Laboratory Hazards

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Contact Chapman University EH&S
with any questions on university-specific practices

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Hazard vs. Risk

- Hazard – an inherent (built-in) property of a material
- Risk – the extent to which that material can cause harm
- One can reduce and/or remove risks associated with a hazardous material, but you can not remove the underlying hazard itself
  - Unless you get rid of the hazardous material

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I. Definition of a "Hazard"

- As assigned by OSHA Standard 1910.1200
- A hazardous chemical is one which is a physical or health hazard
- Physical Hazards are one of two major classes of hazardous materials covered by OSHA.
  - The other major hazard class is Health Hazards
  - Various types of physical hazards and
  - What you need to know to use these materials safely and effectively.

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Hazards

- Physical Hazards - substance for which there is valid evidence that it is combustible, compressed, explosive, flammable, oxidizer, pyrophoric, unstable or water (moisture) reactive.
- Non-chemical related physicals hazards are factors within the environment that can harm the body without necessarily touching it.
  - Noise is an example of a physical hazard.

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Physical Hazards

- Other Examples of non-chemical physical hazards:
  - Heat and Cold
  - Radiation
  - Noise
  - Ergonomics
  - Vibration

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II. Categories of Physical Hazards

- Fire
- Explosion
- Chemical Reactivity

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Fire & Explosion Hazard

- For hydrogen, oxygen, methane, acetylene
  - Hydrogen – when vaporized and ignited, releases 30 times the energy of an equal weight of TNT
- Liquid oxygen makes combustible materials burn much more quickly and violently
- Liquid inert gases, such as liquid nitrogen or helium, are capable of condensing oxygen from the atmosphere and causing oxygen enrichment in unsuspected areas.

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Fire & Explosion Hazard

- Improper labeling, handling or storage of certain material can ~~pose~~ contribute to the ~~a~~ risk of fire or explosion
- Every workplace should have an evacuation plan for getting people out of a building in case of fire and an alarm or alert system to quickly inform employees of an emergency
- Every worker should be trained on what to do in case of an emergency

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Explosives

- A substance or mixture of substances that, when initiated by heat, light, friction, impact, or detonation undergoes a rapid chemical reaction, giving off large volumes of hot gases and are typically accompanied by fires
- Explosives may detonate – create a high pressure wave
- Explosives may deflagrate – rapid decomposition of explosive with little to no high pressure wave
- Many of these compounds become more sensitive as they age or dry out
- May be regulated by the U.S. Bureau of Alcohol, Tobacco, Firearms & Explosives (ATF)

Explosives

- Examples:
  - Hydrogen and Chlorine will react violently in the presence of light
  - Acetylides, Azides, Organic Nitrates, Nitrocompounds and Peroxides are all shock sensitive
  - Picric acid and Picryl Chloride should be kept damp

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Explosives

- Criteria

Category	Criteria
Unstable* explosives or explosives of Division 1.1 to 1.6	For explosives of Divisions 1.1 to 1.6, following are the core set of tests that need to be performed: **Explosibility**: according to UN Test Series 2. Intentional explosives** are not subject to UN Test series 2. **Sensitiveness**: according to UN Test Series 3 **Thermal stability**: according to UN Test 3(c) Further test are necessary to allocate the correct Division.

** Unstable explosives are thermally unstable and/or too sensitive for normal handling, transport and use.*

*** This comprises substances, mixtures and articles which are manufactured with a view to producing a practical, explosive or pyrotechnic effect.*

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Explosives

	Unstable Explosive	Division 1.1	Division 1.2	Division 1.3	Division 1.4	Division 1.5	Division 1.6
Symbol	Exploding bomb	Exploding bomb	Exploding bomb	Exploding bomb	Exploding bomb; or 1.4 on range background *	1.5 on orange backgroun d*	1.6 on orange backgroun d*
Signal word	Danger	Danger	Danger	Danger	Warning	Danger	No signal word
Hazard statement	Unstable Explosive	Explosive; mass explosion hazard	Explosive; severe projection hazard	Explosive; fire, blast or projection hazard.	Fire or projection hazard	May mass explode in fire	No hazard statement

** Applies to substances, mixtures and articles subject to some regulatory purposes (e.g. transport).*

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Reactive Chemicals

- Include those which are:
  - Inherently unstable and susceptible to rapid decomposition
  - Capable of reacting alone or with other substances in an uncontrolled manner, liberating heat, toxic gas or leading to an explosion
- The hazards of reactive chemicals must be understood and they should be handled carefully
  - Some chemicals can create violent explosions with only milligram quantities

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III. Fire Hazards

- Combustible liquid
- Flammable liquid
- Flammable aerosol
- Flammable gas
- Flammable solid
- Oxidizer Pyrophoric

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Combustible Liquid

- OSHA defines as,
  - "any liquid having a flash point $\geq$ 100°F, but below 200°F, except any mixture having components with flashpoints of 200°F, or higher, the total volume of which make up 99% or more of the total volume of the mixture."

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Flammable Liquid

- OSHA defines as,
  - "A liquid having a flash point of not more than 93°C"
  - Flammable liquids are classified in one of four categories for this class according to the following table:

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Flammable liquids

Category	Criteria
1	Flash point <23°C and initial boiling point ≤35°C
2	Flash point <23°C and initial boiling point >35°C
3	Flash point ≥23°C and ≤60°C
4	Flash point >60°C and ≤93°C

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Flammable Liquids

Elements of a label:

	Category 1	Category 2	Category 3	Category 4
Symbol	Flame	Flame	Flame	No Symbol
Signal Word	Danger	Danger	Warning	Warning
Hazard Statement	Extremely flammable liquid and vapor	Highly flammable liquid and vapor	Flammable liquid and vapor	Combustible liquid

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Flammable Aerosol

OSHA defines as,

- "aerosol dispensers containing a gas compressed, liquefied or dissolved under pressure, with or without a liquid, paste or powder, and fitted with a release device."
- Allows contents to be ejected as solid or liquid particles suspension in gas, as a foam, paste or powder or in a liquid or gaseous state
- Aerosols can be considered for classification as flammable if they contain any component which is classified as flammable, i.e.:
  - Flammable liquids
  - Flammable gases
  - Flammable solids
  - Examples: smoke, smog, and tear gas

Flammable Aerosols

- Classified in one of two categories on the basis of its components:
  - Chemical heat of combustion
  - Results of the foam test (for foam aerosols)
  - Ignition distance test
  - Enclosed space test

Flammable aerosols

- Label elements

	Category 1	Category 2
Symbol	Flame	Flame
Signal word	Danger	Warning
Hazard statement	Extremely flammable aerosol	Flammable aerosol

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Flammable Gases

- OSHA defines as,
  - "a gas having a flammable range with air at 20°C and a standard pressure of 101.3 kPa."

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Flammable gas

Criteria:

Category	Criteria
1	Gases, which at 20°C and a standard pressure of 101.3 kPa: (a) Are ignitable when in a mixture of 13% or less by volume in air; or (b) Have a flammable range with air of at least 12 percentage points regardless of the lower flammable limit
2	Gases, other than those of Category 1, which, at 20°C and a standard pressure of 101.3 kPa, have a flammable range while mixed in air

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Flammable gas

Elements of a Label:

	Category 1	Category 2
Symbol	Flame	No Symbol
Signal word	Danger	Warning
Hazard statement	Extremely flammable gas	Flammable gas

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Flammable solids

- Defines as,
  - “a solid which is readily combustible, or may cause or contribute to fire through friction.”
  - Readily combustible solids are powdered, granular, or pasty substances which are dangerous if they can be easily ignited by brief contact with an ignition source, such as a burning match, and if the flame spreads rapidly.

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Flammable Solids

Examples include:

a. Solids which may cause a fire through friction, such as matches

b. Pyrophoric materials, those that can ignite with no external ignition source within five minutes after coming in contact with air

c. Self-heating materials, those that exhibit spontaneous ignition or heat themselves to a temperature of 200°C during a 24-hr test period **[Spontaneous Combustion]**

d. Dangerous when wet material, those that react with water to become spontaneously flammable or to give off flammable gas or toxic gas at a rate greater than 1 liter per kilogram of the material, per hour

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Flammable solids

Classified in one of two categories based on the following criteria:

Category	Criteria
1	Burning rate test: Substances or mixtures other than metal powders: a) wetted zone does not stop fire; and b) burning time < 45s or burning rate > 2.2 mm/s Metal powders: burning time ≤ 5 min
2	Burning rate test: Substances or mixtures other than metal powders: a) wetted zone stops the fire for at least 4 min; and b) burning time < 45s or burning rate > 2.2 mm/s Metal powders: burning time > 5 min and ≤ 10 min

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Flammable solids

Elements of a Label:

	Category 1	Category 2
Symbol	Flame	Flame
Signal word	Danger	Warning
Hazard statement	Flammable solid	Flammable solid

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Oxidizer Pyrophoric

- Literally means “fire-loving”
- These materials can spontaneously ignite in air
- Many are also water reactive, reacting vigorously with water or high humidity, often igniting upon contact
- Typically manipulated in an inert (unreactive) atmosphere of nitrogen or argon using specialized glassware
- Examples:
  - Organometallic reagents such as Alkyllithiums, Alkylzincs, Alkylmagnesiums (Grignards) and some finely divided Metal Powders
  - Specific examples include Diborane, Diethylzinc, tert-Butyllithium, and Diphosphine

IV. Explosion Hazards

Compressed gas explosive

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Compressed Gas Explosive

Three major groups of compressed gases stored in cylinders: Liquefied, non-liquefied and dissolved gases -pressure is commonly given in units of kPa (kilopascals)

- Liquefied Gases
  - Gases which can become liquids at normal temperatures when they are inside cylinders under pressure.
  - They exist inside the cylinder in a liquid-vapor balance or equilibrium.
- Non-Liquefied Gases
  - Also known as compressed, pressurized or permanent gases.
  - Do not become liquid when compressed at normal temperatures, even at very high pressures.
  - Examples: oxygen, nitrogen, helium, and argon
- Dissolved Gases
  - Acetylene is the only common dissolved gas.
  - Very chemically unstable. Can explode at atmospheric pressure but stored in cylinders at high pressures (up to 250 psig at 21°C)
  - Acetylene cylinders are fully packed with inert, porous filler (acetone or suitable solvent) in which the gas can dissolve. Acetylene in solution is stable.

Compressed Gas Explosives

- Hazards present from accidentally broken or leaking valve or from a safety device
  - Even at low pressure, gas can flow rapidly from an open or leaking cylinder
- Some compressed gases are corrosive
  - Can burn and destroy body tissues on contact.
  - Some can attack and corrode metals
- Some can be toxic cause various adverse health effects
  - Based on the specific gas, concentration, length of exposure and route of exposure

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Compressed gas explosives

- Slight temperature/pressure increase, or mechanical shock, can produce unstable chemical reactions
  - Polymerization or Decomposition
  - May result in fire or explosion
  - Examples: 1,3-butadiene, Methyl Acetylene, Vinyl Chloride, Tetrafluoroethylene and Vinyl Fluoride
- Oxidizing gases can react rapidly and violently with combustible materials such as
  1. finely-divided metals
  2. organic (carbon-containing) substances or
  3. other oxidizable substances and fire or explosion can result
  - Fires in atmospheres enriched with oxidizing gases are very hard to extinguish and can spread rapidly

Compressed gas explosives

Criteria as determined below:

Group	Criteria
Compressed gas	A gas which when packaged under pressure is entirely gaseous at -50°C; including all gases with a critical temperature ≤ -50°C
Liquefied gas	A gas which when packaged under pressure, is partially liquid at temperatures above -50°C. A distinction is made between: a) High pressure liquefied gas: a gas with a critical temperature between -50°C and +65°C; and b) Low pressure liquefied gas: a gas with a critical temperature above +65°C
Refrigerated liquefied gas	A gas which when packaged is made partially liquid because of its low temperature.
Dissolved gas	A gas which when packages under pressure is dissolved in a liquid phase solvent

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Compressed gas explosives

Elements of a label:

	Compressed gas	Liquefied gas	Refrigerated liquefied gas	Dissolved gas
Symbol	Gas cylinder	Gas cylinder	Gas cylinder	Gas cylinder
Signal word	Warning	Warning	Warning	Warning
Hazard statement	Contains gas under pressure; may explode if heated	Contains gas under pressure; may explode if heated	Contains refrigerated gas; may cause cryogenic burns or injury	Contains gas under pressure; may explode if heated

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V. Reactive Hazards

- Organic peroxide
- Unstable (reactive)
- Water-reactive

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Organic Peroxides

- Organic peroxides are both fuels and oxidizers in one
- Organic peroxides are extremely sensitive to shock, heat, friction, strong oxidizers and reducing agents
- Some materials form peroxides when exposed to air or light
  - On example - Ethers
  - Date these containers when new and dispose within six months

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Organic peroxides

- Liquid or solid organic substances which contain the bivalent -0-0- structure, may be considered derivatives of hydrogen peroxide
- Thermally unstable, may undergo exothermic self-accelerating decomposition
- May have one or more of the following properties:
  - Be liable to explosive decomposition
  - Burn rapidly
  - Be sensitive to impact or friction
  - React dangerously with other substances

Organic peroxides

Elements of the label:

	Type A	Type B	Type C & D	Type E & F	Type G**
Symbol	Exploding bomb	Exploding bomb and flame	Flame	Flame	**There are no label*
Signal word	Danger	Danger	Danger	Warning	*elements allocated to*
Hazard statement	Heating may cause an explosion	Heating may cause a fire or explosion	Heating may cause a fire	Heating may cause a fire	*this hazard category.**

***should be considered for properties belonging to other hazard classes.*

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Unstable (Reactive) Materials

- These chemical are unstable and may decompose spontaneously
- Decomposition may be from contact from air, water, or other chemicals
- May ignite spontaneously when exposed to oxygen or moisture in the air (while $\leq$ 130 degrees)
- These must be stored under water, mineral oil, or an inert, dry atmosphere depending on the substance
- Examples:
  - Diazomethane, Butadiene, Polymerization Reactions, Highly Nitrated Compounds
  - Phosphorous, Titanium Dichloride, Tributylaluminum, Lithium Hydride

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Water Reactive

- Water reactive chemicals react violently with water
- Many produce hydrogen gas that can ignite when mixed with air
- Others give off large amounts of heat when mixed with water
- Contact with the skin can cause severe thermal and alkali burns
- Examples
  - Alkali Metals, Organometallic Compounds, some Hydrides, Strong Acids and Bases

MSDS Relevance

- Material safety data sheets provide the necessary information to understand and deal with potential hazards associated with a particular substance
- Read carefully before using a hazardous material for the first time or any time you are unsure about the hazards or necessary precautions
- Help to reduce the risks associated with the materials in your workplace
- MSDS's are only required for materials that are hazardous

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