Recognizing Chemical Hazards

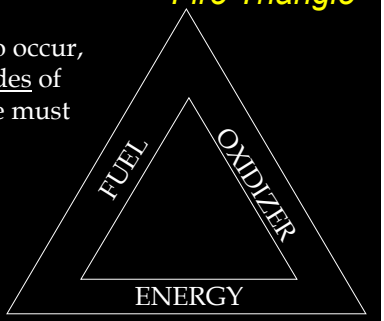
- Flammability
- Oxidizing and Reducing Agents
- Corrosives
- Water Reactive
- Toxic Chemicals
- Sources of Information

Flammability

- Almost all organic compounds (those containing C and H) will burn.
- Burning is the rapid oxidation of a fuel by an oxidizer (usually air) with the liberation of heat and (usually) light.
- A fire can only be started when sufficient energy is present to initiate the reaction.

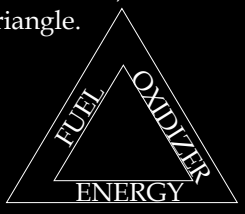
Fire Triangle

- For a fire to occur, all three sides of the triangle must be present.



Fire Control and Flammable Solvent Safety

- The key to safety is removing, or otherwise making inaccessible, at least one side of the fire triangle.



Examples of Flammable Solvent

- Acetone
- Ethanol
- Methanol
- Hexane
- Ether
- Toluene
- Gasoline

Removing the fuel may be the easiest approach

- Store flammable solvents is areas isolated from reactive substances, such as oxidizers, e.g., nitric acid.
- Storage areas should be well-ventilated to prevent build up of vapors.
- When using or dispensing flammable solvents, use a working fume hood.

Removing the fuel side of triangle

- Approved metal safety cans cannot break easily and thus, fuel will not be spilled.
- When transporting solvents that are stored in glass bottles, use an approved safety over-container to eliminate breakage.

Removing the ignition source

- This can be very difficult as there are many possible energy sources.
- Electrical heaters, sparking electrical motors, stirrers, fans, etc.
- Thermostat switches in refrigerators
- Bunsen Burners
- Static electricity can be generated by clothing or by the motion of a solvent being poured out of a container.

Laboratory Safety Instruction

- Recognizing Chemical Hazards
  - Flammability (continued)
  - Oxidizing and reducing agents
  - Corrosives
  - Water reactive compounds

Insidious Hazards of Solvents

- Liquid Density
  - If a solvent is less dense than water, you will not be able to put out a fire with water since the solvent will float on the water.
- Vapor Density
  - The vapors of most solvents are more dense than air and can travel long distances to an ignition source.
  - The vapor "wick" can then permit a flash back to the source.

Insidious Hazards of Solvents

- Water Solubility
  - A water soluble organic solvent (such as ethyl alcohol) may give off sufficient solvent vapor to burn even when diluted with water.
  - Water would not be efficient for extinguishing a fire of such a liquid.

Preventing Fires and Explosions, review

- Know the flammability of the chemicals you use.
- Keep the fire triangle in mind.
- Store and transport solvents safely.
- Beware of ignition sources.
- Electrically ground flammable liquid containers before making transfers.

Fire Extinguishers - Fire Types

- Extinguishers are based on the area of coverage and the type of fire.
- Type A: Wood, paper, rubber, plastic
- Type B: Flammable liquids and greases
- Type C: Electrical equipment
- Type D: Active/combustible metals

Fire Extinguishers to use

- Type A: Water or water/foam
- Type B: Foam, carbon dioxide, dry chemical, $NaHCO_3$, $(NH_4)_3PO_4$
- Type C: carbon dioxide, dry chemical
- Type D: Sand or special powders
- Many common extinguishers are ABC type which means they will work on types A,B, and C, but not on type D.

Fire Extinguishers

- Carbon Dioxide extinguishers must NOT be used to try to put out type D (metal) fires. CO_2 will actually increase the intensity of metal fires.

What To Do When a Fire Occurs

- If the fire is
  - large or
  - compressed gases are nearby or
  - toxic fumes are present,
- you should LEAVE immediately!
- Your first concerns should be:
  - Sound an alarm
  - Evacuate the area
  - Summon assistance

What To Do When a Fire Occurs

- Fighting a fire with a fire extinguisher requires.
  - training and practice at using extinguishers.
  - the proper extinguisher.

What To Do When a Fire Occurs

- If a person's clothing is on fire, use the safety shower. If this is not available, wrap the person in a fire blanket.
  - Caution: Blankets can force flames toward the face and neck.
  - Clothing with chemical contamination should be removed.
- Place clean, wet, cold cloths on burned areas. Wrap the person to avoid shock.
- Get medical attention promptly.

Flammable Liquids video

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Oxidizing and Reducing Agents

- The flammability of organic solvents in air is an example of the more general case of oxidizing and reducing agents.
- Oxygen is the oxidizing agent and the organic material (fuel) is the reducing agent.
- Very vigorous reactions or even explosions can occur when oxidizing and reducing agents are combined.

Common oxidizing agents

- O_2, Halogens: F_2, Cl_2, Br_2
- Peroxides
- Nitric acid, chloric acid, perchloric acid, chromic acid (chlorate salts, perchlorates, chlorites, nitrates, permanganates)

Common Reducing Agents

- H_2, hydrocarbons and their derivatives including alcohols, oils, greases, acetic acid
- Metals and many metal salts
- Ammonia and ammonium salts
- Carbon

Incompatibilities, examples

- Nitric acid(ox.agent) and alcohol(red.agent)
- Ammonia soln.(red.agent) and bleach(sodium hypochlorite,ox. agent)
  - This is a very common household error
  - toxic chloramines are given off
- Do not store incompatibles together

Heat & Shock Sensitive Cmpds.

- Some compounds have reducing atoms or groups and oxidizing atoms or groups in the same molecule or ion. These tend to be heat and shock sensitive. Examples:
- Chlorites, chlorates, perchlorates, nitrates
- Organic nitrates and nitro compounds, (e.g., TNT, trinitrotoluene)

Peroxide Formers

- Peroxides are shock sensitive compounds that often form in the following compounds as a result of partial decomposition/oxidation of these compounds.
- Ethers, dioxane, glyme
- Vinyl compounds (styrene, vinyl acetate)
- Allylic compounds, alkenes (cyclohexene)
- Ketones and cyclic ketones

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Corrosives

- Living tissue as well as equipment is destroyed on contact with corrosives.
  - Ammonia soln.
  - Nitric acid
  - Phophoric acid
  - Sulfuric acid
  - Glacial acetic acid
  - Potassium chromate
  - Hydrochloric acid
  - Hydrogen fluoride
  - Potassium hydroxide
  - Sodium hydroxide

Acid and Base safety

- Always use protective equipment when working with concentrated acids and bases.
- Store acids and bases separately.

Acid and Base safety

- When diluting a concentrated acid:
- Add the acid to water! Why?
  - Lots of heat is generated when acids and bases are diluted. If you add water to the concentrated acid or base, the heat may be enough to boil the water and splash the concentrated solution on you.
  - If you add the acid or base to water, the bulk of the water can absorb the heat fairly quickly without getting hot enough to boil. (That is if you don't add too much too fast.)

Precautions with Corrosives

- Do not breathe chemical vapors.
- Avoid contact with skin, eyes, and clothing.
- Carefully clean equipment that comes in contact with corrosives.
- Use suitable protective equipment.
- Use secondary containment devices when storing, transporting, or dispensing corrosives.

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Water Reactive Compounds

- **Materials that by contact with water become spontaneously flammable or give off a flammable or toxic gas that presents a health hazard.**

  Alkali and alkaline earth metals, e.g., Na, Ca, etc. (give off H_2)

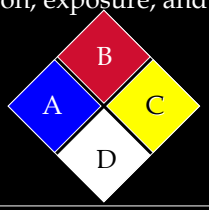
  Anhydrous metal halides, e.g., $FeCl_3$ (gives off HCl)

  Nonmetal halides, e.g., PCl_5 (gives off HCl)

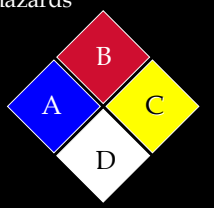
  NaOH (gives off lots of heat, splash hazard)

Fire Diamond

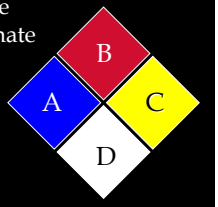
- A hazard rating system for materials developed by the National Fire Protection Association (NFPA). Particularly relevant to fire prevention, exposure, and control.
  - A: Health
  - B: Flammability
  - C: Reactivity
  - D: Special



- A: Degree of health hazard
  - 0=Ordinary combustible hazards
  - 1=Slightly hazardous
  - 2=Hazardous
  - 3=Extreme danger
  - 4=Deadly
- B: Flammability
  - 0=Will not burn
  - 1=Will ignite if preheated
  - 2=Will ignite if moderately heated
  - 3=Will ignite at most ambient conditions
  - 4=Burns readily at ambient conditions



- C: Reactivity, Instability
  - 0=Stable, not reactive with water
  - 1=Unstable if heated
  - 2=Violent chemical change
  - 3=Shock + heat may detonate
  - 4=May detonate
- D: Special Hazard
  - OX = Oxidizer
  - ~~W~~ = Use no water, reacts



Fire Diamond examples

- $Fe(NO_3)_3$

- Mg metal

Fire Diamond examples

- Acetic Acid, glacial

- Acetone

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Exposure to Toxic Chemicals Review

- Acute poisoning: Brief exposure that may have sudden and severe effects.
- Chronic poisoning: Prolonged or repeated exposure over a period of time (months, years). Low level exposure that does not produce immediate observed health change.

Exposure Limits

- Most of the exposure limits we'll look at are guidelines, not absolute boundaries between safe and hazardous conditions.
- Think of them as speed limit signs posted on the roads you travel.

Exposure Limits

- There's no guarantee that if your exposure to a hazardous substance exceeds the limits, you'll automatically experience an adverse health effect.
- However, you can't assume that if you're exposed to permissible levels of a substance, you won't suffer adverse effects.

Agencies that publish limits, OSHA

- Occupational Safety and Health Administration (OSHA) sets Permissible Exposure Limits (PELs) for 550 chemicals. These have the power of law.
- PELs are the allowable limit for an air contaminant to which nearly all workers may be repeatedly exposed day after day without adverse health effects.

Agencies that publish limits, ACGIH

- American Conference of Governmental Industrial Hygienists (ACGIH) has determined Threshold Limit Values (TLVs) for about 850 chemicals. These are advisory only.
- Like PELs, TLVs are the allowable limit for an air contaminant to which nearly all workers may be repeatedly exposed day after day without adverse health effects.

Threshold Limit Values

- Note that TLVs are established for the "average person", a 150 pound male, age 25-44.

Agencies that publish limits, NIOSH

- National Institute of Occupational Safety and Health (NIOSH) has determined Recommended Exposure Limits (RELs). These are advisory only.
- NIOSH seeks to reduce or eliminate adverse health and safety effects of hazardous substances or conditions in the workplace.

PEL, TLV, REL

- Each of these limits may be expressed as:
- Time-weighted averages, TWAs. This is an average exposure weighted for an 8 hour work day.
- Ceiling (C) limits, not to be exceeded during any part of the work day.
- Short-term Exposure Limits (STEL), usually a 15-min. time-weighted average exposure.

Example PELs

- Sulfur dioxide has the following OSHA PELs. Notice the units: ppm or mg/m^3.
  - 8-hr TWA: 2 ppm(5 mg/m^3)
  - 15-min STEL: 5 ppm(10 mg/m^3)
- If you are exposed to 7 ppm of SO_2 for half an hour, 2 ppm for 4 hours, and 1 ppm for 3.5 hours, has your exposure exceeded the OSHA limits?

How are limits determined?

- Toxicity data is obtained by tests on laboratory animals.
  - Since animal and human metabolisms differ, expert interpretation and judgment are needed to apply this data to human exposure.
- Toxicity data is also obtained through industrial experience of workers health and by the analysis of accidents.

Toxicity Data

- LC_{50} lethal concentration 50
  - The concentration of a material in air that is expected to kill 50% of a group of test animals when administered as a single respiratory exposure.
- LD_{50} lethal dose 50
  - The single dose of a substance that causes the death of 50% of an animal population from exposure to a substance *by any route other than inhalation*.

Toxicity Data

- LC_{LO} LD_{LO} lethal concentration/dose low
  - The lowest concentration of substance reported to have caused death in humans or animals by inhalation (LC) or by any route other than inhalation (LD).

Toxicity Data

- TC_{LO} TD_{LO} toxic concentration/dose low
  - The lowest concentration of substance reported to produce any toxic effect in humans or to produce any tumorigenic or reproductive effect in animals or humans by inhalation (TC) or by any route other than inhalation (TD).

Specific Hazards, Carcinogen

- Carcinogen: Substance that is suspected or known to cause cancer.
- Some known carcinogens:
  - Aflatoxins, Asbestos, Benzene, Chromium
  - conjugated estrogens, diethylstilbestrol
  - Soots, tars, mineral oils, coke oven emissions
  - Radon, certain chromium compounds
  - Thiotepa, Vinyl chloride, mustard gas

Compounds anticipated to be human carcinogens

- Partial Listing:Acetaldehyde, carbontetrachloride, chloroform, cisplatin, DDT, estrogens, formaldehyde, glasswool, hydrazine, lead acetate, certain nickel compounds, polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), progesterone, saccharin, crystalline silica, thiourea, urethane.

Specific Hazards, Teratogens

- Teratogen: Substances that cause the production of physical defects in a developing fetus or embryo.
- Some known teratogens:
  - ethylbenzene, boric acid, styrene
  - benzyl alcohol, benzaldehyde, ozone,
  - $CoSO_4 \cdot 7H_2O$, $MnSO_4 \cdot H_2O$,$NiSO_4 \cdot 6H_2O$
  - ferrocene, terephthalic acid, trans-stilbene

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Sources of Information on Chemical hazards, Labels

- Labels should include information on toxicity, flammability, corrosivity, and reactivity.
- All chemical containers must have labels, however, when multiple hazards exist, the label may only indicate the most immediate hazard.
- Read the label before using any chemical!

Sources of Information on Chemical hazards, Labels

- If you store a chemical in a container other than the one it was purchased in or if you prepare a substance in lab and store it in a new container, you must place a secure label on the container that includes:
  - the name of the chemical, concentration
  - the date
  - your name and course name/other reference
  - the hazards of the substance

Sources of information Material Safety Data Sheets

- What do MSDSs provide?
- Name, address and phone number of the manufacturer.
- The date the MSDS was prepared or revised.

What's in an MSDS?

- Material Identification
  - Chemical name (and usually formula). An MSDS for a material that contains a trade secret may list the trade name, not the actual name.
  - synonyms and common names
  - CAS Registry number (not required by OSHA)
- Ingredients and Exposure Limits
  - composition of mixtures
  - OSHA PELs and ACGIH TLVs if these exist
  - Toxicity data may be in this section also

What's in an MSDS?

- Physical and Chemical Characteristics
  - m.p., b.p., v.p., density, solubility, appearance
- Fire and Explosion Hazard Data
  - flash point, autoignition temp., flammability limits, unusual hazards, recommended extinguishing media

What's in an MSDS?

- Reactivity Hazard Data
  - conditions under which it is stable or unstable
  - incompatibilities, hazardous decomp. products
- Health Hazard Data
  - Carcinogenicity, summary of risks
  - Symptoms of exposure, target organs
  - primary entry routes, acute and chronic effects
  - first aid measures

- Spill , Leak, and Disposal Procedures
  - steps for safe cleanup of a spill or leak
  - appropriate waste disposal method
  - regulatory information
- Special Protection Data
  - types of protective equipment to use, safe handling
- Special Precautions and Comments
  - storage requirements, engineering controls
  - transportation (shipping) data

When Reading an MSDS

- Note that:
- only minimum precautions may be outlined.
- Do not assume a substance is hazard free if no particular health effects are cited.
- In many MSDSs, the first aid procedures and handling precautions assume a worst case scenario. Use your common sense.

Recognizing Chemical Hazards

- Know the hazards before doing an experiment.
- Answer three questions:
  - What prudent practices, safety equipment, and protective facilities are needed to minimize exposure to the anticipated hazards?
  - What are the worst accidents that could happen?
  - What must I do to be prepared?
- Never work alone! Always have an informed person within summoning distance for assistance.

Out of Harm's Way video

Think AND Act Safely!

- Act on the knowledge you have acquired in this course.
- If you have knowledge of a hazardous situation, respectfully report it to your instructor or the person responsible for the lab.
- In doing so, you will be creating a safer environment for yourself and others.

Think AND Act Safely!

- All accidents "predict" themselves.
- Analyze all "close calls" to avoid the prophesied accident.
- How many causes can you identify from the story about the liquid algaecide and calcium hypochlorite?
- Act on the knowledge you have acquired in this course.

Safety Examination

- Exam is 90-100 questions, most True/False, some multiple choice, some fill in the blank (acronyms).
- Resources
  - Safety lecture notes on web.
  - Video Study Guides and other handouts.
  - Safety Manual (Sections I, II and III)
- Review all of these. Good luck on the test.