UF Herbert Wertheim College of Engineering
UNIVERSITY of FLORIDA

IPPD Integrated Product & Process Design

Safety Seminar:

CHEMISTRY FOR THE ENGINEER

Learn the WHY behind the safety rules

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http://ippd.ufl.edu/

We are all responsible for safety

- **Personal Protective Equipment (PPE)**
- **Know the rules!**

72 % Of establishments provide occupational safety training

1.2 hr Average per employee

Safety term "Chemical"

chemical is "any element, chemical compound, or mixture of elements and/or compounds." Thus, virtually any product is a "chemical."

- Element - the simplest form of matter. There are currently 109 known elements in the periodic table. Examples of elements are aluminum, carbon, chlorine, hydrogen, mercury and oxygen.
- Chemical compound - a substance consisting of two or more elements combined or bonded together so that its constituent elements are always present in the same proportions.
- Mixture - any combination of two or more chemicals if the combination is not, in whole or in part, the result of a chemical reaction.

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Factors Affecting Reactions

1. **Chemical nature of reactants**
2. **Ability of reactants to come in contact**
3. **Concentrations of reactants**
4. **Temperature**
5. **Presence of Catalysts**
6. **Second Law of thermodynamics**

5

Factors Affecting Reactions

1. Chemical nature of reactants

- What elements, compounds, salts are involved?
- What are fundamental differences in chemical reactivity?
- Safety term: Chemical Compatability

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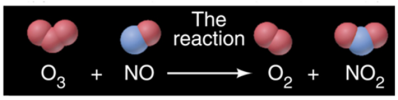
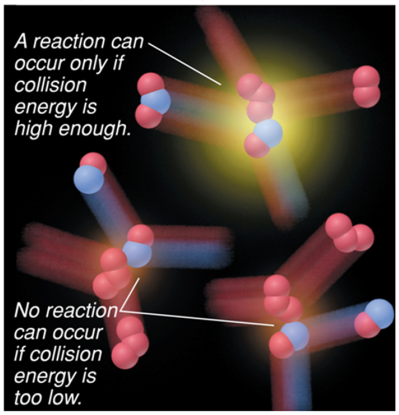
Factors Affecting Reactions

2. Ability of reactants to come in contact

- Reactants must meet in order to react





Collision theory

- molecules must collide to react.
- they must come into contact with sufficient force (E_A) so that chemical bonds break

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2. Ability of reactants to come in contact

The effect of surface area

A hot steel nail glows feebly when placed in O_2.

The same mass of steel wool bursts into flame.

3. Ability of reactants to come in contact

The effect of physical state

- **Gas** or **solution** phase facilitates this
  - Reactants mix and collide with each other easily
  - **Homogeneous** reaction
    - All reactants in same phase
    - Occurs rapidly
  - **Heterogeneous** reaction
    - Reactants in different phases
    - Reactants meet only at interface between phases
    - Surface area determines reaction rate
    - Increase area, increase rate; decrease area, decrease rate

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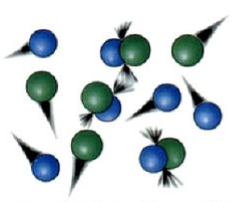
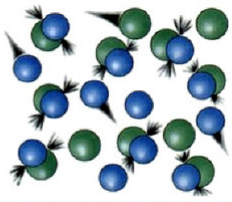
Factors Affecting Reactions

3. Concentrations of reactants



Low concentration = Few collisions



High concentration = More collisions

- Increasing the concertation of reactant, increases the rate of reactions
- The more particles present, the more often they collide
- Rates of both homogeneous and heterogeneous reactions affected by concentration

Factors Affecting Reactions

4. Temperature

- Rates are often very sensitive to temperature
- Raising temperature usually makes reaction faster for two reasons:
  a. Faster molecules collide more often and collisions have more energy
  b. Most reactions, even exothermic reactions, require energy to occur
- Rule of thumb:
  - Rate *doubles* if temperature increases by 10 ° C (10 K)

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Factors Affecting Reactions

5. Presence of Catalysts

- **Catalysts**
  - Substances that increase rates of chemical reactions without being used up
  - Rate-accelerating agents
  - Speed up rate dramatically
    - Rate enhancements of 10^6 not uncommon
  - Chemicals that participate in mechanism but are regenerated at the end
- **e.g.** Enzymes and zeolites

Safety terms

Chemical nature of reactants

Chemical Reactivity

- the tendency of a substance to undergo chemical changes in a system.
- may also mean chemical properties

Chemical Compatibility

- measure of how stable a substance is when mixed with another substance.
- If substances mix and do not change they are considered compatible.

Chemical Equilibrium: When reactants are put together, how far will the reaction go?

Chemical Kinetics: How long will it take to reach an equilibrium state?

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Example: Are Bleach and Ammonia compatible?

First the hydrochloric acid is formed:

$NaOCl \rightarrow NaOH + HOCl$

$HOCl \rightarrow HCl + O$

And then the **ammonia** and chlorine gas react to form **chloramine**, which is released as a vapor:

$NaOCl + 2HCl \rightarrow Cl_2 + NaCl + H_2O$

$2NH_3 + Cl_2 \rightarrow 2NH_2Cl$

Example:

- If ammonia is present in excess (which it may or may not be, depending on your mixture), toxic and potentially explosive liquid **hydrazine** may be formed.
- While impure hydrazine tends not to explode, it's still toxic, plus it can boil and spray hot toxic liquid.

$$2NH_3 + NaOCl \rightarrow \mathbf{N_2H_4} + NaCl + H_2O$$

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Safety term

Hazardous chemical

Physical hazard:

- 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.

Health hazard

- there is statistically significant evidence based on at least one study conducted in accordance with established scientific principles
  - that acute or chronic health effects may occur in exposed employees.

What is Involved in Conducting a Hazard Determination?

1. Selection of chemicals to evaluate;
2. Collection of data;
3. Analysis of the collected data; and
4. Documentation of the hazard determination process and the results obtained.

MATERIAL SAFETY DATA SHEET

DATE OF PREPARATION: 01/16/13

I. General Information

CHEMICAL NAME & SYNONYM:	TRADE NAME: PET URINE NEUTRALIZER
CHEMICAL FAMILY: Synthetic Detergent	FORMULA: Proprietary
PROPER DOT SHIPPING NAME: Cleaning Compound, Liquid	DOT HAZARD CLASSIFICATION: None
SUPPLIER: ZEOFILL INC. 5241 7TH AVE. Hesperia, Ca 92345	SUPPLIER'S PHONE NUMBER: 1-888-926-4785 24-HOUR EMERGENCY PHONE NUMBER: 1-800-535-5053

II. Ingredients

PRINCIPAL COMPONENTS	CAS #	THRESHOLD LIMIT VALUE (UNITS)
MUTANT BACTERIA STRAIN	N/A	N/A
NONIONIC SURFACTANT	90-164-59	N/A
WATER	7732-18-5	N/A
OPACIFIER	N/A	N/A
FRAGRANCE	N/A	N/A

III. Physical Data

BOILING POINT (°F): 212°F	SPECIFIC GRAVITY (H_2O=1): 1.0
VAPOR PRESSURE (MM HG): N/A	PERCENT VOLATILE (%): ~100.0
VAPOR DENSITY (AIR=1): >1	EVAPORATION RATE (WATER = 1): >1
SOLUBILITY IN WATER: Complete	pH: 7
APPEARANCE AND ODOR: Opaque white liquid with characteristic odor	

IV. Fire & Explosion Hazard Data

FLASH POINT (TEST METHOD): NONE (TCC)	LOWER EXPLOSIVE LIMIT (LEL): N/A
AUTO IGNITION TEMPERATURE: NONE	UPPER EXPLOSIVE LIMIT (UEL): N/A
EXTINGUISHING MEDIA: Water, Dry Chemical, CO_2	
SPECIAL FIRE FIGHTING PROCEDURES: NONE	
UNUSUAL FIRE & EXPLOSION HAZARDS: NONE	

V. Health Hazard Data

OSHA-ACGIH THRESHOLD LIMIT VALUE: N/A	
CARCINOGEN -NTP PROGRAM: None	CARCINOGEN - IARC PROGRAM: None
SYMPTOMS OF EXPOSURE: Skin & Eye Irritase	
Medical Conditions Aggravated by Exposure: None	
PRIMARY ROUTES OF ENTRY: Skin, Eyes, Nose, Mouth	

EMERGENCY FIRST AID:

Skin: Flush with water. See a physician.
Eyes: Flush with water for 15 minutes. See a physician.
Ingestion: Give large amounts of water. See a physician.
Inhalation: Remove to fresh air.

VI. Reactivity Data

STABILITY:	UNSTABLE	X	STABLE
INCOMPATABILITY-Material to Avoid: NONE			
HAZARDOUS POLYMERIZATION:	MAY OCCUR	X	WILL NOT OCCUR
HAZARDOUS DECOMPOSITION PRODUCTS: NONE			CONDITIONS TO AVOID: None

VII. Environmental Protection Procedures

SPILL RESPONSE: Contain Spill. Soak up in an absorbant material. Flush area with water.

WASTE DISPOSAL METHOD: In accordance with Federal, State and Local regulations.

VIII. Special Protection Information

EYE PROTECTION: Splash Goggles	SKIN PROTECTION:
RESPIRATORY PROTECTION: None Required	VENTILATION RECOMMENDED: Local Exhaust
OTHER PRECAUTIONS: None	

IX. Special Precautions

HYGIENIC PRACTICES IN HANDLING & STORAGE:	Avoid Skin or Eye contact.
PRECAUTIONS FOR REPAIR & MAINTENANCE OF CONTAMINATED EQUIPMENT:	Flush with water and allow to air dry.
OTHER PRECAUTIONS:	None

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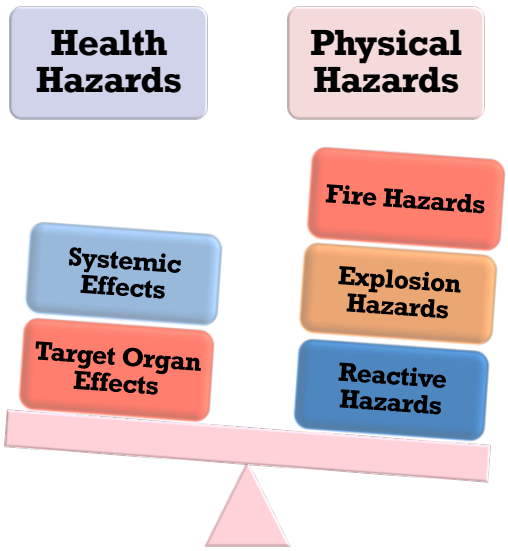
General Hazard Categories



For a hazard determination to be complete, one must consider all possible hazards, and document any hazards that are identified.

Properties of Hazard Chemicals

- A chemical is a physical hazard if it:
  - is likely to burn or support fire;
  - may explode or release high pressures that can inflict bodily injury; or
  - can spontaneously react on its own, or when exposed to water.

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Safety term

Fire Hazards

Combustible and Flammable Liquids

- The ability of a chemical to either burn or support burning is a potentially disastrous physical hazard.
- The two primary measures of the ease with which a liquid will burn are
  - flashpoint
  - autoignition temperature.

Fire Hazards

Definitions

flashpoint

- The is the lowest temperature at which a liquid will emit sufficient vapors to form an ignitable mixture with air.

autoignition

- is the characteristic of a material in which it will spontaneously burn without the aid of an ignition source, such as a spark or flame.

Fuel	Flash point	Autoignition temperature
Ethanol (70%)	16.6 °C (61.9 °F)	363 °C (685 °F)

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Safety term

Fire Hazards

Combustible and Flammable Liquids

- Many agents will burn when ignited whereas there are only a few that will spontaneously erupt into flames.
- While no single measure of flammability is sufficient for all purposes, the most commonly found measure in the literature is the flashpoint.

Safety term

The only difference between a "flammable" and "combustible" liquid is the relative ease (temperature) with which the substance burns or supports burning.

- For a pure chemical compound:
  - flashpoint is between 100F - 210F (37.8° C - 93.3° C), it is a combustible liquid;
  - if the flashpoint is below 100° F (38° C), it is a flammable liquid.
- For chemical mixtures.
  - Not combustible liquid so long as less than 1% of the total volume of components have flashpoints between 100° and 200° F.
  - Not a flammable liquid if it is composed of at least 99% (by volume) of components with flashpoints above 100° F (38° C).

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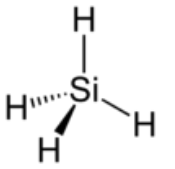
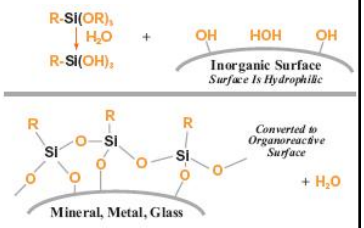
Example: Silane

Flash point	Not applicable, pyrophoric gas
Autoignition temperature	~ 18 °C (64 °F; 291 K)

- Industry use for silane and functionalized silanes.
  - coupling agents to adhere fibers such as glass fibers and carbon fibers, certain polymer matrices, stabilizing the composite material.
  - bio-inert layer on a titanium implant.
  - water repellents,
  - masonry protection,
  - control of graffiti
  - polycrystalline silicon layers on silicon wafers when manufacturing semiconductors,
- sealants.





*Chen, J. R.; Tsai, H. Y.; Chen, S. K.; Pan, H. R.; Hu, S. C.; Shen, C. C.; Kuan, C. M.; Lee, Y. C. & Wu, C. C. (2006). "Analysis of a silane explosion in a photovoltaic fabrication plant". Process Safety Progress. **25** (3): 237–244. doi:10.1002/prs.10136*

Example: Silane

Also health hazard!

- $SiH_4(g) + 2O_2(g) \rightarrow SiO_2(s) + 2H_2O(g)$
- **Hazardous byproducts of combustion**
- $SiH_4(g) + O_2(g) \rightarrow SiO_2(s) + 2H_2(g)$
- $SiH_4(g) + O_2(g) \rightarrow SiH_2O(s) + H_2O(g)$
- $SiH_4(g) + 1/2\ O_2(g) \rightarrow SiH_2O(s) + H_2(g)$
- $SiH_2O(s) + O_2(g) \rightarrow SiO_2(s) + H_2O(g)$

*Chen, J. R.; Tsai, H.Y.; Chen, S. K.; Pan, H. R.; Hu, S. C.; Shen, C. C.; Kuan, C. M.; Lee, Y. C. & Wu, C. C. (2006). "Analysis of a silane explosion in a photovoltaic fabrication plant". Process Safety Progress. **25** (3): 237–244. doi:10.1002/prs.10136*

More examples

- Flammable liquids (with flashpoint temperatures) are:
  - acetone (0°F),
  - ethyl ether (-49°F),
  - ethyl alcohol (55°F),
  - and gasoline (-45°F).

- Combustible liquid to present a fire hazard it must be above normal room temperature.
- Examples are:
  - kerosene (100°-162°F)
  - and Stoddard solvent (102°-110°F).

"paint thinner"

Safety terms

Flammable gas

- burns in air at a concentration of less than 13%; or
- has an LFL of 13% or more with a concentration range for burning in air greater than 12%. The range is the difference between the LFL and the UFL.

Flammable Solid

- "a solid, other than a blasting agent or explosive hat is liable to cause fire through friction, absorption of moisture, spontaneous chemical change, or retained heat from manufacturing or processing, or which can be ignited readily and when ignited burns so vigorously and persistently as to create a serious hazard.
- chemical formulation on the head of matches.
- Some metal powders (such as magnesium) can react with moisture and burn and are thus classified as flammable solids.

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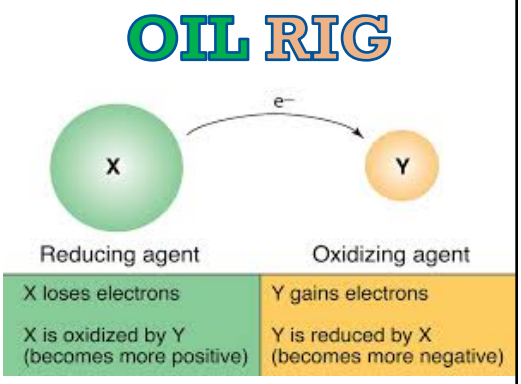
Safety term

Fire Hazards

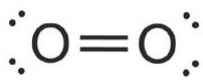
Oxidizer (oxidizing agent)

- chemical or substance that brings about an oxidation reaction.
  - contain oxygen,
  - receive electrons



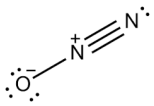
Oxidizer (oxidizing agent)

- Any electron-withdrawing reactant is an oxidizer, whether in gas or liquid phase (solid too).

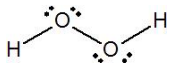


atmospheric oxygen (g)

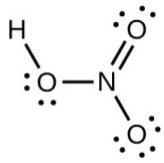
- Examples:
  - The most common oxidizer is atmospheric oxygen
  - Oxygen-containing chemicals
  - halogens (e.g., bromine, chlorine, and fluorine)



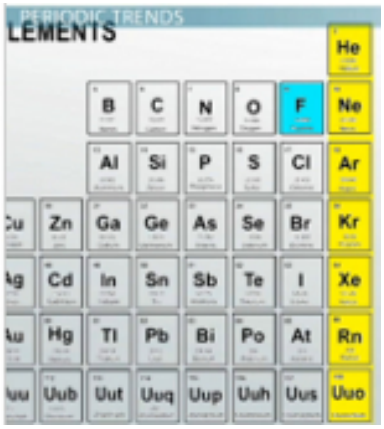
nitrous oxide (3 RS)



hydrogen peroxide (l)



Nitric Acid (2 RS)



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Oxidizer and Chemical Structure

- Polyatomic ions

Charge -1
ClO_4^- perchlorate
ClO_3^- chlorate
ClO- hypochlorite
NO_3- nitrate
NO_2^- nitrite
MnO_4^- permanganate

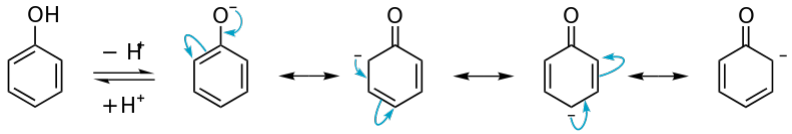
Charge -2
O_2^{2-} peroxide
$Cr_2O_7^{2-}$ dichromate
$S_2O_8^{2-}$ persulfate

- classified as explosives or blasting agents rather than oxidizers
  - Can initiate or greatly accelerate the burning of fuels.
- Oxidizers: Keep away from acids, bases, organics and metals; keep cool. Examples of strong oxidizers: Perchloric acid, nitric acid.
- NOTE: Absolute certainty can only be properly established in the laboratory since oxidation involves not only the oxidizing potential of the oxidizer, but also the chemical formulation of the fuel with which it comes in contact.

Example:

Ensure that phenol crystals are separated from oxidizers

- The majority of these compounds are soluble molecules but the smaller molecules can be volatile.



Phenol-phenolate equilibrium, and resonance structures giving rise to phenol aromatic reactivity.

- Natural phenols are reactive species toward oxidation.
  - Good ones: notably the complex mixture of phenolics, found in food for example, can undergo autoxidation during the ageing process.

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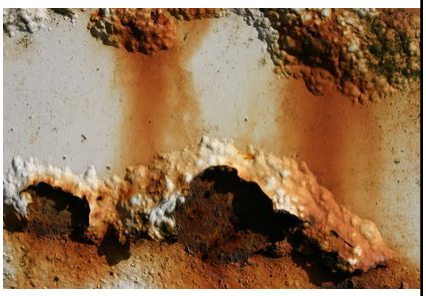
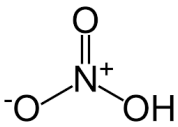
Corrosive Chemicals

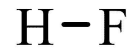
- Corrosives consist of four major classes:
  - acids, bases,
  - dehydrating agents
  - oxidizing agents.
- Inhalation of the vapors of these substances can cause severe respiratory tract irritation. Contact with these chemicals may cause burns to the skin, respiratory tract and eyes.



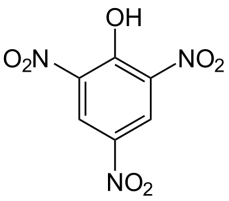
Corrosive Chemicals: Strong acids



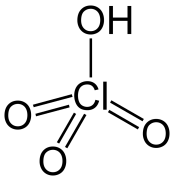
1. **Nitric acid**



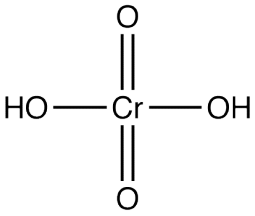
4. **Hydrofluoric acid (HF)**



3. **Picric acid**



2. **Perchloric acid**



Chromic acid/ chromerge solutions

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General Hazard Categories

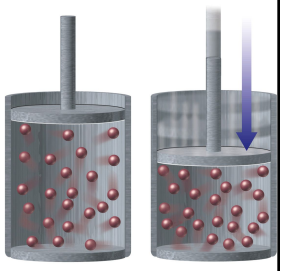
For a hazard determination to be complete, one must consider all possible hazards, and document any hazards that are identified.

Explosive Hazards

Compressed Gas

1. "a gas or mixture of gases having, in a container, an absolute pressure exceeding 40 psi at 70° F (21.1° C): or
2. a gas or mixture of gases having, in a container, an absolute pressure exceeding 104 psi at 130° F (54.4° C) regardless of the pressure at 70° F (21.1° C); or
3. a liquid having a vapor pressure exceeding 40 psi at 100° F (37.8° C) as determined by ASTM D-323-72."

Boyles Law and Thermodynamics



Gas

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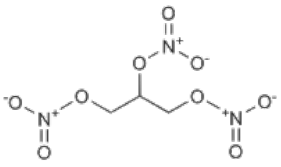
Explosive Hazards

Explosive

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

Type 1: supersonic reactions (detonation), for example, nitroglycerine and TNT.

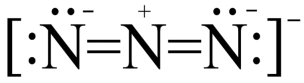
nitroglycerine



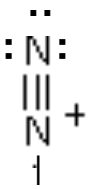
Type 2: materials (usually mixtures) that burn rapidly but at a subsonic rate. Examples of this type are gunpowder, rocket propellants, and pyrotechnic mixtures (fireworks).

Explosive: Structural Trends

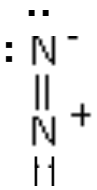
- functional groups

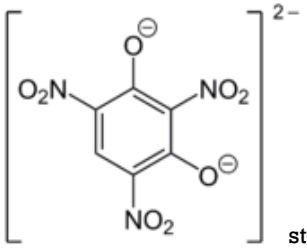


azides



dizonium





styphnate

While the presence of such functional groups suggests explosive potential, it is usually necessary to confirm this hazard via experimental studies.

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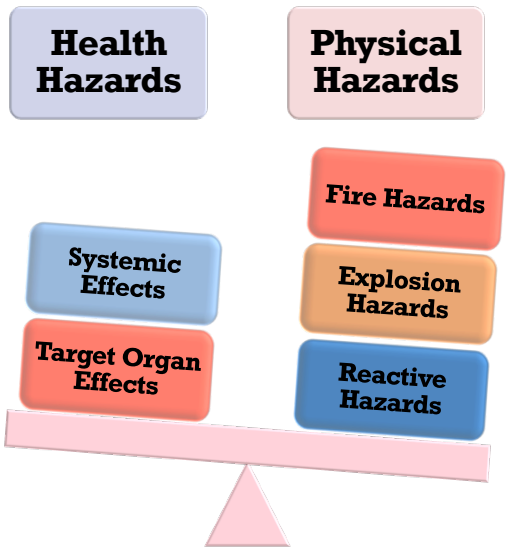
General Hazard Categories



For a hazard determination to be complete, one must consider all possible hazards, and document any hazards that are identified.

Physical hazard: Reactive Hazards

- release of gases that will burn, explode, or produce high pressure that can inflict injury to a person nearby.
- the reactive materials may release substances that are considerably more toxic than themselves.
- types of reactive hazards:
  - organic peroxides,
  - unstable (reactive) materials, a
  - water-reactive materials.
- Mixing incompatible materials may result in the formation of unstable/reactive materials

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But first, comparison of properties

Organic Compound	Inorganic Compounds
Bonding: covalent	Bonding: mostly ionic
Physical State: g, l, s	Physical State: s
Low melting points (<360oC)	High melting point
Soluble in organic solvents. (solubility depend on polarity)	Insoluble in organic solvents
Aqueous solutions do not conduct electricity	Aqueous solutions conduct electricity
Almost all burn	Very few burn
Reactions are usually slow	Reactions are often fast.

Organic Peroxide

- "an organic compound that contains the bivalent -O-O structure and which may be considered a structural derivative of hydrogen peroxide where one or both of the hydrogen atoms has been replaced by an organic radical."
- The peroxide functional group is relatively unstable and most organic peroxides will spontaneously decompose at a slow rate.
  - peroxide ion/functional group (O_2^{2-})
  - sodium peroxide (Na_2O_2), a bleaching agent,
  - barium peroxide (BaO_2), formerly used as a source of hydrogen peroxide.

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Unstable (Reactive) Material

- "chemical which in the pure state, or as produced or transported, will vigorously polymerize, decompose, condense, or will become self-reactive under conditions of shocks, pressure or temperature."
- The main difference between an unstable material and an explosive is the rate of the reaction.
  - While the rate of reaction for unstable materials is less than that in the case of explosives, the unstable materials can still present a serious hazard due to the generation of high temperatures and pressures.
  - In some cases, the reaction may be rapid enough to approach explosive potential.

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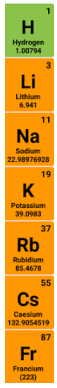
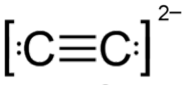
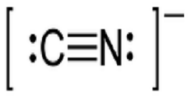
Water-Reactive Material

- "chemical that reacts with water to release a gas that is either flammable or presents a health hazard."
- For example,
- sodium and potassium, when exposed to water, will react and release hydrogen, presenting an explosive hazard.
- Carbides (e.g., calcium carbide) can generate acetylene, a flammable gas, when exposed to water.
- inorganic salt containing cyanide
  - Cyanide compounds must not be stored near acids. (Accidental mixing may release cyanide gas.)

Alkali metals







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Questions?

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