeded, requires certain activities such as exposure monitoring or medical surveillance.

These limits pertain primarily to the inhalation exposure route (cf., skin); so they are airborne concentrations. For this type exposure, the lung is usually the most critical route of entry. Exposures via other routes, such as ingestion and skin absorption, must also be taken into account to determine if an excessive exposure is present.

2.4.f Exposure Risk Assessment

The question then is: How can one gauge exposure risk? Annex 2-2 provides guidelines. The MSDS provides a wealth of information. But, suppose there is no MSDS? One can still consider the MSDS hazard conditions to determine exposure risk:

- ◆ Physical state: vapor pressure, fluidity, loftability, lipid solubility, skin absorption.
- ◆ Chemical properties: air reactivity (flammability), water reactivity (heat, splatter, ignition, gas generation), acidity / basicity, self reactivity (explosive, polymerization) and potency as oxidizer.
- ◆ Toxicity: chronic, acute, sensitizer.

In some cases the Safety Department can measure your workplace air concentrations of chemicals. Call if you are concerned about your exposure or would like advice on controlling chemical exposure. Read the guidelines in Chapter 4 on controlling chemical hazards in the laboratory. Overexposure to hazardous chemicals is a possibility when:

- ◆ Volatile or airborne chemicals are used outside of a fume hood or some other containment.
- ◆ An aerosol results in direct contact with skin or eyes.
- ◆ There is an accidental ingestion.
- ◆ You are in the vicinity of an accidental spill or gaseous release.

If you are concerned about the physical effect from a chemical exposure, see a physician. Information on the signs and symptoms of an overexposure can be obtained from a physician, an MSDS, and the Poison Control Center (262-3702). Students

If you are concerned about effects to your health from exposure to a chemical, see a physician. You may receive medical care from the University Health Service. Call the Safety Department for guidance in seeking medical assistance for chemical exposures. If you feel that you may have had a harmful exposure, see a physician immediately. For emergency care, go to a hospital emergency room. University Police (dial 911) can arrange for emergency transport.

2.5 Review Questions

- A _____ is a chemical known to cause cancer in humans.
a. nephrotoxin b. corrosive c. carcinogen d. mutagen
- A flammable liquid will emit enough vapors to be ignited by a spark source at temperatures:
a. above absolute zero b. above 22 °C (70 °F)
c. below 38 °C (100 °F) d. above its freezing point
- A _____ substance will burst into flames upon contact with air.
a. explosive b. peroxide-former c. teratogenic d. pyrophoric
- Nephrotoxic agents damage the:
a. kidney b. pancreas c. spleen d. liver
- A teratogen can cause birth defects in:
a. anybody b. pregnant women c. postmenopausal women d. males
- A chemical described as having a local effects causes damage that is:
a. widespread b. where the chemical contacts the body
c. inflicted upon everyone in the area d. not inflicted on foreigners and tourists
- The lower the LD₅₀, the _____ the chemical is.
a. less toxic b. more corrosive c. more toxic d. more flammable
- The routes of entry of toxic chemicals into your body include:
a. inhalation b. ingestion c. absorption through skin d. all of the above
- The oral rat LD₅₀ is a commonly used index of:
a. flammability b. corrosivity c. carcinogenicity d. acute toxicity
- A person who develops a rash when contacting nickel salts has been:
a. tagged b. poisoned c. sensitized d. corroded
- The most common chemical route of entry is:
a. ingestion b. inhalation c. skin / eye contact d. injection
- Cryogenic liquids can:
a. displace air in a lab b. freeze skin c. embrittle materials d. explode e. all of the above
- _____ is an example of a blood toxin:
a. formaldehyde b. ozone c. uranium compounds d. nitrites

14. Every lab must have a chemical hygiene plan (CHP) and Material Safety Data Sheets (MSDS).
 - a. true
 - b. false
15. The NFPA label describes a chemical's hazards under everyday use situations.
 - a. true
 - b. false
16. The HMIS label rates the material risks under normal use conditions.
 - a. true
 - b. false
17. _____ toxicity is the toxic effect resulting from repeated, low-level chemical exposure.
 - a. acute
 - b. lethal
 - c. chronic
 - d. general
18. The STEL is a safe exposure limit of no more than four 15-minute exposure periods a day.
 - a. true
 - b. false
19. A "C" (ceiling) is a TLV limit whose concentration should never be exceeded.
 - a. true
 - b. false
20. An exposure risk assessment considers the MSDS hazard conditions of:
 - a. physical state
 - b. chemical properties
 - c. toxicity
 - d. all of the above

Annex 2-1. Glossary of Chemical Hazard Terms

- ACGIH** - The American Conference of Governmental Industrial Hygienists consists of occupational safety and health professionals who recommend occupational exposure limits for many substances.
- Action Level** - An OSHA concentration calculated as an 8-hour time-weighted average, which initiates certain required activities such as exposure monitoring and medical surveillance.
- Acute Health Effect** - A severe effect which occurs rapidly after a brief intense exposure to a substance.
- ANSI** - American National Standards Institute is a private group that develops consensus standards.
- Asphyxiant** - A chemical (gas or vapor) that can cause death or unconsciousness by suffocation.
- Autoignition Temperature** - The lowest temperature at which a substance will burst into flames without a source of ignition like a spark or flame. The lower the ignition temperature, the more likely the substance is going to be a fire hazard.
- Boiling Point** - The temperature of a liquid at which its vapor pressure is equal to the gas pressure over it. With added energy, all of the liquid could become vapor. Boiling occurs when the liquid's vapor pressure is just higher than the pressure over it.
- Carcinogen** - A substance that causes cancer in humans or, because it has produced cancer in animals, is considered capable of causing cancer in humans. Under the OSHA Laboratory Standard, a carcinogen is any chemical that has been found to be a carcinogen or potential carcinogen by the International Agency for Research on Cancer, is listed as a carcinogen or potential carcinogen in the Annual Report on Carcinogens published by the National Toxicology Program, or is regulated by OSHA as a carcinogen.
- CAS Number** - Chemical Abstract Service. Registry of chemicals by assigning numerical identification.
- Ceiling Limit (CL or C)** - An OSHA established concentration exposure limit which must never be exceeded, even for an instant. It is often written as TLV-C.
- Chemical Reactivity** - A chemical's ability to react with other materials. A chemical's ability to change in molecular arrangement or composition alone or with other chemicals. Reactivity implies, at least, a spontaneous action at the conditions, and is often rapid and energetic with dangerous and hazardous effects such as explosions, heat, etc.
- CHEMTREC** - Chemical Transportation Emergency Center. Established by the Chemical Manufacturers Association to provide emergency information on certain chemicals upon request. CHEMTREC has a 24-hour toll free telephone number (800-424-9300).
- Chronic Health Effect** - An adverse effect with symptoms that develop or recur very slowly, or over long periods of time as a result of continued or periodic exposure to the offending agent.
- Combustible** - A material that will burn under most conditions.
- Combustible Liquid** - A liquids or liquid mixture having a flash point at or above 37.8 °C (100 °F), but below 93.3 °C (200 °F).
- Compressed Gas** - Any material which is a gas at normal temperature and pressure, and is contained under pressure as a dissolved gas or liquefied by compression or refrigeration. Other definitions include: (1) a gas or mixture of gases having, in a container, an absolute pressure exceeding 40 psi at 21 °C (70 °F); or (2) a gas or mixture of gases having, in a container, an absolute pressure exceeding 104 psi at 54.4 °C (130 °F) regardless of the pressure at 21 °C (70 °F); or (3) a liquid having a vapor pressure exceeding 40 psi at 37.8 °C (100 °F) as determined by ASTM D-323-72.
- Concentration** - The amount of a substance present per unit of media. The amount of a substance (solute) in a mixture with substance(s) per amount of dominant substance (solvent) or sum of all

substances (solution). These amounts can be mass, volume or molar amount. A single substance can be described by amount, mass or molar, in space. The former is density and the latter is the inverse of molar volume (e.g., water: 55.5 moles per liter).

Corrosive - A chemical which causes visible destruction of or irreversible alterations in, unprotected skin and other tissue as well as metals at the site of contact by chemical action.

Cytotoxin - A substance toxic to cells in culture or to cells in an organism.

Dangerously Reactive Material - A material that can react readily and energetically alone (polymerize, fragment, rearrange) or with ordinarily non-reactive materials like air, water or combustibles. Undesired results can include toxic release, fire, splattering or explosion.

Decomposition - A loss of molecular structure or composition (i.e., breakdown) by loss of simple molecules (water, carbon dioxide) or rearrangement to a simpler structure (loss of information). It is usually thermal, but could also be due to light, hydration or air oxidation.

Density - A measure of anything that is bound by a volume. Usually it is the mass per volume of a single substance at normal (standard) conditions of temperature and pressure. Energy density and power densities are useful measures as well. NFPA gives its highest hazard ratings to materials that generate greater than one kilowatt per cubic centimeter (flames and halogen lights). Energy density has the same units as pressure (i.e., $P = nRT/V$ or $= Q/V$). Specific gravity compares density to other common materials (e.g., water, air). Thus, vapor density, is the ratio of the molecular weight of a vaporized substance to that of standard air, 28.8 g/mole. This ratio is an indicator as to how rapidly the pure vapor will settle out or rise if pushed into the air. If the density of a substance is compared with water (density = 1), then substances with densities < 1 will float on water if they don't dissolve; substances with densities > 1 will sink in water if they don't dissolve.

Dermal / Cutaneous - By or through the skin; pertaining to skin.

Dermatitis - Skin rash; inflammation of the skin.

DOT - U.S. Department of Transportation. Regulates transportation of hazardous materials.

Dyspnea - Shortness of breath, difficulty or labored breathing.

EPA Number - The number assigned to chemicals regulated by the EPA.

Erythema - a reddening of the skin.

Evaporation Rate - How fast a material is converted to vapor (i.e., evaporates) compared to some other chemical at the same temperature and pressure. The known reference material is butyl acetate with a vaporization rate of 1. The higher the number, the more rapidly the liquid evaporates.

Explosive - A chemical that causes a sudden, almost instantaneous release of pressure, gas, and heat when subjected to sudden shock, pressure, or high temperature.

Explosive Limits - The amounts of vapor in air which forms explosive mixtures. Explosive limits are expressed as Lower Explosive Limit (LEL) and Upper Explosive Limit (UEL). These give the range of vapor concentrations in air which will explode if heat is added. Explosive limits are expressed as per cent of vapor in air.

Eye Irritant - A chemical which irritates the eye.

Flammable - A chemical that catches on fire easily and burns readily.

Flammable Gas - A gas that, at an ambient temperature and pressure, forms a flammable mixture with air at a concentration of 13% by volume or less; or, a gas that, at an ambient temperature and pressure forms a range of flammable mixtures with air wider than 12% by volume, regardless of the lower limit. These gases are likely to explode or burn readily if the vapor is exposed to an ignition source.

Flammable Liquid - Liquids with a flash point below 100 degrees Fahrenheit (38 degrees Celsius). Even a small energy spark like static electricity may ignite the vapors, which are usually given off readily under normal temperatures.

Flammable Solid - Solids, other than blasting agents and explosives, which are volatile with vapor in ignitable limits or ignite very easily with ignition source contact or heat radiation and burn intensely. Solids pulverized to fine dust, especially if it is suspendable in air, are a special problem. These don't need to be volatile or reactive, their surface area to volume ratio allows ready, sustainable ignition (e.g., explode or flash) and may even provoke it with static electricity discharge from particle friction.

Flash Point - The lowest temperature at which a liquid gives off enough vapor to catch on fire if heat is applied. Flash point provides an indication of the flammability of a substance.

Fume - A liquid mist or solid particle suspension that has condensed from the vapor state.

Gram - A unit of weight in the metric system. An ounce is about 28 grams, a pound is approximately 450 grams. A teaspoon of sugar weighs about 8 grams.

Grams per Kilogram (g/Kg) - The dose of a substance given to test animals in toxicity studies.

Hazardous Chemical - Defined by OSHA as any chemical for which there is significant evidence that acute or chronic health effects may occur in exposed personnel. They are health or physical hazards.

Hazard Warning - Any words, pictures, symbols, or combination thereof appearing on a label that convey the hazards of the chemical(s) in the container.

Health Hazard - A harmful effect on health if an overexposure occurs. There are acute and chronic health hazards.

Hematopoietic System - The body's blood system, including the production and circulation of blood and the blood itself.

Hepatotoxins - Chemicals that cause liver damage.

Highly Toxic Chemicals - Chemicals which are poisonous in extremely small doses.

Inflammable - Same as flammable.

Ingestion - Taking a substance into the body through the mouth as food, drink, medicine, or unknowingly as on contaminated hands, make-up, cigarettes, etc. (e.g., swallowing).

Inhalation - The breathing in of an airborne substance that may be in the form of gas, fumes, mists, vapors, dusts or aerosols.

Irritants - Chemicals which cause reddening, swelling and pain when it contacts skin, eyes, nose or respiratory system, but are not likely to cause tissue destruction.

Label - Any written, printed, or graphic material displayed on or affixed to containers of hazardous chemicals.

Laboratory - A facility where relatively small quantities of hazardous materials are used on a non production basis.

Laboratory Scale - Work with substances in which the containers used for reactions, transfers, and other handling of substances are designed to be easily and safely manipulated by one person.

Lethal Concentration 50 (LC₅₀) - The concentration of an air contaminant that will kill 50% of the test animals in a group during a single exposure.

Lethal Dose 50 (LD₅₀ or LD_{50/30}) - the dose of a substance or chemical that will kill 50% of the test animals in a group within the first 30 days following exposure.

Material Safety Data Sheet (MSDS) - Written or printed material concerning a hazardous chemical that includes information on the chemical's identity; physical and chemical characteristics; physical and health hazards; primary routes of entry; exposure limits; whether the chemical is a carcinogen; precautions for safe handling and use; control measures; emergency and first aid procedures; the date of preparation of the MSDS or the last change to it; and the name, address, and telephone number of the manufacturer, importer, or employer distributing the MSDS.

Melting Point - The temperature at which a solid substance melts or becomes liquid.

Meter - A meter is about 40 inches.

mg/m³ - A way of expressing the concentration of a substance in air. It means the mass of substance per cubic meter (m³) of air.

Mixture - A heterogeneous association of substances where the various individual substances retain their identities and can usually be separated by mechanical means. Includes solutions or compounds but does not include alloys or amalgams.

MSDS - see Material Safety Data Sheet.

Mutagen - Capable of changing (mutating) genetic material in such a way that future cell generations are affected.

Narcosis - Stupor or unconsciousness caused by exposure to a chemical.

Nephrotoxin - A chemical that can cause kidney damage.

Neurotoxin - A chemical that produces its primary toxic effect on the nervous system.

Occupational Exposure Limits - Maximum allowable concentration of hazardous substances in workroom air to protect workers over a working lifetime.

Odor Threshold - The minimum concentration of a substance at which a majority of test subjects can detect and identify the substance's characteristic odor.

Organic peroxide - An organic compound that contains the bivalent -O-O-structure and may be considered to be a structural derivative of hydrogen peroxide where one or both of the hydrogen atoms has been replaced by an organic radical.

OSHA - The Occupational Safety and Health Administration, United States Department of Labor. OSHA develops and enforces standards for occupational safety and health.

Oxidizer - An oxidizer is a chemical (other than a blasting agent or explosive) that initiates or promotes combustion in other materials, thereby causing fire either of itself or through the release of oxygen or other gases. It may cause the ignition of combustible materials without the aid of an external source of ignition.

Permissible exposure limit (PEL) - An exposure limit established by OSHA expressed as a time-weighted average (TWA) limit, a short-term exposure limit (STEL), or a ceiling exposure limit.

pH - A measure of how acidic or how basic a substance is on a scale of 0 - 14. pH 0 is very acidic; pH 7 is neutral; and pH 14 is very basic. Actually, an expression of the hydrogen ion, (i.e., (H₂O)_nH⁺), concentration in water, as the negative logarithm base 10 of its molarity. It is limited to being a measure in water, even though an analogous measure can be applied to any proton dissociating liquid (e.g., acetic acid). In equilibrium, the product of the concentrations of proton donor and proton receiver is characteristic of the molecule as an acid and a base. For water, the [(H₂O)_nH⁺][(H₂O)_mOH⁻] = 10⁻¹⁴ regardless of the concentration of either. If [H⁺] = 1 molar, then [OH⁻] = 10⁻¹⁴ molar. A very strong acid that is pure, may not be strongly dissociated because a neutral molecule may likely be a weak base for binding another proton. Similarly, liquid ammonia can easily form an ammonium ion with a donated proton but, ammonia is a very weak proton donor, thus a very low dissociation constant

results. An acid stronger than hydronium ion, dissolved in water will produce a nearly equal amount of hydronium ions and protonate any hydroxide ions as well. A practical limit of aqueous acid concentration would be 55.5 moles of a strong monoprotic acid added to a liter of water (55.5 moles of H₂O), forming a salt, H₃O⁺ A⁻, that would likely have a volume greater than one liter. If its molarity is now, say, 25 mole per liter, and it is a liquid, the pH would be -1.40. Most concentrated, strong acids are up to 15 molar (above n = 3.7) and the pH can be thus -1.18. A 50% sodium hydroxide solution is about 17 molar and its pH is 15.23.

The measurement of pH is an artifact. A pH meter is really measuring the electropotential of a proton concentration dependent redox equilibrium against a standard potential (i.e., calomel) and the indicator scale is a voltage meter calibrated to read - Log₁₀ of proton concentration. Hydrofluoric acid or concentrated sodium hydroxide solutions will treat the porous glass probe like it's candy and consume it. Colorimetric indicators, dyes that show different visible light transmissions dependent on protonation of the molecule, change their color at a certain proton concentration in solution given their acid-base characteristics. Distinct color changes of dyes can range from at pH 1 to 13. A clever combination of four dyes that are water soluble, universal indicator, results in a prism color spectrum from red at pH of 4 to blue at pH of 10 with purple at about 11. This will only indicate truly in aqueous systems; solvent mixtures can protonate or deprotonate the dyes at conditions other than what water, acidic or basic, will do. The colors can be off-spectrum, interesting in themselves, but not really saying anything.

Physical Hazard - A chemical for which there is scientifically valid evidence that it is a combustible liquid, a compressed gas, explosive, flammable, an organic peroxide, an oxidizer, pyrophoric, unstable (reactive), or water-reactive.

pK - An acid or base equilibrium constant, pKa or pKb, as the negative logarithm (- Log₁₀) of proton or hydroxide molar concentrations, times the conjugate ion concentration, [A⁻] or [BH⁺], divided by the un-dissociated species concentration. Water concentration, certainly a participant in the equation, is not included (i.e., dilute solutions will be 55.5 molar water). For acids stronger than hydronium, protonated water, pKa = 0, the pKa has limited meaning for aqueous systems; hydronium ion is the acid. To obtain a pK value, it is necessary to know the reaction that the pK is being referred to. Experimentally determined pK values depend on temperature, ionic strength, and the microenvironment of the ionizable group. Generally, only the pKa's are listed for both acids and bases. That is because pKb is 14 - pKa, just as pOH = 14 - pH. The pKa of an amine, that obviously doesn't donate a proton in normal cases, is the pKa of its conjugate, BH⁺; thus pKa = - Log₁₀{[B][H⁺]/[BH⁺]} and pKb = - Log₁₀{[BH⁺][OH⁻]/[B]}, pKa + pKb = - Log₁₀{[H⁺][OH⁻]} = pKw = 14.

Polymerization - A chemical reaction, usually carried out with a catalyst, in which two or more small molecules combine to form larger molecule that contain repeating structural units of the original molecules. A hazardous polymerization occurs when the reaction results in an uncontrolled release of energy.

ppm - Parts per million. An expression of concentration of a gas or vapor in air or a solute in a solvent, but can also express precision. It can be dimensionless (e.g., micromoles per mole, milligram per kilogram), or it can be mixed units (e.g., milligram per liter [i.e., liter equated to kilogram by water density] or even milliliter per kilogram) if necessary. In these situations, it is important to know what it means in terms of the units.

Pyrophoric - A chemical that will ignite spontaneously in air at a temperature of 54.4 °C (130 °F) or below.

Reactivity - The ability of a substance to undergo a chemical change alone or with other substances, without energy input and usually with a release of energy and/or volatiles. Highly reactive substances may burn, explode or produce corrosive or toxic emissions. See also **Dangerously Reactive**.

Reproductive Toxin - A chemical that affects the reproductive capabilities including chromosomal damage (mutations) and effects on fetuses (teratogenesis).

Respirator - A device which is designed to protect the wearer from inhaling harmful contaminants.

Respiratory Hazard - A particular concentration of an airborne contaminant that, when it enters the body by way of the respiratory system results in some bodily function impairment.

Routes of Entry - Ways in which a chemical can come into contact with the body. Included are the skin, the eyes, the mouth, the nose and the lungs.

Sensitizer - A chemical that may cause no reaction in a person during initial exposure, but afterward, further, repeated exposures will cause an allergic reaction in normal tissue in a substantial proportion of exposed people or animals exposed to the chemical.

Short term exposure limit (STEL) - A term used by the ACGIH to express the maximum concentration most workers can tolerate for a 15-minute exposure period (with a maximum of four periods a day with at least 60 minutes between exposure periods and provided that the TLV-TWA is not exceeded) without adverse effects.

Solvent - A substance, usually a liquid in which other substances are dissolved. The most common solvent is water.

Specific Gravity - A ratio of the density of a substance with the density of water, which has a relative value of 1 when metric units are used. The gram was defined as being the mass of one cubic centimeter of water (note: initially the meter was one ten millionth the distance from the Equator to the North pole along the Greenwich meridian). Finer measurements showed water has a maximum density at 3.98 °C, so the milliliter was defined as being the volume of one gram of water at maximum density (i.e., 0.999972 ml = 1.000000 cm³ @ 3.98 °C [Merck Index]). If the chemical's specific gravity is greater than 1, the chemical is heavier than water and will sink in water.

Systemic - Spread throughout the body, affecting many or all body systems or organs;; not localized in one spot or area.

Teratogen - An agent or substance that may cause physical defects in the developing embryo or fetus when a pregnant female is exposed to the substance.

Toxic- Poisonous. Causes adverse health effects when the body is exposed.

Target Organ Effect - Chemically caused health effects from exposure to a substance on specific organs i.e., lungs, kidneys, nervous system, blood or blood-forming organs, eyes, skin, etc.

Threshold Limit Value (TLV) - Term used by the ACGIH to express the maximum airborne concentration of a material to which most workers can be exposed during a normal daily and weekly work schedule (i.e., day-after-day) without adverse health effects.

Time Weighted Average (TWA) - A technique for averaging individual variant measurements over an 8-hour workday.

Toxic - causing acute or chronic injury to the human body or suspected of being able to cause disease or injury under some conditions. The terms *toxic* and *highly toxic* are defined specifically by the chemical's median lethal dose and median lethal concentration for laboratory animals.

Unstable (reactive) - A chemical that in the pure state or as commercially produced or transported, will vigorously polymerize, decompose, condense, or will become self-reactive under conditions of shock, pressure, or temperature. Equivalently, a single chemical or mixture that has a low energy of activation threshold to self reaction or mutual reactivity which then delivers a greater energy leading to even more reaction. The activating energy can be thermal as well as mechanical friction or shock.

An instability may be a slow, easy and low energy yielding reaction of decomposition or change that may build up products to sufficient levels to seriously react. Some examples include:

- ◆ Nitroesters, such as nitroglycerine and even nitrocellulose will slowly decompose by moisture hydrolysis of the ester to nitric acid, which furthers hydrolysis of esters leading to combustion or explosion involving nitric acid produced.
- ◆ Silver diamine ion from silvering solutions will slowly disproportionate to ammonia, silver amide, imide and nitride, as well as air oxidize to trisilver tetranitride, all of which silver compounds are very mechanically sensitive and powerful explosives.
- ◆ Air oxygen slowly and non-energetically adducts with certain alkenes (polymer monomers) which slowly adduct more alkene to an extent that it later becomes a vigorous, heat producing reaction runaway.
- ◆ Pyruvic acid and formic acid both will auto-decompose producing carbon dioxide and carbon monoxide respectively, which builds internal pressure that is not limited by pressure, thus bursting the container if tightly sealed.

Vapor - The gaseous state of substances which are normally in the liquid or solid state (i.e., condensed phase) at normal / ambient room temperature and pressure. Vapors evaporate into the air from liquids such as solvents. The gaseous versus condensed state amounts (i.e., equilibrium vapor pressure) are determined by the transition temperature (i.e., boiling or sublimation point), temperature of material and the energy of transition to gas phase. The ratio of molar transition energy to absolute temperature of transition is approximately constant for most non-ionic substances.

Vapor Density - Whether a substance is heavier or lighter than air (which has a vapor density of 1). A vapor with a density lighter than 1 is lighter than air and will rise in air. Specifically, it is the density of the vapor of a substance at normal atmospheric pressure, but at a temperature that is above its boiling point, compared to air at that temperature. Using ideal gas behavior (i.e., $PV = nRT$), this allows the molecular weight of the substance as a ratio to normal air (i.e., 28.8 g/mole), to be the density of the vapor. The true density of an escaping vapor must be based on its vapor pressure in air, at the prevailing temperature. Just as air's density is a composite, the vapor density of a volatile liquid will be a composite calculated using molecular weight and mole fraction in air (i.e., vapor pressure). $D_v = [P_v M_w + (1 - P_v) \times 28.8] / 28.8$. For example, ether vapor: $D_v = [440/760 \times 74 + (1 - 440/760) \times 28.8] / 28.8 = 1.91$ -times that of air.

Vapor Pressure - The pressure that a solid or liquid exerts when it is in equilibrium with its vapor at a given temperature. It relates to how quickly a substance becomes airborne within the workplace and how quickly a worker could be exposed to it. The pressure of the gas phase of a liquid or solid, whether the only component of an atmosphere or as a partial pressure in a mixture (e.g., in air at normal pressure, in equilibrium with the condensed phase); it is the same. If a material evaporates in a closed space with enough vapor to achieve vapor pressure and there is some condensed phase of the material remaining, there exists a dynamic equilibrium. If the air is being replaced in the space or the pool is in open air, the material will continue to evaporate (and steal heat from its surroundings) until it is gone (i.e., evaporated). The **evaporation rate** of a condensed substance depends on the vapor pressure at pool temperature (i.e., this may be depressed from the ambient due to evaporation energy requirement) minus any vapor concentration already in air (e.g., a puddle of water on a humid day), the air speed over the pool, the length of pool to be traversed (i.e., air saturates with vapor) and the total area of the pool. Diffusivity and fluid viscosity are factors in this as well. The vapor concentration exponentially decreases with height above pool in a simple model of plume formation. It may be hard to predict the particular scaling of this profile in any situation.

Viscosity - A measure of how slowly a substance pours or flows. Very viscous substances, like honey, pour very slowly. Slightly viscous substances, like water, pour and splash easily.

Volatility - A measure of how quickly a substance forms vapor at ordinary temperatures. Equivalently, a measure of equilibrium vapor pressure of a liquid or solid but also denotes how quickly a substance forms vapor. See **evaporation rate** under **vapor pressure**

Water-reactive - A chemical that reacts with water to release a gas that either is flammable or presents a health hazard. On mixing with water the substance produces heat, splattering or gas which is toxic or flammable (possibly with enough temperature rise to ignite the gas). The reaction can be hydration of a small ion like a proton from an acid (sulfuric) or hydroxide from a base (sodium hydroxide), hydrolysis of a weakly bonded ligand (chloride to silicon bond), protonation of a base like phosphide to form phosphine or hydride to form hydrogen, oxidation of an active metal (sodium) to form hydrogen and metal hydroxide or reduction of an oxidizer (fluorine) to form oxygen gas.

Work Area - A room or defined space in a workplace where hazardous chemicals are used, produced or stored, and where employees are present.

Annex 2-2. Quick Guide to Hazardous Chemical Risk Assessment

The following 7-step outline, extracted from the National Research Council's *Prudent Practices in the Laboratory: Handling and Disposal of Chemicals*, provides a summary of the steps that laboratory workers should use to assess the risks from handling toxic chemicals. Besides the MSDS, the Prudent Practices Committee developed 88 Laboratory Chemical Safety Summaries (LCSSs) which they believe provide more appropriate information for laboratory workers. A listing of these LCSSs can be found at <http://www.qrc.com/hhmi/science/labsafe/lcss/>.

- 1. Identify chemicals to be used and circumstances of use.** Identify the chemicals involved in the proposed experiment and determine the amounts that will be used. Is the experiment to be done once, or will the chemicals be handled repeatedly? Will the experiment be conducted in an open laboratory, in an enclosed apparatus, or in a fume hood? Is it possible that new or unknown substances will be generated in the experiment? Are any of the workers involved in the experiment pregnant or likely to become pregnant? Do they have any known sensitivities to specific chemicals?
- 2. Consult sources of information.** Consult an up-to-date MSDS or LCSS for each chemical involved in the planned experiment. In cases where substances with significant or unusual potential hazards are involved, it may also be advisable to consult more detailed chemical references. Depending on the worker's level of experience and the degree of potential hazard associated with the proposed experiment, it may also be necessary to obtain the assistance of supervisors and safety professionals before proceeding with risk assessment.
- 3. Evaluate type of toxicity.** Use the above information obtained to determine the type of toxicity associated with each chemical involved in the proposed experiment. Are any of the chemicals to be used acutely toxic or corrosive? Are any of the chemicals to be used irritants or sensitizers? Will any select carcinogens or possibly carcinogenic substances be encountered? For many substances, it will be necessary to consult the listings of carcinogens (see Appendix D) to identify chemical similarities to known carcinogens. Are any chemicals involved in the proposed experiment suspected to be reproductive or developmental toxins or neurotoxins?
- 4. Consider possible routes of exposure.** Determine the potential routes of exposure for each chemical. Are the chemicals gases, or are they volatile enough to present a significant risk of exposure through inhalation? If liquid, can the substances be absorbed through the skin? Is it possible that dusts or aerosols will be formed in the experiment? Does the experiment involve a significant risk of inadvertent ingestion or injection of chemicals?
- 5. Evaluate quantitative information on toxicity.** Consult the information sources to determine the LD₅₀ for each chemical via the relevant routes of exposure. Determine the acute toxicity hazard level for each substance, classifying each chemical as highly toxic, moderately toxic, slightly toxic, and so forth. For substances that pose inhalation hazards, take note of the threshold limit value time-weighted average (TLV-TWA), short-term exposure limit (STEL), and permissible exposure limit (PEL) values.
- 6. Select appropriate procedures to minimize exposure.** Use the basic prudent practices for handling chemicals, which are discussed in Chapter 4, for all work with chemicals in the laboratory. In addition, determine whether any of the chemicals to be handled in the planned experiment meet the definition of a particularly hazardous substance due to high acute toxicity, carcinogenicity, and/or reproductive toxicity. If so, consider the total amount of the substance that will be used, the expected frequency of use, the chemical's routes of exposure, and the circumstances of its use in the proposed experiment. Use this information to determine whether it is appropriate to apply the additional procedures for work with highly toxic substances and whether additional consultation with safety professionals is warranted.
- 7. Prepare for contingencies.** Note the signs and symptoms of exposure to the chemicals to be used in the proposed experiment. Note appropriate measures to be taken in the event of exposure or accidental release of any of the chemicals.

Preliminary Chemical Hazard Assessment Form[†]

Chemical: _____

Risks = Hazards X the Probability of Exposure

Hazards:

Health Hazards (check hazards that apply):

- Carcinogen
- Corrosive
- Irritant
- Sensitizer (allergy producer)
- Target Organ Effect
 - Hepatotoxin (liver)
 - Nephrotoxin (kidney)
 - Neurotoxin (nervous system)
 - Agent which acts on the Hematopoietic System (blood-forming cells)
 - Agent which Damages the Lungs
 - Reproductive Toxin
 - Teratogen (affects unborn)
 - Mutagen (chromosomal changes)
 - Cutaneous Hazard (skin)
 - Eye Hazard Others (list) _____
- Toxic
- Highly Toxic

Physical Hazards (check hazards that apply):

- Combustible Liquid
 - Compressed Gas
 - Explosive
 - Flammable
 - Aerosol, Flammable
 - Gas, Flammable
 - Liquid, Flammable
 - Solid, Flammable
 - Oxidizer
 - Organic Peroxide (oxidizer and fuel)
 - Pyrophoric
 - Unstable (reactive)
 - Water-Reactive
 - Flammable Hazards Formed: _____
 - Health Hazards Formed: _____
- (repeat assessment for any other flammable or health hazards formed)

Risks = Hazards X the Probability of Exposure

Risks:

Acute Health Effects

(check / list acute symptoms of exposure):

- Irritation
- Burning
- Nausea
- Dizziness
- Difficulty Breathing
- Sensitization (allergies)
- Others (list): _____
- _____
- _____
- _____
- _____
- _____

Chronic Health Effects

(check / list chronic effects):

- Cancer
- Teratogenesis (effects on unborn)
- Mutagenesis (chromosomal changes)
- Others (list): _____
- _____
- _____

Physical Effects (check / list physical effects):

- Fire
- Explosion
- Excessive Temperature
- Release of Pressure
- Release of Toxic/Flammable Gases/Vapors
- Others (list): _____
- _____

[†]this form was developed by the University of Arizona's Department of Risk Management & Safety

Risks = Hazards X the Probability of Exposure

Factors Indicating the Degree of Hazard or the Probability of Exposure

Also Consider: The number of individuals exposed, their individual susceptibility, and The manner of use, storage and disposal
(place "X's" in the appropriate boxes)

Indicators	Factors	LESS RISKY ▶▶▶▶▶▶▶▶▶ MORE RISKY				
Acute Health Hazard Indicators	Corrosivity (pH, oxidizer status)	pH 6-9 OR not an oxidizer	pH 5-6 or 9-10	pH 3-5 or 10-12 OR moderate oxidizer	pH 1-3 or 12-14	pH <1 or >14 OR strong oxidizer
	Toxicity (LD₅₀) oral, rat (mg/kg)	>5000	500-5000	50-500	1-50	<1
	inhalation, rat (ppm)	>10,000	1,000-10,000	100-1,000	10-100	<10
Chronic Health Hazard Indicator	Excretion (bio. half-life)	minutes	hours	days	weeks	years
Exposure Hazard Indicators	Quantity	small quantities low conc.		intermediate quantities and conc.		large quantities, high conc.
	Physical Form	solids, granules	liquids	dusts/mists	vapors, fume	gases
	Routes of Exposure	ingestion		skin contact, ingestion		inhalation, skin contact, ingestion
	Detection / Warning Properties	appearance,	established odor/irritation levels, odor/irritation less than PEL/TLV	odor/irritation,	odor/irritation levels not established odor/irritation levels above PEL/TLV	analytical methods
	Vapor Pressure (mmHg @20°C)	<1	1-10	10-100	100-760	760
	Exposure Limits (PEL or TLV) [†]	>1000 ppm	100-1000 ppm	10-100 ppm	1-10 ppm	<1 ppm
	Vapor Hazard Ratio [‡]	<10	10-1000	1000-10,000	10,000-100,000	>100,000
Flammable Hazard Indicators	Flash Point (°F)	>200	150-200	100-150	0-100	< 0
	Flammable Range (0-100%)	narrow flammable range, flammable range in higher percentage range		intermediate flammable range flammable range in middle percentage range		broad flammable range, flammable range in lower percentage range

[†]ppm = (mg/M³)(24.45/MW)

[‡][(VP at temp. of use)(10⁶/atmospheric pressure)]/TLV or PEL (atmospheric pressure is 760 @ sea level)

Degree of Hazard Chart

	Factor Measure	Slight	Low	Moderate	High	Dangerous
Reactivity						
Oxidizer[§]	Electropotential, Acidic	< 0.5	0.75	1	1.25	> 1.5
Reducer[§]	Electropotential, Basic	< 0.75	1.00	1.25	1.50	> 1.75
Acid[†]	$-\log_{10}([H_3O^+][A^-]/[HA])$, pKa	> 6	5	4	3	< 2
Base[†]	$-\log_{10}([OH^-][BH^+]/[B])$, pKb	> 6	5	4	3	< 2
Aqueous pH, Acid		> 3.5	2.5	1.5	0.5	< - 0.5
Aqueous pH, Base		< 10	11	12	13	> 14
Flammability	Flash Point, °C	> 75	50	25	0	< - 25
Auto-ignition Temperature °C		> 850	650	450	250	< 50
Flammability Range	U.E.L. - L.E.L. %	10	30	50	70	90
Water Reactivity	Observation	hydrates	warms	heating	splatters	gas/ignition
Self Reactivity	Energy/mass, kJ/g	< 0.25	0.5	1.0	2.0	> 4.0
Reaction Energy / Heat Capacity °C		< 50	100	150	200	> 250
Molar heat capacity for solids is ~ 1 J/g °C x [sum]Mw (g/mole), use J/mole for reaction energy. Heat capacity of water is 4.18 kJ/liter °C, organic solvents are ~ 1.6 kJ/liter °C						
Toxicity						
Inhalation Hazard	LC ₅₀ x t, ppm-Hr	> 10,000	5,000	2,000	6,00	< 200
Ingestion, Oral	LD ₅₀ mg/Kg animal	> 5,000	1,500	500	150	< 50
Occupational	log ₁₀ [STEL/vp]	> 0	- 1	- 2	- 3	< - 4
Bio half-life	½ burden excreted, days	< 0.2	2	20	200	> 2000
Mobility						
Vapor	mm of Hg	< 2.5	10	45	180	> 760
pressure @ 25 °C						
Gage Pressure (cylinders)	Atmosphere	0	5	20	100	> 250
Amount of something dangerous	grams	< 0.1	1	10	100	> 1000
Viscosity, kinematic	Stoke (cm ² /sec)	> 10	1	0.1	0.01	< 0.001
(of something dangerous) glycerol = 9 octanol = 0.1 H ₂ O = 0.009 Hg = 0.0011						
Friability, low density, high MP, brittle, non-compact, organic crystal	Melting Point in °C	< 60	150	250		

[†]Acid pKa and base pKb (14 - pKa) hazard assessed for the case of skin or eye contact with undissolved material.

Hydrofluoric and acetic acids are more dangerous than their pKa's indicate. Skin is more sensitive to aqueous base than acid, thus the factor of 3 (0.5 log) off-set.

[§]Use of electropotential is out of the hazard context of an oxidizer or reducer. It's oxidizer with cellulose and reducer with oxygen in air that is a better context. Potential is what is more widely available. **Some markers:**
Acidic Oxidizers -- quinone: 0.70; nitric: 0.93; oxygen: 1.23; dichromate: 1.23; bromate: 1.42; permanganate: 1.68; peroxydisulfate: 2.0; fluorine: 2.87.

Basic Reducers -- ferrous hydroxide: 0.56; sulfite: 0.93; phosphite: 1.05; borohydride: 1.24; zinc: 1.25; phosphorus: 1.71; aluminum: 2.31; lithium: 3.04

Annex 2-3. Explanation of Material Safety Data Sheet Information

Although OSHA does not mandate a specific MSDS format, the use of the 16-section American National Standards Institute (ANSI) MSDS has increased because it's easy to use and the form helps companies meet international requirements. The Chemical Manufacturers Association worked with OSHA and ANSI to develop the format. A standardized format enables supervisors, employees and emergency responders to find detailed, consistent information about workplace chemicals. Lets look at the type of information found in each of the sections of an ANSI-format MSDS (cf. ANSI Z400.1-2004).

Section 1. Chemical, Product and Company Identification

This section tells the name of the chemical as it appears on the container label. The name on the MSDS will always be the same as the name on the container label, providing a direct link of the chemical to the MSDS. Also listed is the name and address of the manufacturer and an emergency phone number where questions about toxicity and chemical hazards can be directed. A common emergency number found is for CHEMTREC, a center established by the Chemical Manufacturers Association. Their 24-hour, toll-free number is 1-800-424-9300.

If one generic MSDS is used to cover various grades of a material, all grades must be listed as well as known synonyms. If an optional number or code is used by the manufacturer to help identify the MSDS, it should appear in this section and on every page of the MSDS. Remember, thousands of materials with many similar names are found in workplaces. A mistake on the supplier's part in sending you the wrong MSDS needs to be caught immediately before you put your trust in the wrong information.

Section 2. Hazard Identification

This section is divided into two parts. The first part describes the material's physical appearance and provides the most significant immediate concerns for emergency personnel. Examples include:

Chlorine is a greenish-yellow gas with a pungent, suffocating odor. It is a highly toxic and corrosive gas which is irritating to the eyes and mucous membranes. Although noncombustible, it is a strong oxidizer and supports the combustion of other organic materials. It is an extremely reactive and explosive gas. Chlorine reacts with many common substances such as acetylene, ammonia, hydrogen, ether, fuel gas, hydrocarbons, turpentine, and finely divided metals.

Sweet smelling clear liquid. Evaporates quickly at normal temperatures. High concentrations in immediate area can reduce oxygen and result in dizziness, unconsciousness, and even death with longer exposures. Keep people without self-contained breathing apparatus out of area. Not a fire hazard in open areas. Water fog can be used on fires. Contain large spills and keep liquid out of water sources.

This information is important to both workers and emergency responders since it describes a chemical's normal appearance and odor and describes how the chemical will behave when it is released. Workers are expected to be trained in recognizing a chemical's hazard.

The second part of this section provides information on the most significant immediate concerns including emergency overview, OSHA regulatory status, potential health effects and symptoms associated with exposure to the material, and potential environmental effects.

Here is a list all the routes of entry (i.e., eye, skin, inhalation, ingestion) pertinent to this material and it also lists the actual health hazard of the chemical, both acute (effects that show up immediately after exposure) and chronic (effects that develop over time, usually following prolonged exposure). If the material is *Particularly Hazardous* and considered a confirmed or suspected carcinogen by IARC, NTP, or OSHA, a teratogen (causes physical defects in a developing embryo or fetus), a mutagen (causes genetic mutations), toxic to aquatic life or a danger to the environment, this fact may be included here or in other sections of the MSDS.

Signs and symptoms of exposure are noted here. They can range from minor skin irritation to chronic lung disease. Some chemicals may harm a *target organ* such as the heart, liver, lungs, etc. Chronic effects are particularly dangerous because workers may not experience discomfort in the presence of the material but may develop severe health problems later in life as a result of the exposure. There is a

possibility that exposure to some chemicals will aggravate preexisting medical conditions such as heart or respiratory problems. Remember, sickness and even death from improper exposure can be prevented if workers are aware of the potential hazards before they use a chemical.

Section 3. Composition, Information on Ingredients

This section describes what is hazardous in the chemical. It identifies the chemical by both its common and scientific name. If it is a chemical compound, this section describes the percent composition of the substance, listing chemicals present in the mixture which contribute to its hazardous nature. Otherwise, it lists all carcinogens and ingredients making up more than 1%. This section may also include the chemical family or group of chemicals with related physical and chemical properties, the chemical formula, and the *Chemical Abstract Services (CAS)* Registry number.

The chemical's exposure limits are also listed here. There may be several values and types of limits. The most common are: Permissible Exposure Limit (PEL), Time Weighted Average (TWA), Threshold Limit Value (TLV), Short Term Exposure Limit (STEL) and Ceiling Limit (CL). OSHA and other organizations establish exposure limits. OSHA sets the *permissible exposure limit (PEL)*. The *threshold limit value (TLV)* is recommended by the American Conference of Governmental Industrial Hygienists (ACGIH). Both the PEL and TLV specify the maximum amount of exposure a worker can have to a substance averaged over an 8-hour workday. The limits are usually expressed in parts per million parts of air (ppm) or milligrams of dust or vapor per cubic meter of air (mg/m³). OSHA's PEL is the enforceable standard while others are recommendations and may be different than OSHA. When comparing hazards, the lower the ppm value, the more hazardous the chemical. Thus, a chemical with a PEL or TLV of 2 ppm is far more hazardous than one listed as 200 ppm. The PEL is often expressed as a *time weighted average (TWA)*. TWA is a technique for averaging individual variant measurements over an 8-hour workday. The *short term exposure limit (STEL)* is a term used by the ACGIH to express the maximum concentration most workers can tolerate for a 15-minute exposure period without adverse effects (with a maximum of four periods a day and at least 60 minutes between exposure periods). The ACGIH also establishes a *ceiling limit (CL)*, the exposure limit that should never be exceeded, even instantaneously.

If established, the chemical's exposure limits are listed. Some compounds may not have an established exposure limit and this would be blank. If the MSDS shows "8-hr TWA: 100 ppm or 300 mg/m³" it is a guideline establishing an exposure limit which should not be exceeded when averaged over an 8-hour workday. If the MSDS shows "STEL: 100 ppm" it is a guideline for an exposure level not to be exceeded over a 15-minute continuous exposure. A "skin" notation means that skin exposure is significant in contributing to the overall exposure. These exposure levels are set for healthy adult workers, based on the average 150-pound male, age 25 - 44. Lower exposure levels may be necessary for workers at higher risk (e.g., those who are young or elderly, pregnant, smokers, etc.) or for those who have already been exposed to other materials for which exposure limits have been set. Exertion increases the effects of exposure. Exposure to more than one hazardous substance at a time may be especially harmful because the combined effects of more than one material may be more damaging than the additive effects of each material. Thus, both smoking and asbestos can cause lung cancer; however, if a smoker is also exposed to asbestos, the danger of lung cancer is far greater (e.g., by a factor of 10) than just adding the separate risks from the two exposures.

Section 4. First Aid Measures

This describes medical and first aid treatment for accidental exposure by route of exposure (i.e., inhalation, skin, eye, ingestion). Clear instructions including known antidotes that may be administered by a lay person or specially trained health care professional will be indicated. In accidents, give a copy of the MSDS to attending physicians. A subsection entitled **Note to Physicians** may also be found here. This will provide specific medical information on treatment and diagnostic procedures which trained medical personnel can apply.

Section 5. Fire Fighting Measures

This section describes the fire and explosive properties of the material, the proper extinguishing materials, and the precautions and procedures to safely and effectively fight the fire. If a chemical has a high fire or explosion potential, the work area should be inspected carefully before it is used and all ignition sources should be removed.

The flammable properties combined with the physical and chemical properties give a good indication of how hazardous a material is in a fire situation. The **flash point** of a chemical is the lowest temperature at which the chemical's vapors are concentrated enough to ignite if an ignition source is present. The lower the flash point, the more dangerous the material. Gasoline's flash point is - 45 °F. The **autoignition temperature** is the lowest temperature at which a liquid will give off enough flammable vapors or heat energy to ignite and burn by itself. Thus, it tells how hot a material must be before it will set itself on fire without a flame or spark. Other properties include the upper and lower **flammable limits**, the concentration in the air between which the substance is likely to ignite, and the upper and lower **explosion limits** (**UEL** and **LEL**), the minimum and maximum concentration of the chemical's vapor in the air where an explosion could occur.

With most fires, often the greatest danger to human life comes not from the heat of the fire, but from the toxic smoke that can quickly fill a work area. Known or anticipated hazardous products of combustion would be listed here. Thus, carbon disulfide, when burned, produces toxic gases and irritants, including carbon monoxide and sulfur oxides.

There is also a discussion of the best way to safely and quickly extinguish fires. Some burning materials may react with water and are best smothered with foam, carbon dioxide gas, or a dry chemical. Certain chemicals may also present unusual fire hazards (e.g., strong oxidizer, explosive potential), these would be discussed here.

Section 6. Accidental Release Measures

Spill, leak, and response procedures for emergency responders and environmental professionals as well as evacuation procedures, containment and cleanup techniques, and other emergency advice to protect the health and safety of the responders as well as the environment.

Section 7. Handling and Storage

Information for employees, health and safety professionals, and employers on safe handling practices and storage procedures for the substance. Under safe handling, the precautions listed are specific for the material's unique properties. There may be general warnings, "*Do not breathe dust*" and general practices to prevent continued exposure, "*Practice good personal hygiene after using this material, especially before eating, drinking, smoking, using the toilet, or applying cosmetics.*" Handling practices, such as how to prevent vapor release, the need for a totally enclosed system, and recommendations to prevent injury would also be found here. Information like, "*To avoid sudden release of pressure, loosen closure cautiously before opening*" and "*To reduce potential for static discharge, bond and ground containers when transferring materials*" are warnings about the substance which must be followed.

Information about appropriate storage practices, including explanations of necessary storage conditions to avoid damage to containers, contact with incompatible materials and subsequent dangerous reactions, evaporation or decomposition of stored material, or flammable and explosive atmospheres in the storage area. Examples of specific storage procedures to avoid dangerous conditions include, "*Keep away from oxidizing materials*," "*Keep containers closed, store in the dark at temperatures less than 20 °C (68 °F)*," and "*Protect these containers from physical damage, shield them from direct sunlight, and maintain their temperature at less than 38 °C (100 °F)*."

Section 8. Exposure Controls / Personal Protection

Methods that safety professionals and employers can employ for reducing worker exposure to hazardous materials are presented. Control measures are often divided into engineering and administrative controls.

Engineering controls include things like ventilation, process controls (e.g., isolation, enclosure, etc.), sampling devices and concentration monitoring. These are important because they do not require any action by the workers to be protected. Administrative controls include training, labeling, warning devices, operating procedures, etc. Administrative controls require the workers to take an active part in their safety. Guidance for appropriate **personal protective equipment (PPE)** is also found here. PPE is discussed in greater detail in Chapter 4. Protection of the workers is the employer's responsibility. To accomplish this, employers must provide engineering and administrative controls and PPE. The workers must be trained to use the right PPE correctly. Employees are responsible for handling chemicals as instructed and using the PPE provided. Both managers and workers are responsible for insuring protection systems are inspected and properly maintained to provide the proper amount of protection.

Section 9. Physical and Chemical Properties

This section lists the physical and chemical properties that characterize the material. Physical data such as evaporation rate, vapor density, etc. is important because it tells what circumstances (e.g., temperature) could change a chemical's normal state. It can also be used to determine conditions for exposure and allow workers to judge how a chemical will react to changes in condition and how it will disperse into the atmosphere. For example, certain kinds of jobs could increase the temperature in the work area and that could change the chemical and its hazards. Some of the common characteristics listed for a chemical are:

- ♦ **Appearance/Odor** - color, physical state at room temperature, size of particles, consistency, odor, etc. Odor threshold refers to the concentration required in the air before vapors are detected or recognized.
- ♦ **Melting Point** - the temperature at which a solid begins to change to a liquid
- ♦ **Boiling Point** - the temperature at which liquid changes to a gas or to its vapor state
- ♦ **Evaporation Rate** - how fast the chemical turns into a vapor, usually expressed as a time ratio with ethyl ether (or butyl acetate) = 1, unless otherwise specified. A chemical with a higher number evaporates faster; one with a lower number evaporates slower.
- ♦ **Solubility in Water** - the percentage of material that will dissolve in water, usually at ambient temperature. Since much of the human body is made of water, water soluble substances are more readily absorbed and distributed.
- ♦ **Specific Gravity** - the ratio of volume weight of material to equal volume weight of water (water = 1).
- ♦ **Vapor Density** - the weight of a gas or vapor compared to the weight of an equal volume of air (air = 1). A vapor density greater than 1 indicates it is heavier than air, less than 1 indicates it is lighter than air (i.e., it will rise in air). Vapors heavier than air can flow just above ground, where they may pose a fire or explosion hazard or may displace breathable air.
- ♦ **Vapor Pressure** - a measure of how volatile a substance is and how quickly it evaporates. For comparison, the VP of water (at 20 °C) is 17.5 mm Hg, Vaseline (nonvolatile) is close to 0 mm Hg, and diethyl ether (very volatile) is 440 mm Hg. The higher the number the faster it evaporates.
- ♦ **Viscosity** - internal resistance to flow exhibited by a fluid, normally measured in centiStoke time or Saybolt Universal Secs.

Section 10. Stability and Reactivity

There are many different ways that materials may react with one another. Some substances are unstable and can react with other substances or under specific kinds of situations and/or changes in conditions (e.g., temperature, humidity, light, etc.). The MSDS would list materials and circumstances that could be hazardous when combined with the material covered by the MSDS.

The MSDS will warn about the possibility of reactions and the conditions that create them. Some unstable chemicals will react when the temperature changes, or when they are exposed to sunlight, air, or water. Many chemicals will react violently when exposed to water. If the chemical is incompatible with another chemical, the MSDS lists the materials so they are not stored in close proximity and they are kept far apart on the job. For example, if the material reacts with metal, it should be stored on nonmetal shelves. If the material reacts with natural rubber, you shouldn't wear a respirator or gloves made of natural rubber or use a rubber stopper to close the bottle.

Decomposition products or hazardous byproducts, such as toxic gases that the chemical could generate, along with their hazards, are also listed here. It is common knowledge that mixing bleach (sodium hypochlorite) with an acid gives off toxic and irritating chlorine gas; bleach mixed with an ammonia solution produces toxic and irritating chloramines. Polymerization is also a reactivity hazard. In this instance the material changes form usually releasing a lot of heat.

Knowledge of the physical and chemical properties and a chemical's stability and reactivity potential can be used in selecting proper personal protective equipment, storage or shelving, and choice of containers.

Section 11. Toxicological Information

Here information on toxicity testing of the material and / or its components is discussed. Usually the information reflects animal testing, although some human data will be available if accidental human poisonings have occurred and the exposure amounts are known, or if epidemiological studies have been

conducted. The information is intended for medical and health and safety professionals. Data includes acute, sub-chronic, and chronic studies through various routes of exposure (inhalation, ingestion, skin, etc.). A typical example of data might be "*Rat, Oral, LD₅₀: 200 mg/kg*" which means that 200 milligrams of the chemical per each kilogram of body weight is the lethal dose that killed 50% of a group of test rats following oral administration. These data are then used to help estimate the degree of hazard to humans.

Section 12. Ecological Information

This information assists in evaluating the effect a chemical may have if it is released to the environment. Ecotoxicity data may include information on acute and long-term toxicity to fish and invertebrates, or plant and microorganism toxicity. Chemical behavior in the air, soil, or water is also important data when evaluating environmental contamination. Other information may include persistence and degradation, soil mobility, bioaccumulation, and photolytic (i.e., decomposition by light) stability.

Section 13. Disposal Considerations

The MSDS provides proper disposal information for environmental professionals or persons responsible for waste management activities. The information may include special disposal methods or limitations per Federal, state, or local regulations, and waste management options (e.g., recycling, reclamation) and may include RCRA waste classification and / or EPA waste identification numbers and descriptions.

Section 14. Transportation Information

This section provides basic classification information and special precautionary information to help a knowledgeable user prepare the material for shipment. It is not intended to contain every regulatory detail involving the transportation. If the material is regulated, shipping information includes DOT hazardous materials description / proper shipping name, hazard class, and identification numbers. This information helps shippers properly prepare materials for shipment.

Section 15. Regulatory Information

Regulatory information useful for employers and personnel to assure compliance with health, safety and environmental regulations is listed. This includes reportable quantities (RQ) for spills or discharges and threshold planning quantities (TPQ). All of this helps management to comply with various regulatory requirements. The content and organization of this section depends on where the material is manufactured or used, but is not intended to be a comprehensive list of all regulations that may apply.

Section 16. Other Information

This section provides a location for additional information that may be useful. It may include label text, a list of references, keys / legends explaining abbreviations used in the MSDS, or preparation and revision indicators. Hazard ratings defining the acute health, flammability, and reactivity hazards of a material may also be included.

Annex 2-4. HMIS and NFPA Label Rating Systems

There are two major labeling systems in use. The Hazardous Materials Information System pertains to routine uses and the NFPA (diamond) pertains to hazards of the chemical in a fire situation. Both systems use numbers to rate the hazard level, 0 being a minimal hazard, 4 being an severe hazard.



Hazardous Materials Information System (HMIS)

I. Health Hazard Rating (blue)

- 0 Minimal - No significant risk to health.
- 1 Slight - Irritation or minor reversible injury possible.
- 2 Moderate - Temporary or minor injury may occur.
- 3 Serious - Major injury likely unless prompt action is taken and medical treatment is given.
- 4 Severe - Life-threatening, major or permanent damage may result from single or repeated exposures.

II. Flammability Hazard Rating (red)

- 0 Minimal - Materials that are normally stable and will not burn unless heated.
- 1 Slight - Materials that must be preheated before ignition will occur. Flammable liquids in this category have flash points (the lowest temperature at which ignition can occur) at or above 93.4 °C [200 °F (NFPA Class IIIB)].
- 2 Moderate - Materials that must be moderately heated before ignition will occur, including flammable liquids with flash points at or above 37.8 °C (100 °F) and below 93.4 °C [200 °F (NFPA Class II and Class IIIA)].
- 3 Serious - Materials capable of ignition under almost all normal temperature conditions, including flammable liquids with flash points below 22.8 °C (73 °F) and boiling points above 37.8 °C (100 °F) and liquids with flash points between 22.8 °C (73 °F) and 37.8 °C [100 °F (NFPA Class IB and IC)].
- 4 Severe - Very flammable gases or very volatile flammable liquids that have their flash points below 22.8 °C (73 °F) and boiling points below 37.8 °C [100 °F (NFPA Class IA)].

III. Physical Hazard Rating (orange)

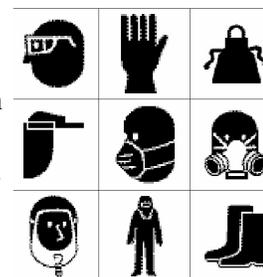
- 0 Minimal - Materials that are normally stable, even under fire conditions and will not react with water.
- 1 Slight - Materials that are normally stable, but can become unstable at high temperatures and pressures. These materials may react with water, but they will not release energy violently.
- 2 Moderate - Materials that, in themselves, are normally unstable and that readily undergo violent chemical change, but will not detonate. These materials may also react violently with water.
- 3 Serious - Materials that are capable of detonation or explosive reaction but which require a strong initiating source or which must be heated under confinement before initiation; or materials that react explosively with water.
- 4 Severe - Materials that are readily capable of detonation or explosive decomposition at normal temperatures and pressures.

IV. Chronic Effects Information

Chronic health effects are not rated because of the complex issues involved and the lack of standardized classifications and tests. However, based on information provided by the manufacturer/supplier, chronic effects may be indicated by (1) use of an asterisk (*) or other designation after the Health hazard rating corresponding to other information that may be available; or (2) written warnings in the upper white section of the HMIS label.

V. Personal Protective Equipment

Information provided by the manufacturer/supplier is used to determine the proper personal protective equipment. This is represented by a letter coding system which refers to a series of protective equipment configurations. In some instances, icons may be used instead of the codes. Although use of icons is not endorsed by HMIS, the icons are more specific than having employees try to remember a bunch of codes or consult a chart, something that could lead to confusion and/or a fatal accident.



NFPA Hazard Rating- Fire Diamond

I. Health Hazard (Blue). Degree of hazard; level of short-term protection.

- 0 Ordinary Combustible Hazard in a Fire
- 1 Slightly Hazardous
- 2 Hazardous
- 3 Extreme Danger
- 4 Deadly

II. Flammability (Red). Susceptibility to burning.

- 0 Will Not Burn - Any material that will not burn in air when exposed to a temperature of 815.5 °C (1500 °F) for a period of 5 minutes.
- 1 Will Ignite if Preheated - Materials that will burn in air when exposed to a temperature of 815.5 °C (1500 °F) for a period of 5 minutes or less; liquids, solids, and semi-solids having a flash point above 93.4 °C [200 °F (i.e., Class IIIB combustible liquids)].
- 2 Will Ignite if Moderately Heated - Liquids having a flash point above 37.8 °C (100 °F), but not exceeding 93.4 °C [200 °F (i.e., Class II and Class IIIA combustible liquids)]; solid materials in a dust, fibrous, or shredded form that may burn rapidly or readily give off flammable vapors, but do not form explosive atmospheres with air.
- 3 Will Ignite at Ambient Conditions - Liquids having a flash point below 22.8 °C (73 °F) and having a boiling point at or above 37.8 °C (100 °F) and those liquids having a flash point at or above 22.8 °C (73 °F) and below 37.8 °C [100 °F (i.e., Class IB and Class IC flammable liquids)]; materials that can form explosive mixtures with air and materials that burn with extreme rapidity.
- 4 Burns Readily at Ambient Conditions - Flammable gases; flammable cryogenic materials; any liquid or gaseous material that is liquid while under pressure and has a flash point below 22.8 °C (73 °F) and a boiling point below 37.8 °C [100 °F (i.e., Class IA flammable liquid)]; materials that ignite spontaneously when exposed to air.



III. Reactivity, Instability (Yellow). Energy released if burned, decomposed, or mixed.

- 0 Stable Even Under Fire Conditions and Not Reactive with Water
- 1 Unstable if Heated
- 2 Violent Chemical Change
- 3 Shock and Heat May Detonate
- 4 May Detonate at Normal Temperatures and Pressures

IV. Special Hazard (White).

OX = Oxidizer

ACID = acid (pH < 7.0)

W = Use No Water, reacts!

-- = No Special Hazard

COR = corrosive (either acid or base)

ALK = alkaline or base, caustic (pH > 7.0)

 = poison / highly toxic

 = radioactive

 = explosive metal