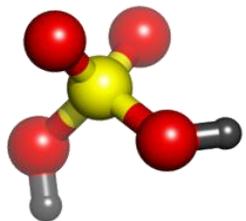


Chemical Hazards and Risks

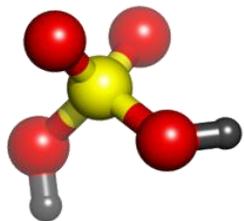
SAND No. 2011-0720P, SAND No. 2012-5234C

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.



Overview of Presentation

- ▶ Chemical Hazards in Laboratories
- ▶ Chemical Hazards in Industrial Processes
- ▶ Identifying Process Hazards
- ▶ Sources of Chemical Hazard Data



Laboratory Hazards

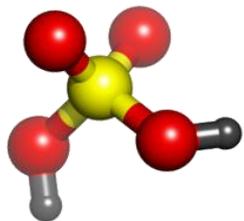


- ▶ Chemical Hazards
 - Toxic
 - Flammable
 - Reactive
 - Explosive
 - Chemicals of Concern (COCs)

- ▶ Physical Hazards

- ▶ Biological Hazards

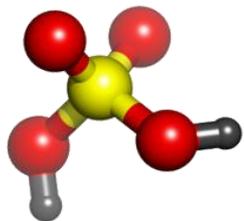
- ▶ Radiological Hazards



Chemical Hazards: Principles of Toxicity

Toxicity Depends on Dose & Exposure

<u>Chemical</u>	<u>Beneficial Dose</u>	<u>Toxic Dose</u>
Aspirin	300–1000 mg	1000–30,000 mg
Vitamin A	500 units/d	50,000 units/d
Oxygen	20% in air	50–100% in air
Water	~1-2 L/day	~13 L



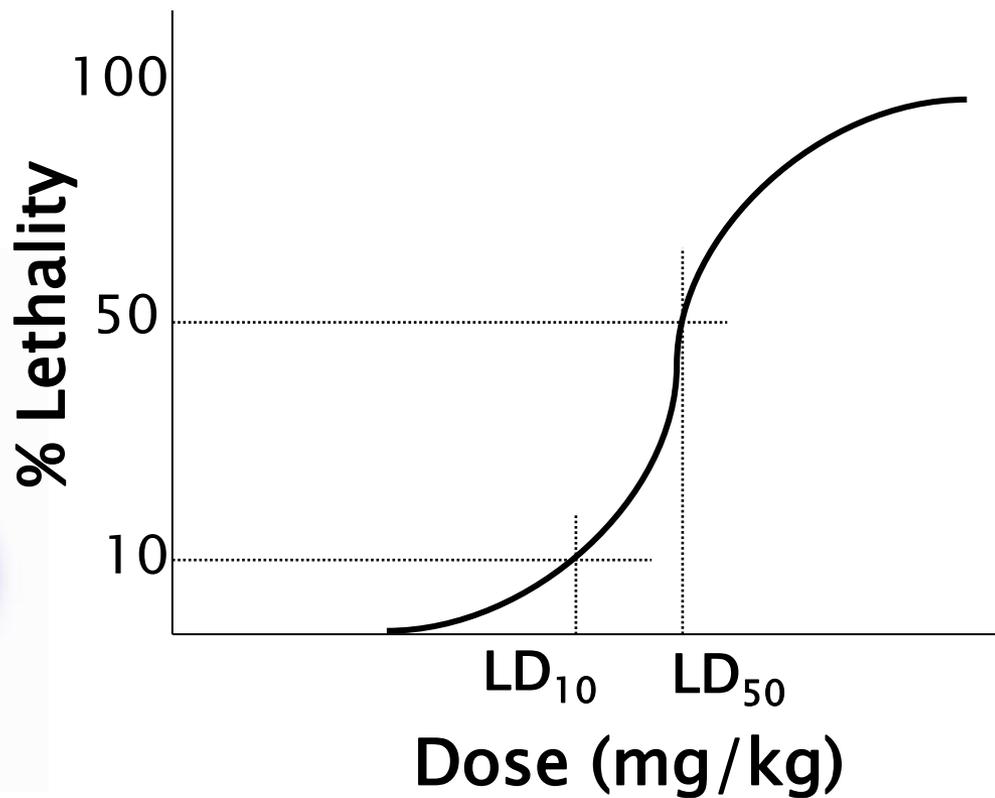
Chemical Hazards: Principles of Toxicity

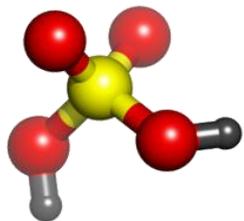
Toxicity is Measured by Lethality

- LD_{50} (mg/kg)
- “Lethal Dose 50%”



Dose-Response Curve





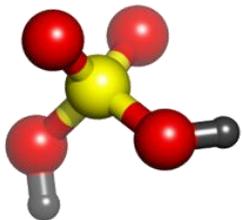
Chemical Hazards: Principles of Toxicity

Extremely wide range of toxicities between different substances

Agent	LD ₅₀ (mg/kg)
Ethanol	7060
NaCl	3000
Formaldehyde	800
Caffeine	192
Nicotine	1
Dioxin	0.0001

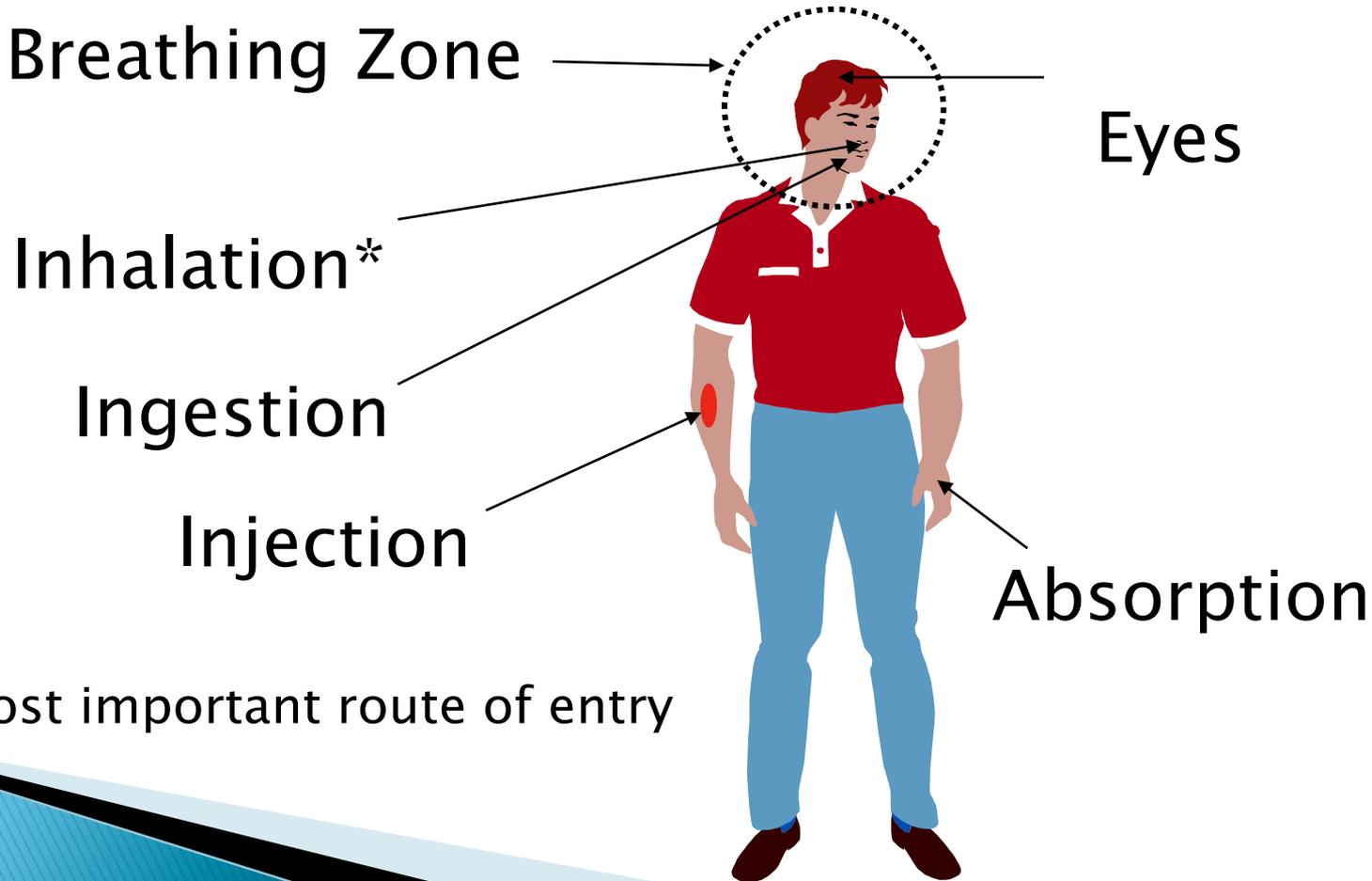


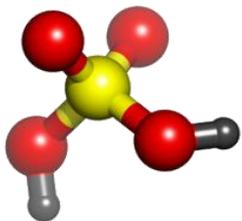
Toxicity depends on a variety of factors



Chemical Hazards: Principles of Exposure

Routes of Exposure



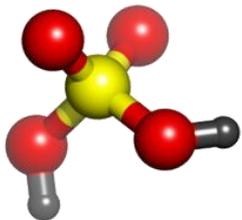


Chemical Hazards: Acute Toxins

- ▶ Includes highly toxic chemicals/poisons
 - Phosgene
 - Strychnine
- ▶ Includes common lab chemicals
 - Cyanides
 - Chlorine gas

Need to ensure safety and security when using and storing acute toxins





Chemical Hazards: Irritants, Allergens, and Corrosives

▶ Irritants

- Effects are local and reversible



▶ Corrosives

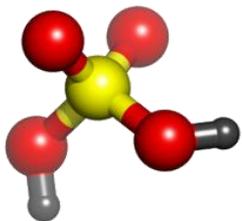
- Effects are local
- Acids and bases
 - $\text{pH} \leq 2$ or ≥ 12.5
- React with and damage living tissue



▶ Allergens (and sensitizers)

- Cause a reaction of the immune system



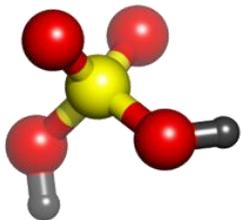


Chemical Hazards: Organ-Targeting



- ▶ Neurotoxins
 - Ethanol, Hg, CS₂, xylene, *n*-hexane
- ▶ Reproductive and Developmental Toxins
 - Harm fertility or reproductive ability
 - Harm fetus
- ▶ Other Organs
 - Liver, kidneys, lungs, etc.
 - Chlorinated or aromatic hydrocarbons, some metals

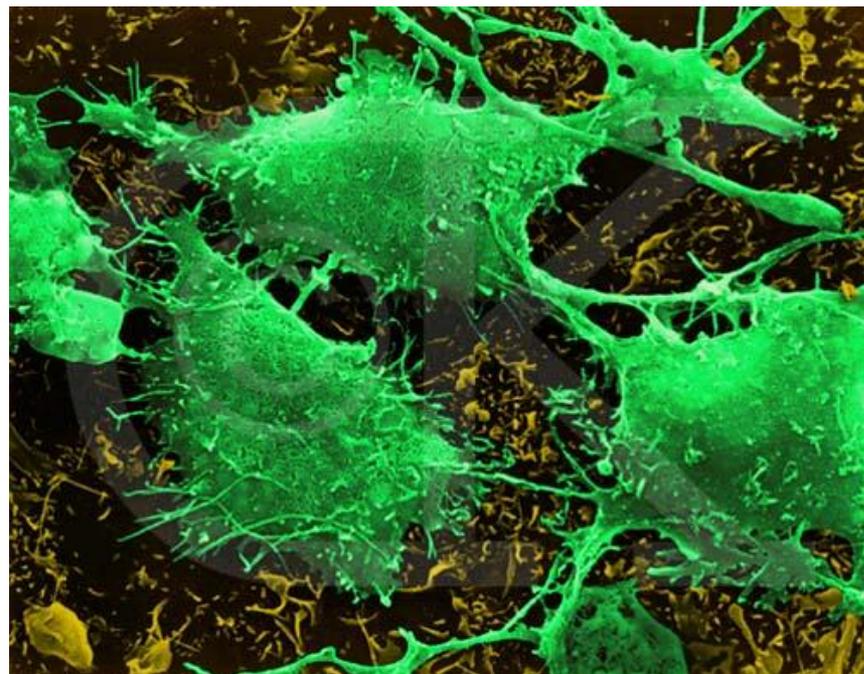




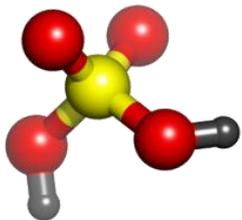
Chemical Hazards: Carcinogens



- ▶ Chronically Toxic
 - Vinyl chloride (liver cancer)
 - Asbestos (mesothelioma)
- ▶ Carcinogenicity of most chemicals is untested
 - Precautions taken may consider amount and frequency of use
- ▶ Treat known carcinogens as particularly hazardous



http://www.alternative-cancer.net/images/Cancer_cell,%20brain.jpg



Chemical Hazards: Flammable

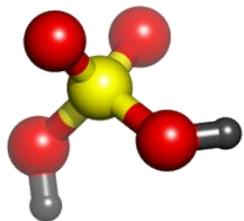
- ▶ Fuel: Solids, Liquid, or Gases
 - Compressed or liquefied gases are especially hazardous
- ▶ Oxidant
 - Oxygen in air
 - Other oxidants
 - Cl_2 , HNO_3
- ▶ Ignition
 - Spark
 - Heat



University of California, Santa Cruz, 2002

- Lab fire, cause not determined
- Lost equipment, notes, samples, etc.
- Labs took 2 years to reopen



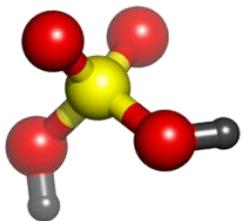


Chemical Hazards: Reactive

- ▶ Water-reactive
- ▶ Pyrophoric materials
- ▶ Incompatible Chemicals
 - Combination leads to reactive or toxic hazards
 - Concentrated oxidizing or reducing agents



http://science.pixeladdiction.co.uk/?page_id=57



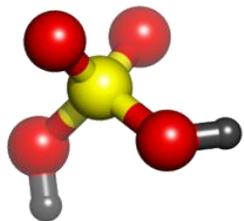
Chemical Hazards: Explosive

- ▶ Initiated by
 - Heat
 - Light
 - $\text{H}_2 + \text{Cl}_2$
 - Mechanical shock
 - Nitro, peroxy, chlorates
 - Certain catalysts
 - Acid/base catalyzed polymerization
- ▶ Dusts
- ▶ Peroxide-formers
 - Dialkyl ethers



- ▶ Texas Tech University Chemistry Lab, 2010
 - Synthesis of explosive compound
 - Scaled-up without precautions
 - One graduate student severely injured

http://www.csb.gov/investigations/detail.aspx?SID=90&Type=2&pg=1&F_InvestigationId=90



Chemical Hazards: Chemicals of Concern

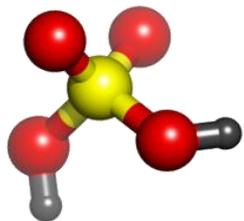
- ▶ Presence or suspected presence of COCs in your laboratory could make you and your institution a target
 - Outsider Threat
 - Insider Threat

Example: Outsider Threat

- ▶ Chicago, USA, 2002
 - Joseph Konopka arrested in tunnels under the University of Illinois
 - Had cyanide compounds on him and a stockpile of stolen chemicals including cyanides in subway
 - Sentenced to 13 years in prison for “possessing a chemical weapon” and other charges

http://articles.cnn.com/2002-03-12/us/chicago.cyanide_1_cyanide-in-chicago-subway-sodium-cyanide-chicago-police?_s=PM:US

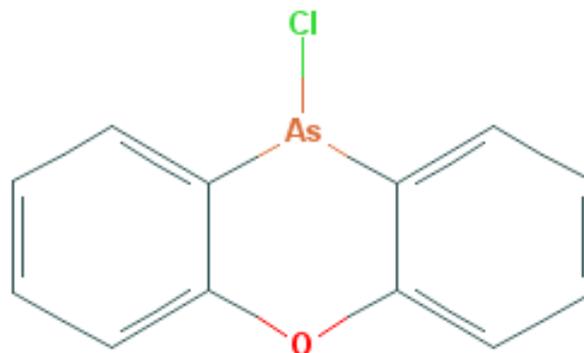
http://articles.chicagotribune.com/2004-01-04/features/0401040453_1_tunnels-urban-exploration-city-hall



Chemical Hazards: Chemicals of Concern

Example: Insider Threat

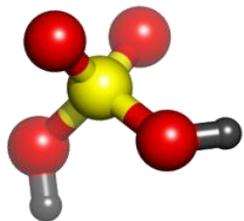
- ▶ Philadelphia, USA, 2007
 - Carol Anne Bond, microbiologist
 - Stole 10-chlorophenoxyarsine from work
 - Attempted to poison her husband's lover
 - Case is still in court



It is important to recognize the safety and security hazards posed by chemicals

http://articles.cnn.com/2011-06-16/justice/us.scotus.poisoned.paramour_1_potassium-dichromate-myrlinda-haynes-carol-anne-bond?_s=PM:CRIME

<http://www.chemindustry.com/chemicals/0437452.html>



Laboratory Hazards



☑ Chemical Hazards

☑ Toxic

- ☑ Principles of Toxicity
- ☑ Acute Toxins
- ☑ Irritants, Corrosives, and Allergens
- ☑ Organ-targeting
- ☑ Carcinogens

☑ Flammable

☑ Reactive

☑ Explosive

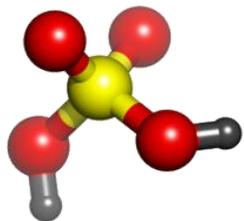
☑ Chemicals of Concern (COCs)

▶ Physical Hazards

- Compressed gases
- Cryogenics, Pressure, and Temperature
- Electrical
- Mechanical and Other

▶ Biological Hazards

▶ Radiological Hazards

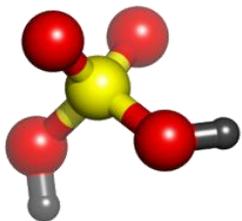


Physical Hazards: Compressed Gases



- ▶ Pressure
- ▶ Also chemical hazard depending on gas
 - Toxic
 - Reactive
 - Flammable
- ▶ Asphyxiation





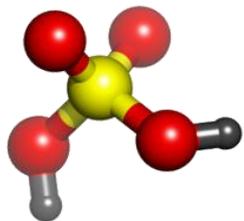
Physical Hazards: Cryogenics, Pressure, and Temperature

- ▶ Cryogenics
 - Dry ice
 - Liquid nitrogen
 - Contact
 - Oxygen condensation
 - Asphyxiation
 - Pressure

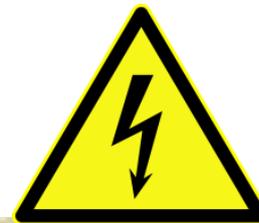
- ▶ Pressure
 - High, above ~1 atm
 - Vacuum work

- ▶ Temperature



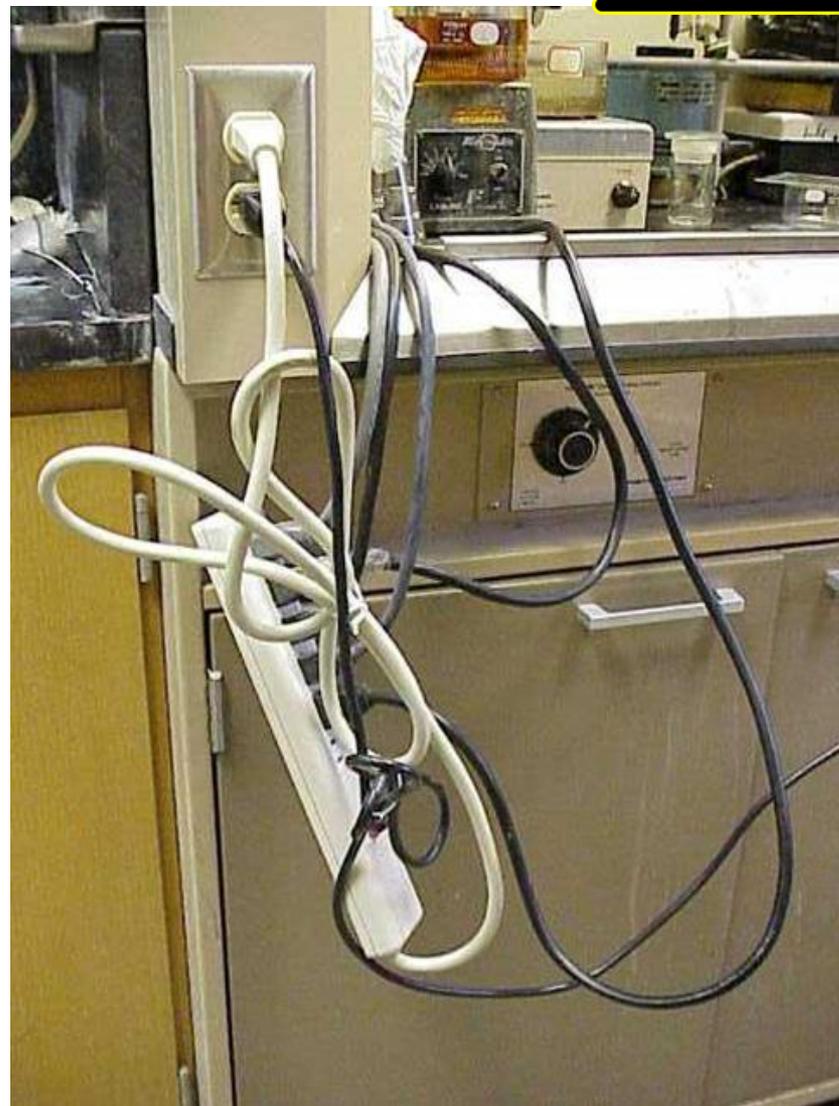


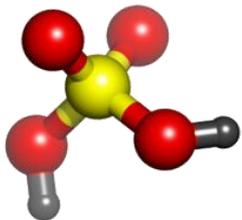
Physical Hazards: Electrical



- ▶ Power outages
- ▶ Shock
- ▶ Fire

- ▶ Frayed cords
- ▶ Overloaded circuits
- ▶ Static electricity





Physical Hazards: Mechanical and Other



▶ Mechanical

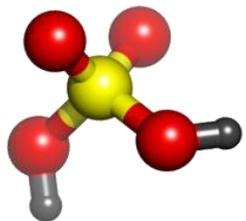
- Noise
- Moving parts
 - Yale University, 2011
 - Student dies after getting hair caught in lathe (machine shop of chemistry lab)

▶ Other

- Sharps
- Slips, trips, falls
- Housekeeping
 - Fire
 - Blocked exits



<http://www.waterfront-woods.com/Projects/Lathe/lathe1.JPG>



Laboratory Hazards



☑ Chemical Hazards

☑ Toxic

- ☑ Principles of Toxicity
- ☑ Acute Toxins
- ☑ Irritants, Corrosives, and Allergens
- ☑ Organ-targeting
- ☑ Carcinogens

☑ Flammable

☑ Reactive

☑ Explosive

☑ Chemicals of Concern (COCs)

☑ Physical Hazards

☑ Compressed gases

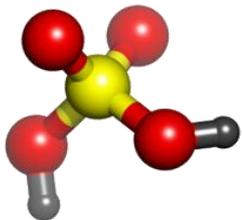
☑ Cryogenics, Pressure, and Temperature

☑ Electrical

☑ Mechanical and Other

▶ Biological Hazards

▶ Radiological Hazards

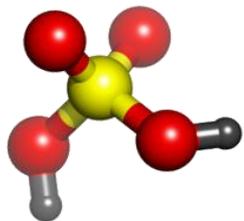


Laboratory Hazards: Biological

Pathogens

- ▶ Route of infection
 - Food or water borne
 - Salmonella
 - Blood borne
 - Hepatitis, HIV
 - Airborne
 - Tuberculosis
- ▶ Reason for exposure
 - Diagnostic work
 - Research work





Laboratory Hazards: Radiological

▶ Ionizing Radiation

- X-rays
- Gamma rays
- Alpha particles
- Beta particles
- Neutrons

▶ Ionizing Radiation Sources

- Radioactive isotopes
 - ^3H , ^{14}C , ^{32}P , ^{35}S , ^{131}I
- Instruments
 - Diffractometer
 - Electron microscope

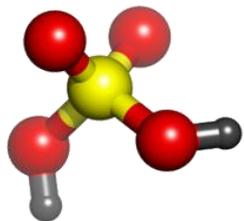
▶ Nonionizing Radiation

- Ultraviolet
- Infrared



- Primarily an eye hazard

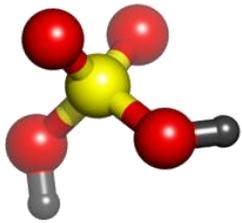




Overview: Chemical Hazards

Process Hazards

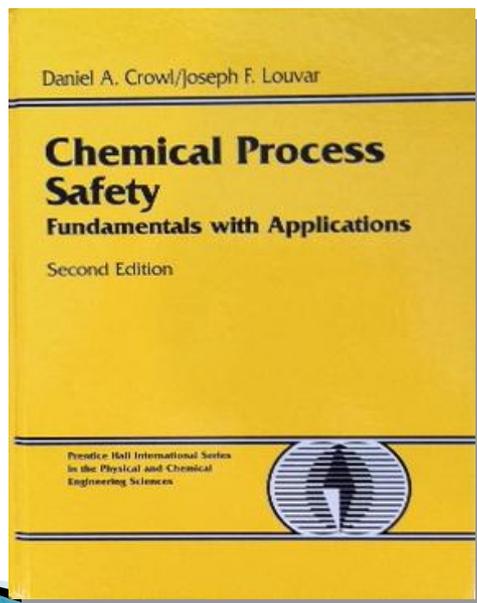
- Process safety resources
- “Process hazard” defined
- Difference from laboratory hazards
- Types of process hazards
- Methods for systematically identifying process hazards
- Chemical hazard data



Process Safety Resources

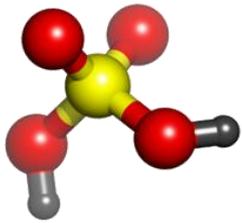
D.A. Crowl and J.F. Louvar 2001.

Chemical Process Safety: Fundamentals with Applications, 2nd Ed., Upper Saddle River, NJ: Prentice Hall.



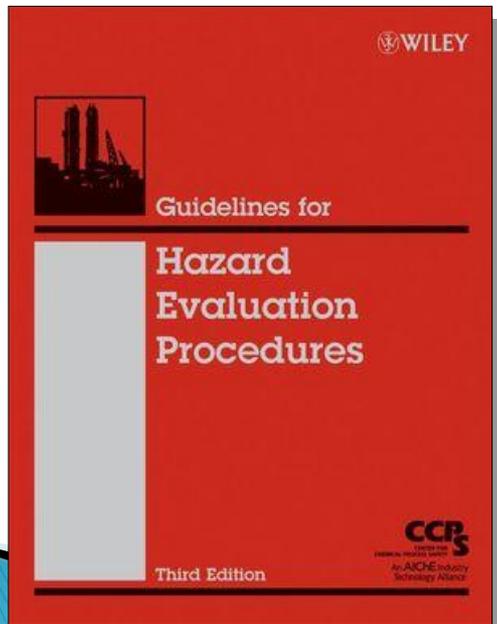
Chapter

- 2 • Toxicology
- 4 • Source Models
- 5 • Toxic Release and Dispersion Models
- 6 • Fires and Explosions
- 10 • Hazards Identification

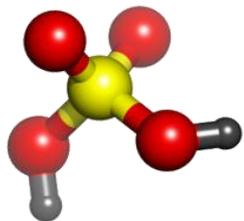


Process Safety Resources

CCPS 2008a. Center for Chemical Process Safety, *Guidelines for Hazard Evaluation Procedures, Third Edition*, NY: American Institute of Chemical Engineers.



- Chapter 3 • Hazard Identification Methods**
- 3.1 Analyzing Material Properties and Process Conditions**
 - 3.2 Using Experience**
 - 3.3 Developing Interaction Matrixes**
 - 3.4 Hazard Identification Results**
 - 3.5 Using Hazard Evaluation Techniques to Identify Hazards**
 - 3.6 Initial Assessment of Worst-Case Consequences**
 - 3.7 Hazard Reduction Approaches and Inherent Safety Reviews**



Process hazard definition

*Presence of a
stored or connected*



material or energy with

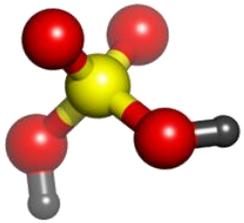
inherent characteristics



having the potential for

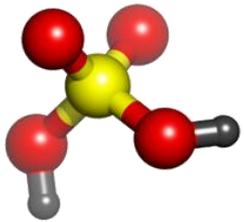
causing loss or harm.





Process Chemical Hazards

- ▶ Differ from laboratory chemical hazards
 - Larger scale
 - Environmental conditions: temperature and pressure
- ▶ Two types of chemical process hazards:
 - Inherent material hazards
 - Chemical interaction hazards

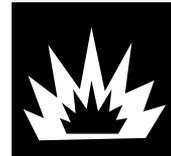


Inherent Material hazards

Inherently hazardous characteristics:



Flammability



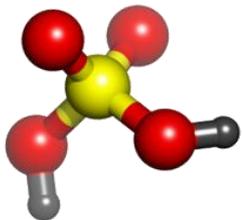
Instability



Toxicity



Corrosivity



Toxicity/corrosivity hazards

Nature of hazard

Potential exposure of people to materials having toxic and/or corrosive properties

What is required

Presence or generation of toxic/corrosive material + mechanism for physical contact

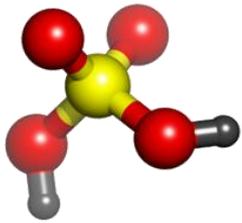
Typical examples

Chlorine used for water treatment; hydrogen sulfide as hydrocarbon impurity; sulfuric acid used for pH control

Consequences

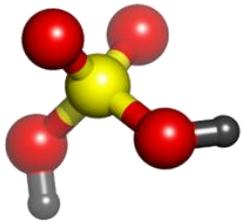
Contact with toxic/corrosive material can cause various health effects, depending on material characteristics, concentration, route of exposure and duration of contact (see Day 1 information)





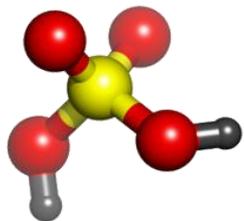
Types of process hazards & potential consequences

- ▶ Toxicity and corrosivity hazards
- ▶ **Asphyxiation hazards**
- ▶ Combustion hazards
- ▶ Detonation hazards
- ▶ Chemical reactivity hazards
- ▶ Rapid phase transition hazards (BLEVEs)
- ▶ Bursting vessel explosion hazards
- ▶ Other physical hazards



Asphyxiation hazards

- ▶ An *asphyxiant* is a gas that can cause unconsciousness or death by suffocation (*asphyxiation*).
 - *Chemical asphyxiants* chemically interfere with the body's ability to take up and transport oxygen
 - *Physical asphyxiants* displace oxygen in the environment
- ▶ *Simple asphyxiants* have no other health effects
- ▶ Most simple asphyxiants are colorless and odorless.



Asphyxiation hazards

▶ Common industry asphyxiant: Nitrogen



▶ Other simple asphyxiants:

◦ Hydrogen



◦ Argon, helium, neon

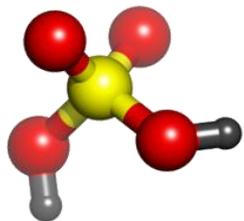


◦ Hydrocarbon gases (e.g., methane, ethane, ethylene, acetylene, propane, propylene, butane, butylene)



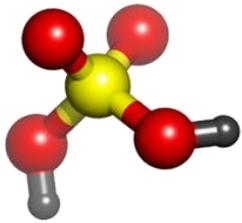
◦ Carbon dioxide





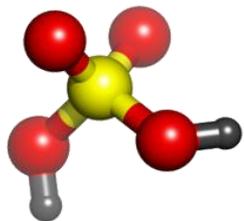
Asphyxiation hazards

What is required	Reduced-oxygen atmosphere + situation allowing breathing of the atmosphere
Typical examples	Entry into vessel inerted with nitrogen; oxygen depletion by rusting over time; oxygen depletion by combustion; natural gas leak into enclosed room or area
Video	http://www.csb.gov/videoroom/detail.aspx?vid=11&F=0&CID=1&pg=1&F_All=y
Boundaries	<ul style="list-style-type: none">• US OSHA: oxygen deficiency exists if concentration is less than 19.5%• ACGIH[®]: deficiency exists below 18% oxygen at 1 atm (equivalent to a partial pressure pO₂ of 135 torr)



Types of process hazards & potential consequences

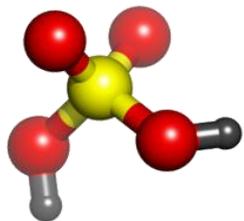
- ▶ Toxicity and corrosivity hazards
- ▶ Asphyxiation hazards
- ▶ **Combustion and flammability hazards**
- ▶ Detonation hazards
- ▶ Chemical reactivity hazards
- ▶ Rapid phase transition hazards (BLEVEs)
- ▶ Bursting vessel explosion hazards
- ▶ Other physical hazards



Combustion hazards

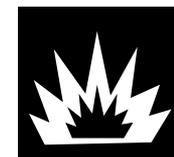
Nature of hazard	Potential for uncontrolled release of the heat of combustion upon rapid oxidation of a combustible material
What is required	A <u>fuel</u> (pyrophoric or flammable gas; pyrophoric, flammable or combustible liquid; or finely divided combustible solid) + an <u>oxidant</u> (usually atmospheric O ₂) + an <u>ignition source</u> (unless pyrophoric)

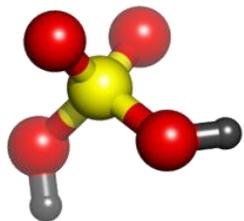




Combustion hazards

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Possible consequences	<ul style="list-style-type: none">• Flash fire, pool fire and/or jet fire• Confined vapor explosion• Vapor cloud explosion• Dust or mist explosion• Toxic combustion products





Combustion hazards

Free program

www.epa.gov/emergencies/content/cameo/aloha.htm

(can be used to calculate release rates, extent of a flammable vapor cloud, and vapor cloud explosion effect distances)

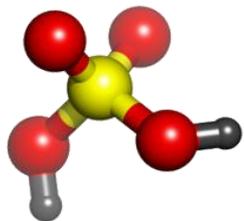
Online reference

Gexcon Gas Explosion Handbook,
www.gexcon.com/handbook/GEXHBcontents.htm

Other references

CCPS 2010; Crowl and Louvar 2001

(See also the Chemical Data Sources at the end of this presentation)



Flammability limits



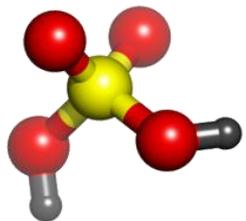
LFL Lower flammability limit

Below LFL, mixture will not burn, it is too lean.

UFL Upper flammability limit

Above UFL, mixture will not burn, it is too rich.

- **Defined only for gas mixtures in air**
- **Both UFL and LFL defined as volume % fuel in air**



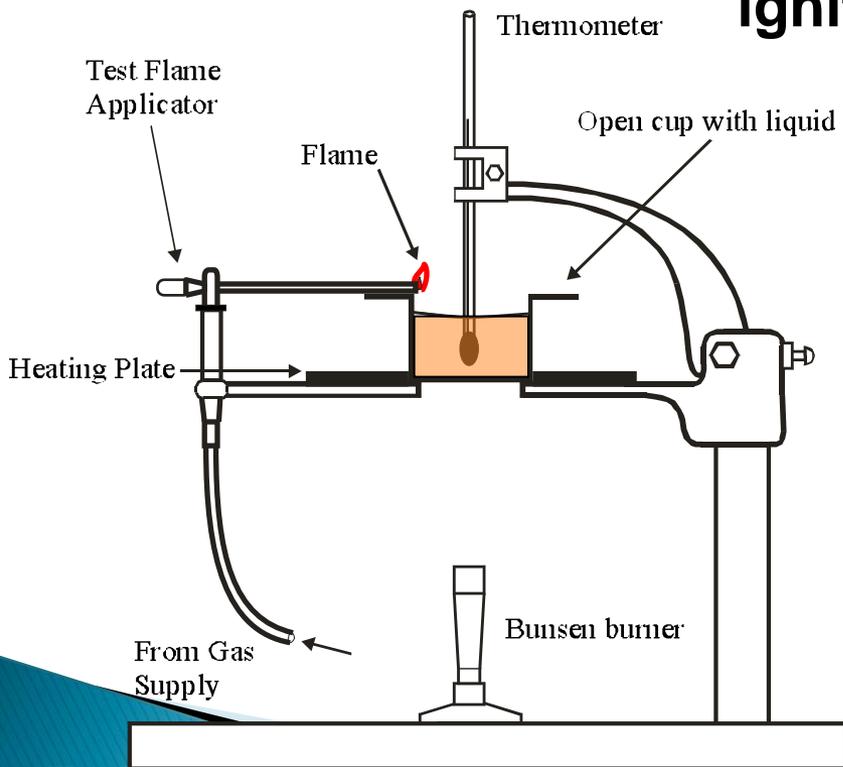
Flash point

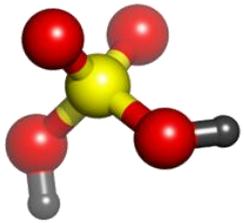


Flash Point

Temperature above which a liquid produces enough vapor to form an ignitable mixture with air

(Defined only for liquids at atmospheric pressure)

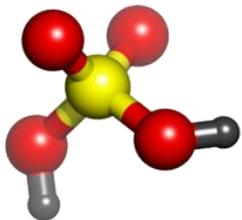




Example values

	<u>LFL</u>	<u>UFL</u>
Methane	5%	15%
Propane	2.1%	9.5%
Butane	1.6%	8.4%
Hydrogen	4.0%	75%

	<u>Flash point</u>
Methanol	12.2 °C
Benzene	-11.1 °C
Gasoline	-40 °C
Styrene	30.5 °C



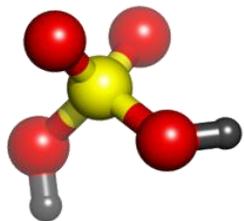
Autoignition temperature

Autoignition Temperature (AIT): Temperature above which adequate energy is available from the environment to start a self-sustaining combustion reaction.

Example values:

	AIT
Methane	632 °C
Ethane	472
1-Pentene	273
Toluene	810
Acetaldehyde	185

***There is great variability
in reported AIT values!
Use lowest reported value.***



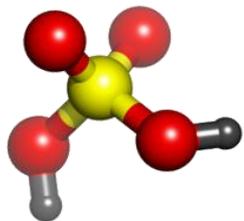
Limiting oxygen concentration

Limiting oxygen concentration (LOC):

Oxygen concentration below which combustion is not possible, with any fuel mixture, expressed as volume % oxygen.

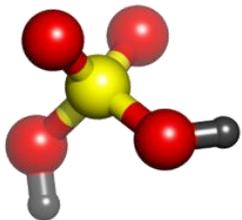
Also called: Minimum Oxygen Concentration (MOC)
Max. Safe Oxygen Concentration (MSOC)

Examples:	<u>LOC (volume % oxygen)</u>
Methane	12 %
Ethane	11 %
Hydrogen	5 %



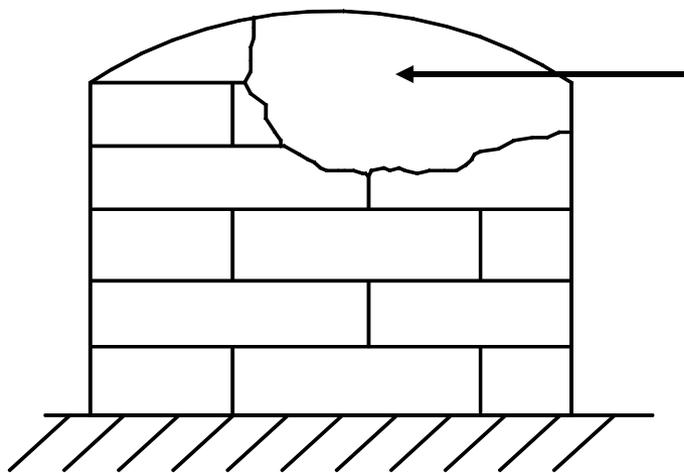
Design Criteria

- 1 Avoid flammable mixtures**
- 2 Eliminate ignition sources**

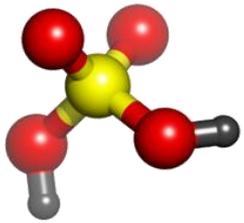


Avoid Flammable Mixtures By Inerting and purging

Purpose: To reduce the oxygen or fuel concentration to below a target value using an inert gas (e.g., nitrogen, carbon dioxide)

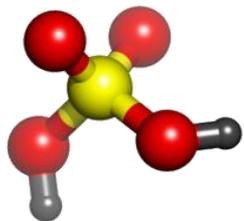


E.g., reduce oxygen concentration to $< \text{LOC}$



Eliminate Ignition sources

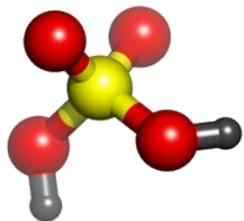
- ▶ **Identify ignition sources**
 - Continuous ignition sources; e.g., fired equipment
 - Potential/intermittent ignition sources; e.g., traffic
- ▶ **Identify what could be ignited**
 - Flammable atmospheres
 - Potentially flammable atmospheres
 - Likely leak/release locations
 - Avenues to unexpected locations; e.g., drains, sumps
- ▶ **Analyze for adequate control**



Examples: Ignition sources

- ▶ Obvious (e.g., flames, welding, hot surfaces)
- ▶ Spontaneous ignition at moderate temp's
- ▶ Electrical sources
 - Powered equipment
 - Static electricity
 - Stray currents
 - Radio-frequency pickup
 - Lightning
- ▶ Chemical Sources
 - Catalytic materials
 - Pyrophoric materials
 - Thermite reactions
 - Unstable chemical species formed in system
- Physical sources
 - Adiabatic compression
 - Heat of adsorption
 - Friction
 - Impact

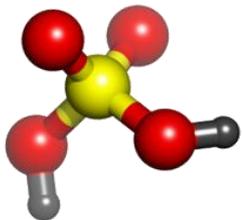




DISCUSSION

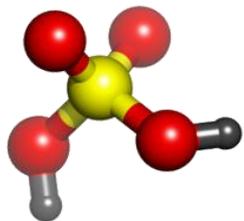
Which of these two design criteria can be more easily and reliably attained?

- 1 Avoid flammable mixtures**
- 2 Eliminate ignition sources**



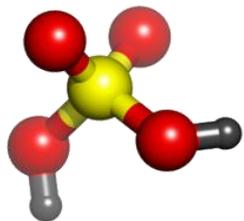
Types of process hazards & potential consequences

- ▶ Toxicity and corrosivity hazards
- ▶ Asphyxiation hazards
- ▶ Combustion hazards
- ▶ **Detonation hazards**
- ▶ Chemical reactivity hazards
- ▶ Rapid phase transition hazards (BLEVEs)
- ▶ Bursting vessel explosion hazards
- ▶ Other physical hazards



Detonation hazards

Nature of hazard	Potential for generating a damaging blast wave by extremely fast chemical reaction
What is required	One of two typical mechanisms: (1) Direct initiation of a solid or liquid explosive material or mixture, or (2) Acceleration of a propagating gas-phase reaction to detonation velocity
Typical examples	(1) TNT; picric acid; unstable peroxides; commercial explosives (2) Vapor cloud explosion; flame acceleration in a long pipeline containing a flammable mixture



Detonation hazards

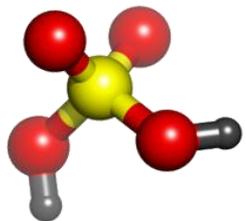
Possible consequences

- **Blast wave** (sometimes more than one)
- Shrapnel (usually small fragments)
- Toxic decomposition products

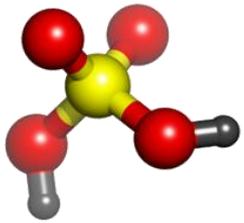
See calculation example for Bursting vessel explosion hazards

Video

www.youtube.com; search term **Pepcon explosion**

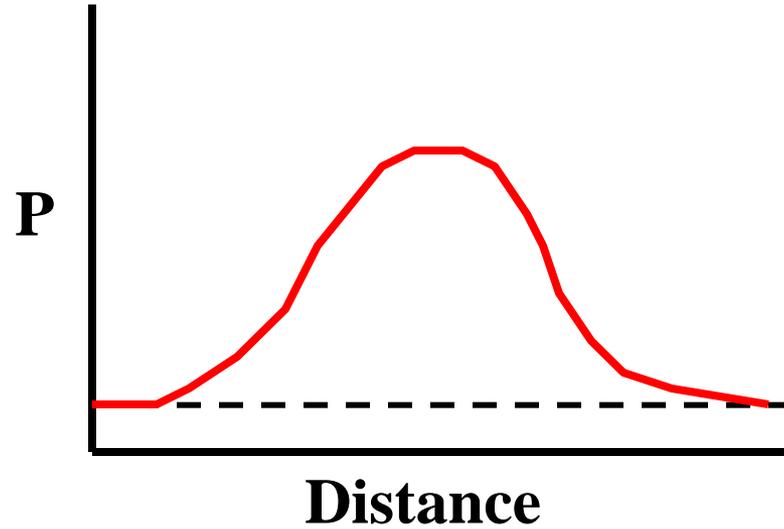
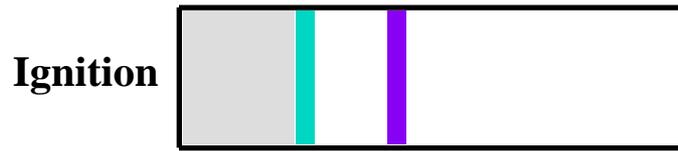


Pepcon Explosion Video



Deflagration vs Detonation

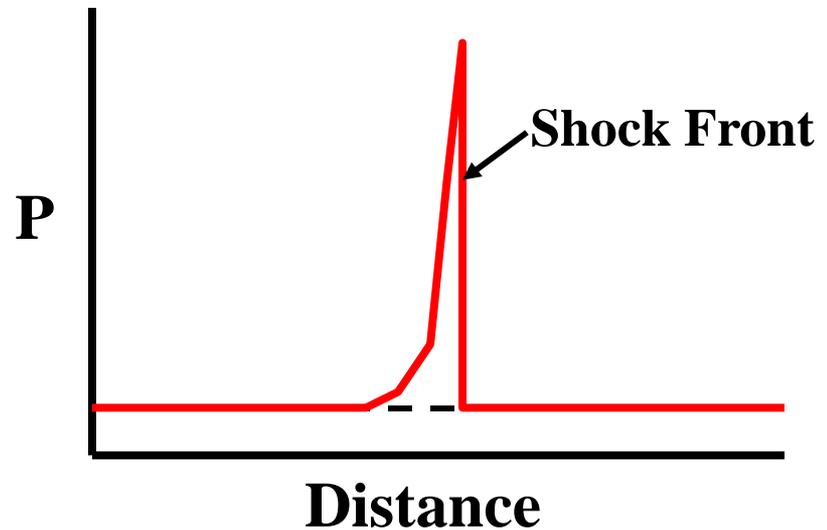
Deflagration:

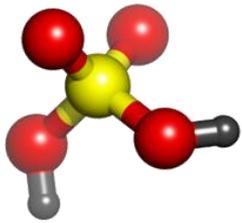


Detonation:



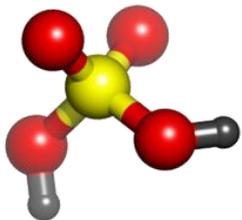
- Reacted gases
- Reaction / Flame Front
- Pressure Wave
- Unreacted gases





Types of process hazards & potential consequences

- ▶ Toxicity and corrosivity hazards
- ▶ Asphyxiation hazards
- ▶ Combustion hazards
- ▶ Detonation hazards
- ▶ **Chemical reactivity hazards**
- ▶ Rapid phase transition hazards (BLEVEs)
- ▶ Bursting vessel explosion hazards
- ▶ Other physical hazards

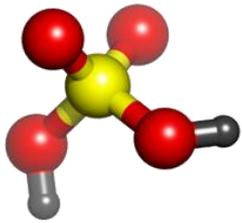


Reactive interactions

Example Compatibility Chart for an Acetic Anhydride Handling Facility

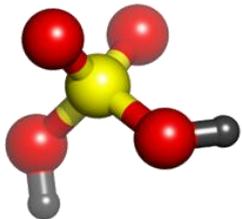
<i>Will These Two Materials React?</i>	Acetic Acid	Acetic Anhydride	Cooling Water	Sulfuric Acid	50% Caustic	Lube Oil	Cleaning Solution
Acetic Acid							
Acetic Anhydride	<i>Reactive</i>						
Cooling Water	<i>Not reactive</i>	<i>Reactive</i>					
Concentrated Sulfuric Acid	<i>Reactive</i>	<i>Reactive</i>	<i>Reactive</i>				
50% Caustic	<i>Reactive</i>	<i>Reactive</i>	<i>Reactive</i>	<i>Reactive</i>			
Lube Oil	<i>Not reactive</i>	<i>Not reactive</i>	<i>Not reactive</i>	<i>Reactive</i>	<i>Reactive</i>		
Cleaning Solution	<i>Find out what the cleaning solution contains, then determine reactions</i>						

From CCPS 2001



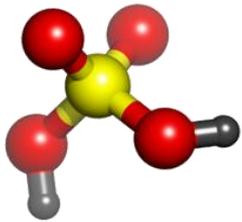
Types of process hazards & potential consequences

- ▶ Toxicity and corrosivity hazards
- ▶ Asphyxiation hazards
- ▶ Combustion hazards
- ▶ Detonation hazards
- ▶ Chemical reactivity hazards
- ▶ **Rapid phase transition hazards (BLEVEs)**
- ▶ Bursting vessel explosion hazards
- ▶ Other physical hazards



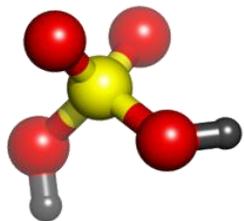
Rapid phase transition hazards

Nature of hazard	Near-instantaneous phase transition from liquid to gas, with large volume increase
Also known as	Boiling-liquid-expanding-vapor explosion (BLEVE)
What is required	<u>Any</u> liquefied gas stored under pressure above its boiling point
Typical example	Propane storage tank engulfed in fire with flame impinging on vapor space of tank, weakening the metal to point of failure
Consequences	Blast energy from both phase transition and bursting vessel; large tank fragments; huge fireball also if flammable liquid



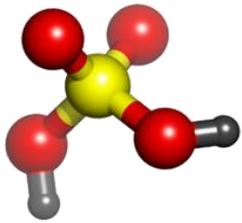
Types of process hazards & potential consequences

- ▶ Toxicity and corrosivity hazards
- ▶ Asphyxiation hazards
- ▶ Combustion hazards
- ▶ Detonation hazards
- ▶ Chemical reactivity hazards
- ▶ Rapid phase transition hazards (BLEVEs)
- ▶ **Bursting vessel explosion hazards**
- ▶ Other physical hazards



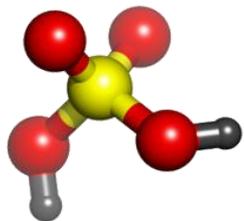
Bursting vessel explosion hazards

Nature of hazard	Near-instantaneous release of energy stored by a compressed vapor or gas
Also known as	Containment overpressurization; Vessel rupture explosion
What is required	Vapor or gas at elevated pressure inside some form of containment
Typical examples	Overpressurization of a reaction vessel from an unrelieved runaway reaction; ignition of flammable vapors in a tank
Consequences	Blast energy from bursting vessel; large vessel fragments thrown; expelling of remaining tank contents; follow-on effects



Types of process hazards & potential consequences

- ▶ Toxicity and corrosivity hazards
- ▶ Simple asphyxiation hazards
- ▶ Combustion hazards
- ▶ Detonation hazards
- ▶ Chemical reactivity hazards
- ▶ Rapid phase transition hazards (BLEVEs)
- ▶ Bursting vessel explosion hazards
- ▶ **Other physical hazards**



Other physical hazards

Physical hazard

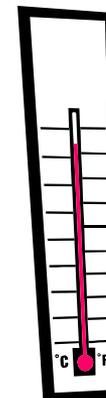
Typical examples

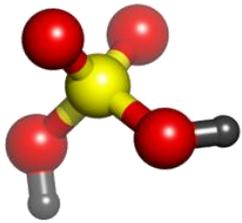
Hydraulic pressure

High-pressure hydraulic fluid:
Jet spray from pinhole leak can cause severe cuts

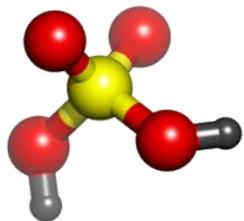
Vacuum

Contained sub-atmospheric pressure:
Pumping out of a tank or condensing steam with inadequate venting can cause tank implosion





A railcar steam cleaning team went to lunch - but before they left, they put the manway back on the car on a cool and cloudy day. The steam condensed and created a vacuum.



Other physical hazards

Physical hazard

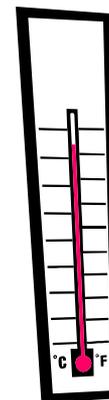
Typical examples

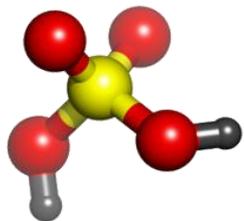
Elevated temperature

High gas, liquid or surface temperature:
Contact with hot surface or leaking hot material can cause severe burns; prolonged exposure to high area temperature can cause heat exhaustion

Cryogenic temperature

Liquid nitrogen; flashing liquefied gas:
Skin contact can cause cryogenic burns





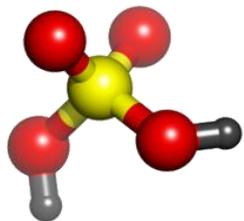
Other physical hazards

Physical hazard

Typical examples

Mass storage

Very large liquid storage tanks, silos:
Catastrophic failure can lead to fatalities



Other physical hazards

Physical hazard

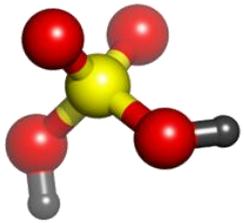
Obscuring vapor cloud

Typical examples

Acid gases, titanium tetrachloride, cryogenic liquids:

Dense vapors, dust or condensed humidity can obscure vision and lead to e.g. vehicle collisions



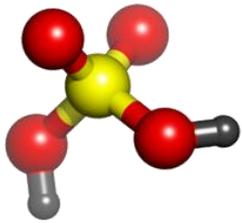


Identification of Hazards and Potential Consequences

- ▶ “Process hazard” defined
- ▶ Types of hazards and potential consequences
- ▶ **Approaches and methods for identifying process hazards**



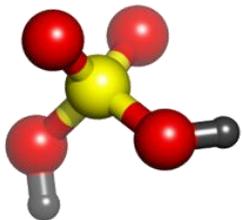
US Chemical
Safety Board



Approaches and methods for identifying process hazards

Some “HAZID” approaches and methods:

- ▶ Analyze material properties
- ▶ Analyze process conditions
- ▶ Use company and industry experience
 - Knowledge of the process chemistry
 - Experience at a smaller scale e.g. pilot plant
 - Examination of relevant previous incidents
 - Use relevant checklists e.g. CCPS 2008a Appx B
- ▶ Develop chemical interaction matrices

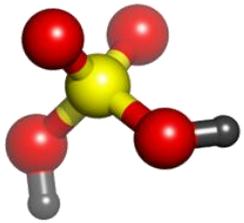


Approaches and methods for identifying process hazards

Typical hazard identification results:

- List of flammable/combustible materials
- List of toxic/corrosive materials and by-products
- List of energetic materials and explosives
- List of explosible dusts
- List of hazardous reactions; chemical interaction matrix
- Fundamental hazard properties e.g. flash point, toxic endpoint
- Others e.g. simple asphyxiants, oxidizers, etc.
- Total quantities of each hazardous material
- List of chemicals and quantities that would be reportable if released to the environment
- List of physical hazards (e.g., pressure, temperature, etc.) associated with a system
- List of contaminants and process conditions that lead to a runaway reaction

Reference: CCPS 2008a, Table 3.4

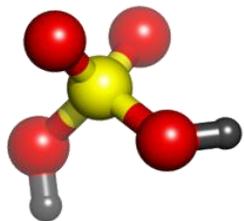


Identification of Hazards and Potential Consequences

- ▶ “Process hazard” defined
- ▶ Types of hazards and potential consequences
- ▶ Approaches and methods for systematically identifying process hazards
- ▶ **Chemical hazard data**



US Chemical
Safety Board



Chemical hazard data

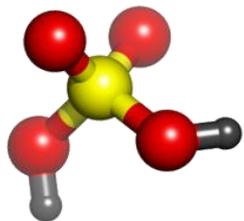
Some sources of chemical hazardous property data:

- ▶ Safety Data Sheets from chemical supplier
- ▶ Chemical industry-specific sources (e.g., Chlorine Institute)
- ▶ Many books and handbooks (NFPA 704)

NFPA 704

Summary
of material
hazards for
emergency
response

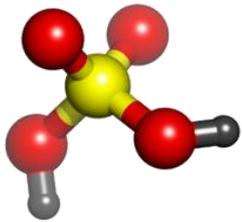




SDSs

Safety Data Sheets

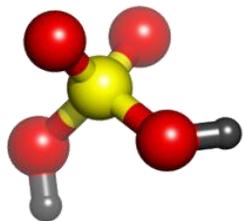
- ▶ More complete summary of hazards
- ▶ Required to be accessible in workplace
- ▶ All hazardous materials on-site
- ▶ Available from suppliers, internet sources
- ▶ Give only basic chemical reactivity info
- ▶ Often inconsistent from source to source



Limitations for Identifying Process Hazards

NFPA 704 diamonds and SDSs only give properties of individual hazardous materials

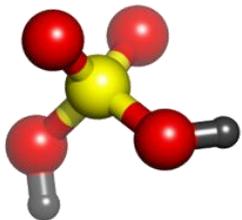
- Hazardous energies not identified
- Some hazardous chemical interactions not identified
- Connected hazards may not be identified



Chemical hazard data

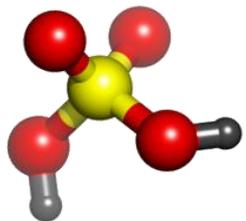
Some internet-accessible data sources:

- ▶ **International Chemical Safety Cards**
www.ilo.org/legacy/english/protection/safework/cis/products/icsc/dtasht/index.htm
- ▶ **CAMEO Chemicals**
cameochemicals.noaa.gov
- ▶ **Chemical Reactivity Worksheet**
response.restoration.noaa.gov/CRW
- ▶ **NIOSH Pocket Guide to Chemical Hazards** www.cdc.gov/niosh/npg
- ▶ **Wireless Information System for Emergency Responders**
wiser.nlm.nih.gov



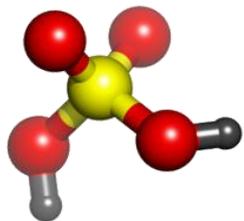
DISCUSSION

- ▶ Select a familiar type of simple chemical process either laboratory or industrial process
- ▶ Identify what *process hazards* are present; i.e., generate a hazard inventory
- ▶ Discuss what could happen if the hazards were not contained and controlled

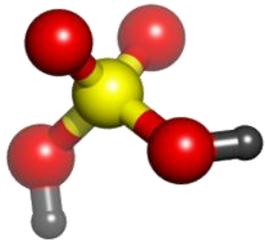


Summary of Presentation

- ▶ Chemical Hazards in Laboratories
- ▶ Chemical Hazards in Processes
- ▶ Identifying Process Hazards
- ▶ Sources of Chemical Hazard Data



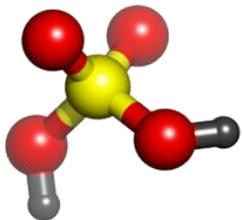
TEA BREAK!



Globally Harmonized System of Classification

SAND No. 2012-5234C

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.



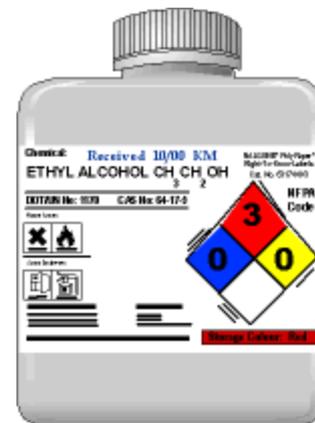
Labeling Basics

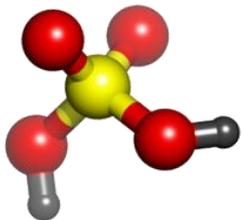
- ▶ Proper Labeling of Laboratory Hazards
 - Chemical
 - Physical
 - Biological
 - Radiological



Just ignore the label...
The worst stuff isn't listed anyway.

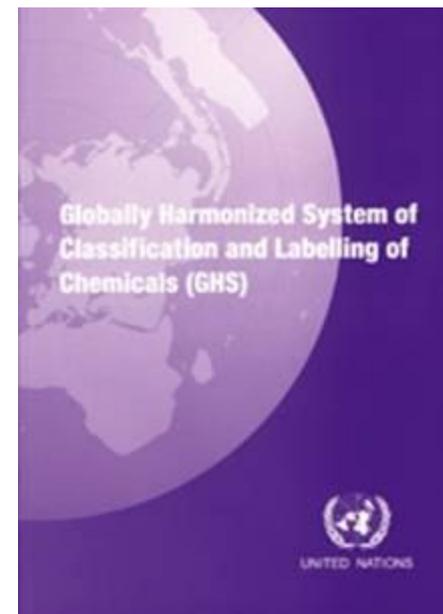
- ▶ Globally Harmonized System (GHS) Hazard Labels



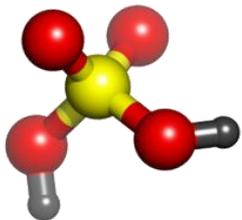


The Globally Harmonized System (GHS) of Classification and Labeling of Chemicals

- ▶ A system for standardizing and harmonizing the classification and labeling of chemicals
- ▶ Not a regulation or a standard.
 - establishes agreed hazard classification and communication provisions with explanatory information on how to apply the system
- ▶ GHS Labels and Safety Data Sheets (SDS)

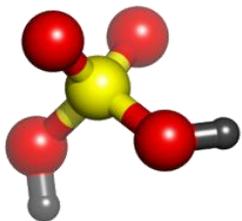


<http://www.osha.gov/dsg/hazcom/ghs.html>

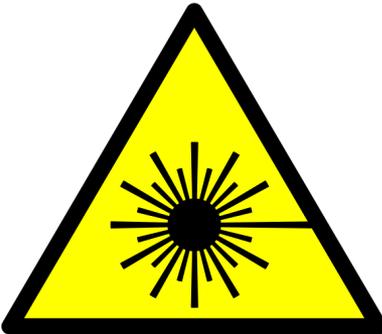


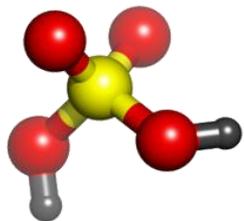
Globally Harmonized System (GHS) Hazard Labels

Corrosive 	Irritant 	Health Hazard 	Acute Toxicity 
Flammable 	Explosion 	Oxidizer 	Compressed Gas 



Globally Harmonized System (GHS) and Other Hazard Labels

Environmental 	Electricity 	Hot Surface 	Pinch Point 
Biohazard 	Radioactive 	Laser Beam 	Optical Radiation (UV) 



GHS Labels Elements: Example Bottle Label



ToxiFlam (Contains: XYZ)

Danger! Toxic If Swallowed, Flammable Liquid and Vapor



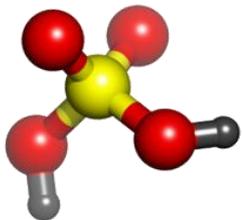
Do not eat, drink or use tobacco when using this product. Wash hands thoroughly after handling. Keep container tightly closed. Keep away from heat/sparks/open flame. - No smoking. Wear protective gloves and eye/face protection. Ground container and receiving equipment. Use explosion-proof electrical equipment. Take precautionary measures against static discharge.
Use only non-sparking tools. Store in cool/well-ventilated place.

IF SWALLOWED: Immediately call a POISON CONTROL CENTER or doctor/physician. Rinse mouth.

In case of fire, use water fog, dry chemical, CO₂, or "alcohol" foam.

See Material Safety Data Sheet for further details regarding safe use of this product.

MyCompany, MyStreet, MyTown NJ 00000, Tel: 444 999 9999



GHS Labels Elements: Example Bottle Label

Symbols (Hazard Pictograms)

ToxiFlam (Contains: XYZ)

Danger! Toxic If Swallowed, Flammable Liquid and Vapor

Do not eat, drink or use tobacco when using this product. Wash hands thoroughly after handling. Keep container tightly closed. Keep away from heat/sparks/open flame. - No smoking. Wear protective gloves and eye/face protection. Ground

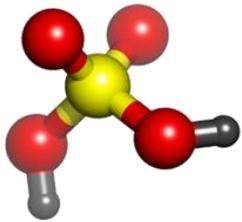
Signal Word ("Danger" for the more severe hazards, and "Warning" for the less severe hazards)

IF SWALLOWED: Immediately call a POISON CONTROL CENTER or doctor/physician. Rinse mouth.

In case of fire, use water fog, dry chemical, CO₂, or "alcohol" foam.

See Material Safety Data Sheet for further details regarding safe use of this product.

Precautionary Statement (prevention, response in cases of accidental spillage or exposure, storage, and disposal)



Example Labels

Label Creation

	Chemical Name _____
	Common Name _____
	Manufacturer _____
	MSDS# _____ Date _____

Chemical Liquor

CLASS: **A** GRADE: **5** TYPE: **II** % w/w active: **7%**

Chemical Agents Solution. This product conforms to U.S. EN 890-2005

UN No: 1700 CAS No: 18029-22-5 AGH / RID: Class 3, PG I HMG: DATA, Class 3, PG I

Risk Phrases:

- Irritating to eyes and skin.

Subst. Phrases:

- In case of contact with skin, clean immediately with plenty of water and seek medical attention.
- May contain proteins causing allergic and/or other reactions.

Hazard pictograms: GHS05 (Corrosive), GHS08 (Explosive), GHS09 (Health Hazard)

Hazard diamond: 8

Company Name, Street, Town, County...
www.chemtrec.com Tel: 800-424-9300 Fax: 800-424-9300

Chemical: Received 10/00 KM
ETHYL ALCOHOL CH₃CH₂OH

UN No: 1170 CAS No: 64-17-5 MFR Code

Hazard diamond: 3 (Blue), 0 (Yellow), 0 (White), 0 (Red)

Storage Color: Red

CHEMICAL NAME _____

Mfr. (Emergency Phone) _____

DANGER	DANGER
FLAMMABLE	CORROSIVE
TOXIC	OXIDIZER
ALKALI	WATER REACTIVE
ACID	USE VENTILATION
DANGER EYE PROTECTION REQUIRED	CAUTION USE FACE SHIELD
DANGER USE SELF-CONTAINED AIR RESPIRATORS	CAUTION RESPIRATOR REQUIRED
DANGER HAND PROTECTION REQUIRED	CAUTION USE PROTECTIVE CLOTHING
DANGER EXTREME HAZARD STOP	CAUTION USE CHEMICAL RESISTANT
DANGER NO SMOKING OR OPEN FLAME	CAUTION GROUND BEFORE POURING

Hydrogen Peroxide 35% FOOD GRADE

Danger! STRONG OXIDIZER, Causes eye and skin burns. May cause permanent eye damage. Can react violently with water, acids and other materials.

FIRST AID: Skin-Flush area with water for 15 minutes. DOT SHIPPING NAME/UN#: Hydrogen Peroxide 5.1, UN2014, PGII

Eye: Flush eyes for 15 minutes. Contact a physician immediately. **INGESTION:** Do not induce vomiting. Give large quantities of water. Contact a physician immediately. **INHALATION:** Remove to fresh air. Contact a physician immediately.

PREVENTION: Use chemical gloves and clothing to prevent skin contact, safety goggles or full face mask.

SPILL/DISPOSAL: Caution: This product may react strongly with acids or water. Scoop spilled product into marked disposal containers. Flush spill area with water.

STORAGE/USE/HANDLING: Do not add any other product to this container. Avoid contamination from any source.

CAS # 7722-84-1 / 7732-18-5

LOT No. 662531

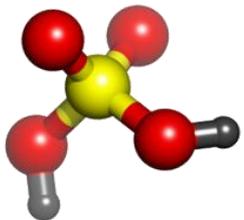
CODE No. 041

NET WT: 500LBS (145LBS CARBOY)

Hazard pictogram: GHS05 (Corrosive)

Hazard diamond: 8

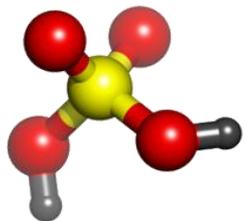
FOR CHEMICAL EMERGENCY SPILL, LEAK, FIRE, EXPOSURE OR ACCIDENT ONLY
Call: CHEMTREC - DAY OR NIGHT - 1-800-424-9300



Other Labeling Considerations

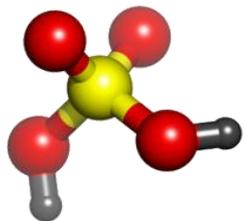
- ▶ Chemical Resistance
- ▶ Environmental Resistance
 - Heat, Fridge, Freezer
- ▶ Age
- ▶ Size
 - Label
 - Container
- ▶ Attachment to Bottle





(M)SDS Basics

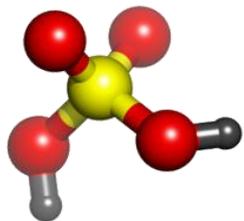
- ▶ Can use videos to demonstrate concepts and basics
 - <http://www.youtube.com/watch?v=yFHvuDnEEK0&feature=related>



GHS Safety Data Sheets

- ▶ Serve the same function as an MSDS does in ISO, EU and ANSI requirements
- ▶ Most comprehensive source of information
 - Hazards, including environmental hazards
 - Advice and safety precautions
 - Transportation, emergency responders, poison centers
- ▶ Product related and not specific to workplace or task
 - Written and supplied by manufacturer
- ▶ Only for pure substances and some mixtures

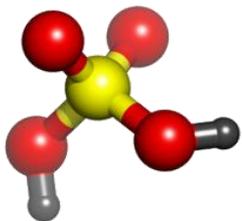
<http://www.osha.gov/dsg/hazcom/ghs.html>



SDS Format

16 Sections

1. Identification
2. Hazard(s) identification
3. Composition/information on ingredients
4. First-aid measures
5. Fire-fighting measures
6. Accidental release measures
7. Handling and Storage
8. Exposure controls/ personal protection
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



Safety Data Sheet

Example: Benzene

SDS Section 2: Hazards Identification

▶ OSHA Hazards

- Flammable liquid, Carcinogen, Target Organ Effect, Irritant, Mutagen

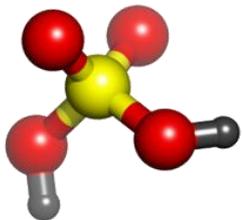
▶ GHS Classification

- Flammable liquids (Category 2)
- Acute toxicity, Oral (Category 5)
- Skin irritation (Category 2)
- Eye irritation (Category 2A)
- Germ cell mutagenicity (Category 1B)
- Carcinogenicity (Category 1A)
- Aspiration hazard (Category 1)
- Acute aquatic toxicity (Category 2)

▶ GHS Label elements, including precautionary statements

▶ Signal word: Danger





Safety Data Sheet

Example: Benzene

SDS Section 4: First Aid Measures

▶ General advice

- Consult a physician. Show this safety data sheet to the doctor in attendance. Move out of dangerous area.

▶ If inhaled

- If breathed in, move person into fresh air. If not breathing, give artificial respiration. Consult a physician.

▶ In case of skin contact

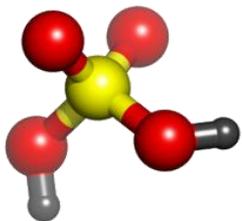
- Wash off with soap and plenty of water. Consult a physician.

▶ In case of eye contact

- Rinse thoroughly with plenty of water for at least 15 minutes and consult a physician.

▶ If swallowed

- Do NOT induce vomiting. Never give anything by mouth to an unconscious person. Rinse mouth with water. Consult a physician.



Safety Data Sheet

Example: Benzene

SDS Section 4: Accidental release measures

▶ Personal precautions

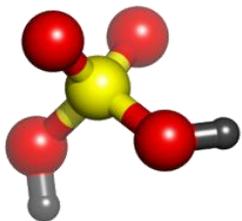
- Use personal protective equipment. Avoid breathing vapors, mist or gas. Ensure adequate ventilation. Remove all
- sources of ignition. Evacuate personnel to safe areas. Beware of vapours accumulating to form explosive concentrations. Vapours can accumulate in low areas.

▶ Environmental precautions

- Prevent further leakage or spillage if safe to do so. Do not let product enter drains. Discharge into the environment must be avoided.

▶ Methods and materials for containment and cleaning up

- Contain spillage, and then collect with an electrically protected vacuum cleaner or by wet-brushing and place in container for disposal according to local regulations.



Safety Data Sheet

Example: Benzene

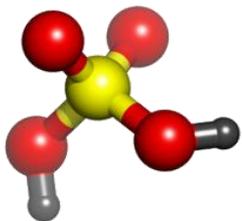
SDS Section 8: Exposure Controls/PPE

Exposure Limits

- ▶ TWA = 0.5 ppm USA. ACGIH Threshold Limit Values (TLV)
- ▶ Leukemia Substances for which there is a Biological Exposure Index or Indices (see BEI[®] section)
- ▶ Confirmed human carcinogen Danger of cutaneous absorption
- ▶ STEL = 2.5 ppm USA. ACGIH Threshold Limit Values (TLV)
- ▶ TWA = 10 ppm USA. Occupational Exposure Limits (OSHA) – Table Z2

Respiratory protection

- ▶ Where risk assessment shows air-purifying respirators are appropriate use a full-face respirator with multi-purpose combination (US) or type ABEK (EN 14387) respirator cartridges as a backup to engineering controls. If the respirator is the sole means of protection, use a full-face supplied air respirator. Use respirators and components tested and approved under appropriate government standards such as NIOSH (US) or CEN (EU).



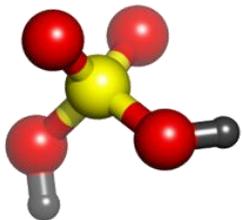
Safety Data Sheet

Example: Benzene

SDS Section 8: Exposure Controls/PPE

Hand protection

- ▶ Handle with gloves. Gloves must be inspected prior to use. Use proper glove removal technique (without touching glove's outer surface) to avoid skin contact with this product. Dispose of contaminated gloves after use in accordance with applicable laws and good laboratory practices. Wash and dry hands.
- ▶ Immersion protection
Material: Fluorinated rubber
Minimum layer thickness: 0.7 mm
Break through time: > 480 min
Material tested: Vitoject® (Aldrich Z677698, Size M)
- ▶ Splash protection
Material: Fluorinated rubber
Minimum layer thickness: 0.7 mm
Break through time: > 30 min
Material tested: Vitoject® (Aldrich Z677698, Size M)



Safety Data Sheet

Example: **Benzene**

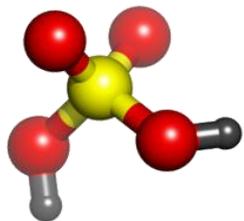
SDS Section 13: Disposal

▶ Product

Burn in a chemical incinerator equipped with an afterburner and scrubber but exert extra care in igniting as this material is highly flammable. Offer surplus and non-recyclable solutions to a licensed disposal company. Contact a licensed professional waste disposal service to dispose of this material.

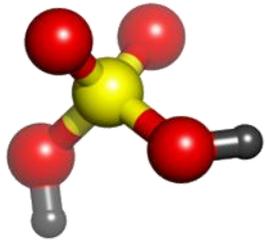
▶ Contaminated packaging

Dispose of as unused product.



GHS Safety Data Sheets (SDS)

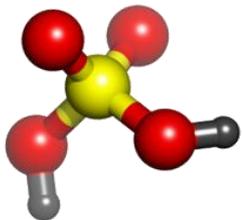
- ▶ Benefits of the SDS
 - The SDS contains comprehensive information for chemical management in one place
- ▶ Drawbacks
 - Not always current
 - Lack of toxicity information for most chemicals
 - Industry focus, not specific to laboratory scale
 - Sometimes inconsistent
- ▶ Keep a SDS for each chemical in your inventory
- ▶ Ensure all SDSs are accessible to workers and auditors



Chemical Toxicity and Exposure Standards

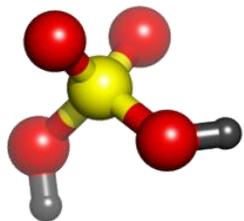
2012-1601C

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.



Overview

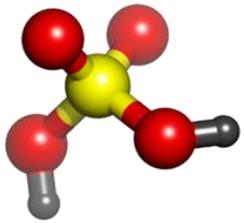
- ▶ Definitions
- ▶ Exposure
- ▶ Dose response
- ▶ Exposures
- ▶ Health effects
- ▶ Exposure limits
- ▶ Evaluating exposure
- ▶ Control banding



Definitions

- ▶ Toxicology: the study of the adverse effects of chemicals (xenobiotics) on living organisms.
- ▶ Toxicity: ability of a chemical to produce an unwanted effect.
- ▶ Hazard: presence of an agent that has inherently hazardous properties and the potential to cause harm.
- ▶ Exposure: Contact with the chemical substance.
- ▶ Dose: the amount of the chemical that has the potential to produce injury or death.

Klassen, C. (2001). Casarett and Doulls Toxicology
Plog, B. (2002). Fundamentals of Industrial Hygiene



Exposure

Inhalation

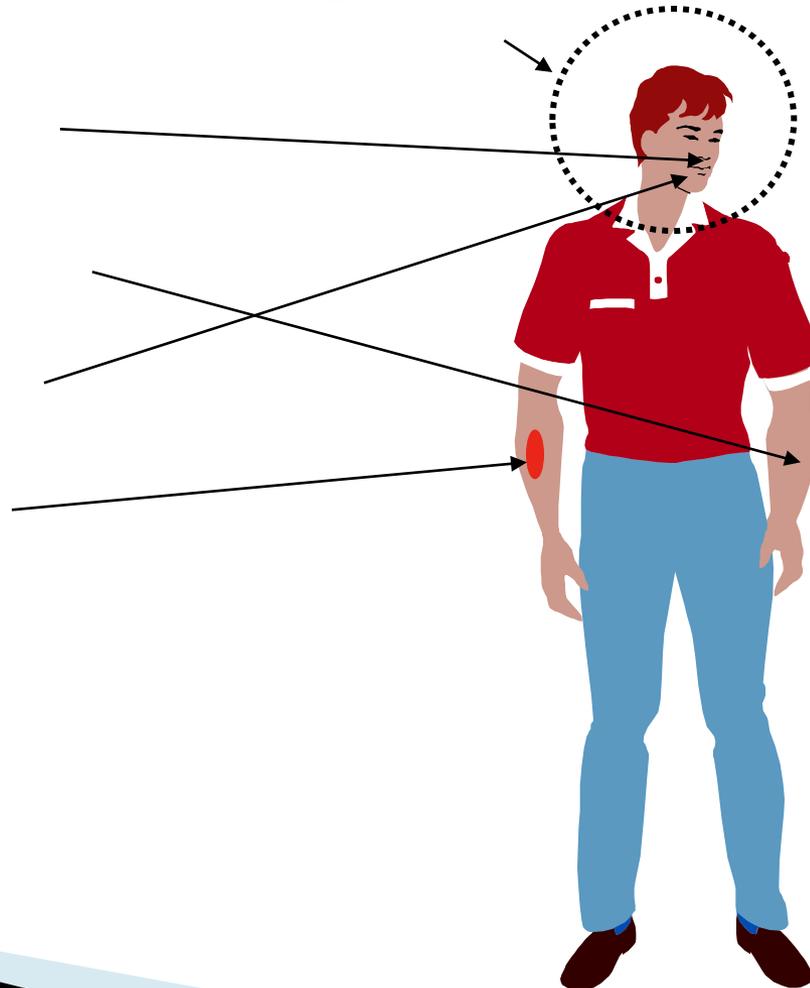
Absorption

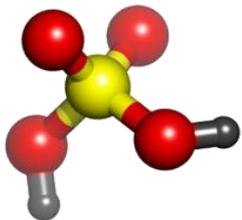
Ingestion

Injection

Breathing Zone

Eyes





Exposure: Inhalation

- Most important route of exposure for workers
 - Gases, solvent vapors, acid mists, dusts, particles, and metal fumes
- Exposure is dependent on:
 - Duration and frequency of task
 - Breathing rate
 - Concentration of the chemical
 - Particle size
 - Inhalable size = 0.1 μm to 10 μm
 - Solubility of gases & vapors
 - Formaldehyde versus chloroform

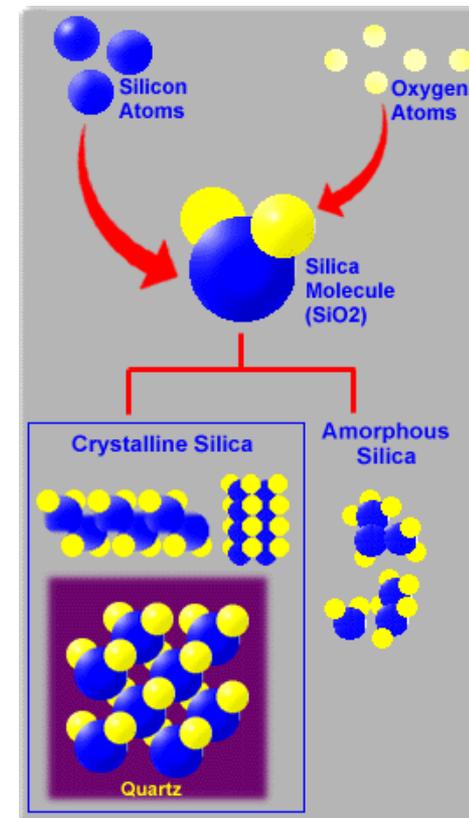
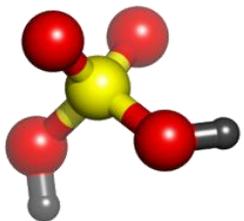
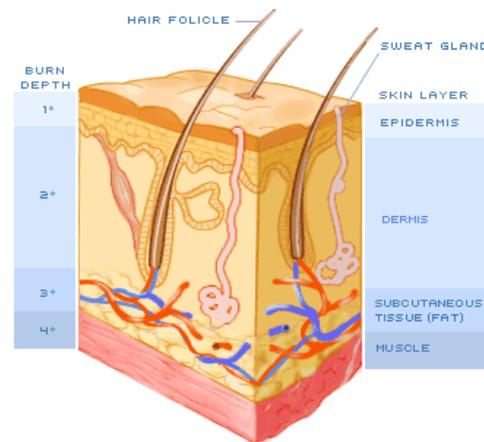


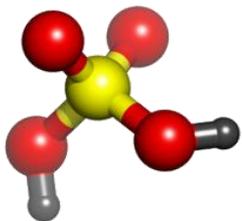
Photo Credit: US OSHA



Exposure: Skin Absorption

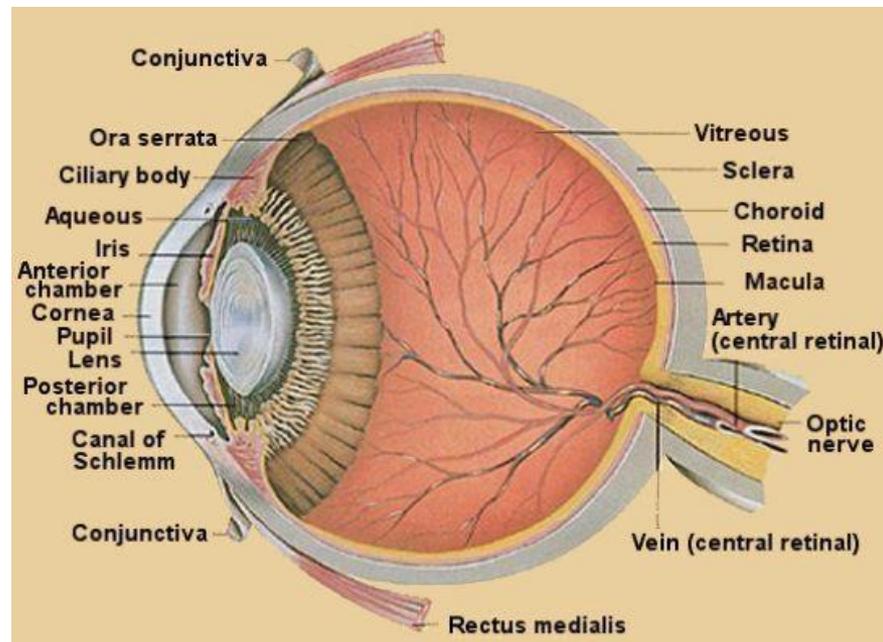
- Depends on skin location and thickness
 - Palms of the hands are thickest
 - Skin on abdomen is thin
- Depends on skin condition
 - Dry and broken skin more susceptible
 - Sweat increases absorption
- Duration of contact
- Properties of the chemical
 - Concentration
 - Solubility (in fat or water)
 - Molecular size (nanoparticles)

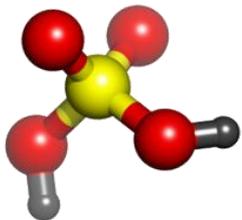




Exposure: Eyes

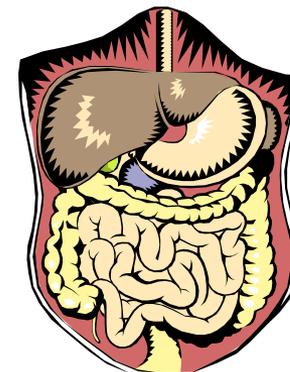
- ▶ Corneal irritation or trauma
 - Gases, particles
- ▶ Corneal burns
 - Acids, ammonia
 - Mustard agents
- ▶ Optic nerve damage
 - Thallium, methanol (ingested)

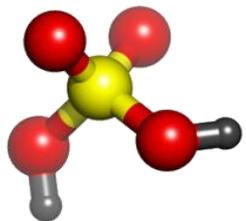




Exposure: Ingestion

- Rare exposure route, but possible
 - Swallow chemicals after inhaling
 - Eating, drinking, smoking in work areas
- Factors affecting absorption
 - Ionized versus nonionized form of compound
 - Weak base absorbed in intestines
 - Weak acid absorbed in stomach

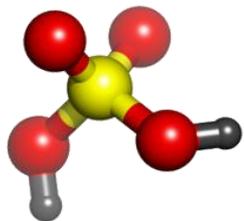




Pharmakokinetics

- Absorption
 - Chemical enters the body by exposure route
- Distribution or storage
 - Distributed to organs, or
 - Stored in bone, proteins, fat
- Metabolism
 - Liver, kidney enzymes
 - May metabolize to a more toxic chemical
- Excretion
 - Sweat, urine, feces

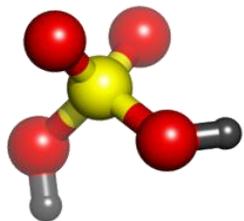




Dose Response

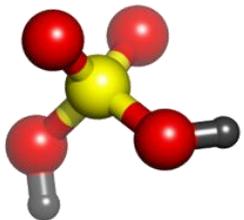
“All substances are poisons;
There is none which is not a poison.
The right dose differentiates a
poison from a remedy...”
–Paracelsus (1493–1541)





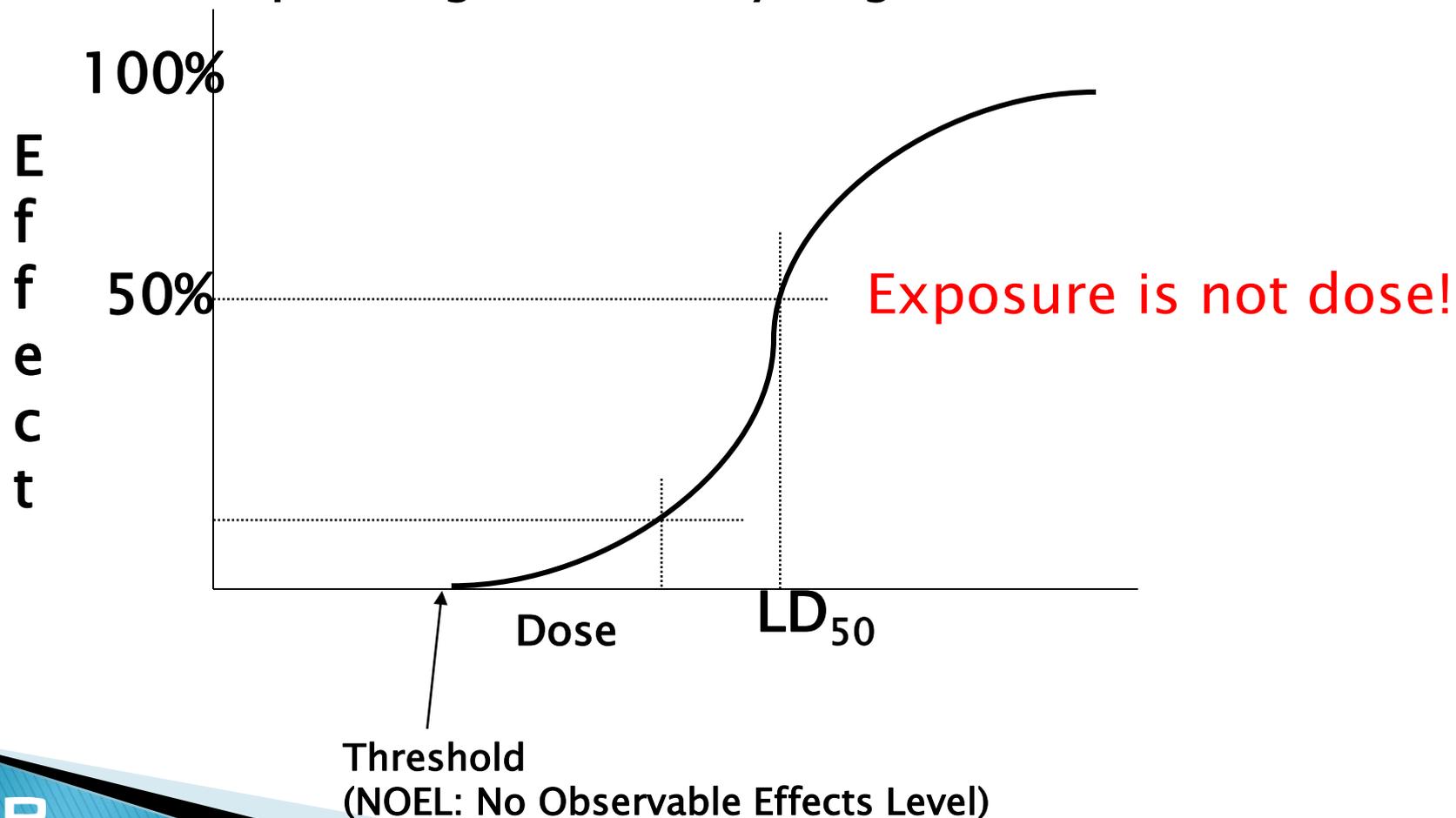
Dose Response Terminology

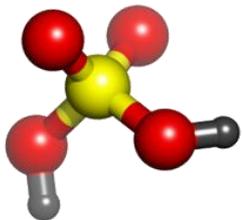
- ▶ TD_{10} – Toxic dose low – lowest dose for effect
- ▶ LD_{50} – Lethal dose 50% – dose that causes death in 50% of the test population
- ▶ TC_{10} – Toxic concentration low – used to express toxic concentration *via* inhalation
- ▶ LC_{50} – Lethal concentration 50% – concentration that causes death in 50% of the test population *via* inhalation



Dose Response

Dose is measured in milligrams of toxicant per kilograms of body weight

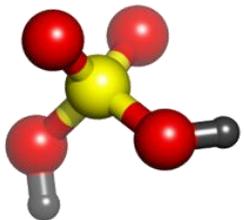




Health Effects

- ▶ Acute Health Effects—severe injury or death
 - High concentration of chemical over short time period
 - Chemicals with acute effects:
 - Toxic gases: hydrogen sulfide, phosgene
 - Asphyxiants gases: nitrogen, methane
 - Corrosive gases and liquids: chlorine, acids

- ▶ Chronic Health Effects—chronic disease
 - Low concentration over long time period
 - Chemicals with chronic effects:
 - Carcinogens: benzene, asbestos, arsenic
 - Reproductive agents: glycol ether acetates, lead, carbon disulfide
 - Sensitizers—glutaraldehyde, toluene diisocyanate



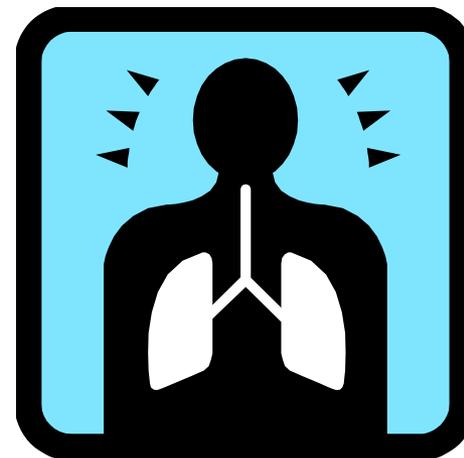
Health Effects

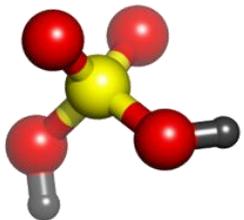
▶ Local

- Effect occurs at site of contact
- Skin rash, burns, coughing
- Chemicals with local effects:
 - Solvents, acids
 - Nickel allergy

▶ Systemic

- Chemical distributed by circulation
- Effect occurs in body organs
- Chemicals with systemic effects:
 - Methylene chloride to heart muscle
 - Lead to bone and brain

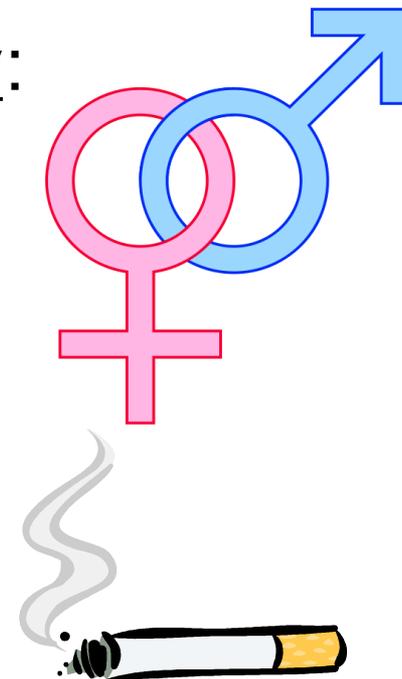


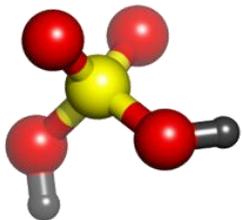


Health Effects

Chemicals affect people differently:

- ▶ Age
- ▶ Gender
- ▶ Genetic makeup
- ▶ Disease or stress
- ▶ Nutrition
- ▶ Lifestyle
- ▶ Interactions between chemical toxicants





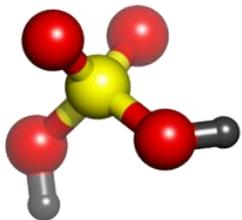
Health Effects Chemical Interactions

▶ Additive Effect

- Combined effect of 2 chemicals equals sum of each agent alone...($2 + 3 = 5$)
- Example: **Parathion, methyl-parathion pesticides**

▶ Synergistic Effect

- Combined effect of 2 chemicals is greater than sum of each agent alone...($2 + 3 = 20$)
- Example: **Carbon tetrachloride & ethanol**



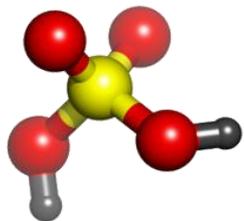
Health Effects Chemical Interactions

▶ Potentiation

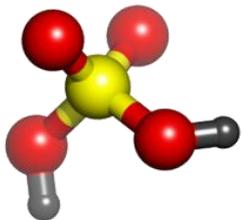
- One substance does not have toxic effect on certain organ or system, but when added to another chemical, it makes the latter more toxic...(0 + 2 = 10)
- Example: **Isopropanol & carbon tetrachloride**

▶ Antagonism

- 2 chemicals, when given together, interfere with each other's actions or one interferes with the action of the other chemical...(4 + 6 = 8)
- Example: **BAL (chelating agent) and lead**



Exposures



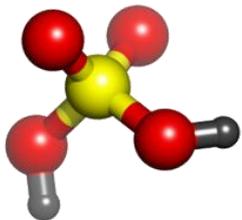
Exposures: Metals

Exposure primarily by inhalation:

- **Particulates**
 - Processes: grinding, cutting, sanding, mixing
 - Examples: copper, nickel, zinc
- **Fumes**
 - Processes: welding, smelting
 - Examples: lead, manganese, hexavalent chromium, zinc
- **Mists (soluble metal compounds)**
 - Processes: spraying anticorrosives, metal plating
 - Examples: hexavalent chromium, nickel chloride

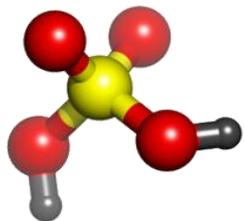


<http://www.millerwelds.com/>



Health Effects of Metals

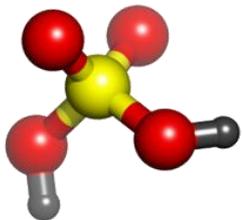
- ▶ Sensitizers (skin and lungs)
 - Skin rash, asthma
 - Nickel, beryllium, chromium
- ▶ Metal fume fever
 - Flu-like symptoms
 - Oxides of zinc, magnesium, and copper
- ▶ Organ toxicity
 - Damage specific organs
 - Arsenic—nervous system, liver
 - Cadmium—kidney, lungs
 - Lead—nervous system, blood, kidney, reproductive systems
- ▶ Carcinogens
 - Cause cancer
 - Arsenic, soluble nickel, hexavalent chromium



Exposures: Solvents

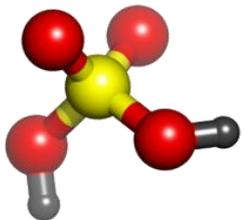
Exposure is by inhalation and skin absorption:

- **Process: transfer, mixing, spraying, high vapor pressure solvents**
 - Examples: ethers, ketones, chloroform, benzene
- **Process: Heating solvents**
 - Examples: styrene, dimethyl formamide
- **Process: skin immersion in process baths, parts cleaning**
 - Examples: acetone, trichloroethylene, dimethyl sulfoxide (DMSO)



Health Effects: Solvents

- ▶ Skin irritants, dermatitis (rash)
 - Acetone, alcohols
- ▶ Organ toxicity
 - Nerve damage–hexanes
 - Liver–chloroform, vinyl
 - Heart damage–methylene
- ▶ Carcinogens
 - Benzene, formaldehyde
- ▶ Reproductive toxicants
 - Cause women to miscarry
 - Glycol ether acetates

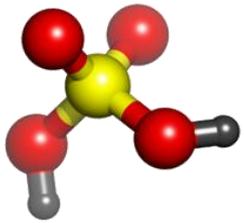


Exposures: Pesticides

Exposure primarily by skin absorption and inhalation of aerosols:

- Processes: mixing, spraying (aerosols), waste handling
- Organochlorine (DDT, Chlordane, Dieldrin)
 - **NOTE: poorly absorbed through the skin**
- Carbamates (Aldicarb, Carbofuran),
- Organophosphates (Malathion, Parathion)

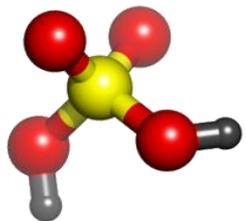
Exposure by ingestion from pesticide residue on foods



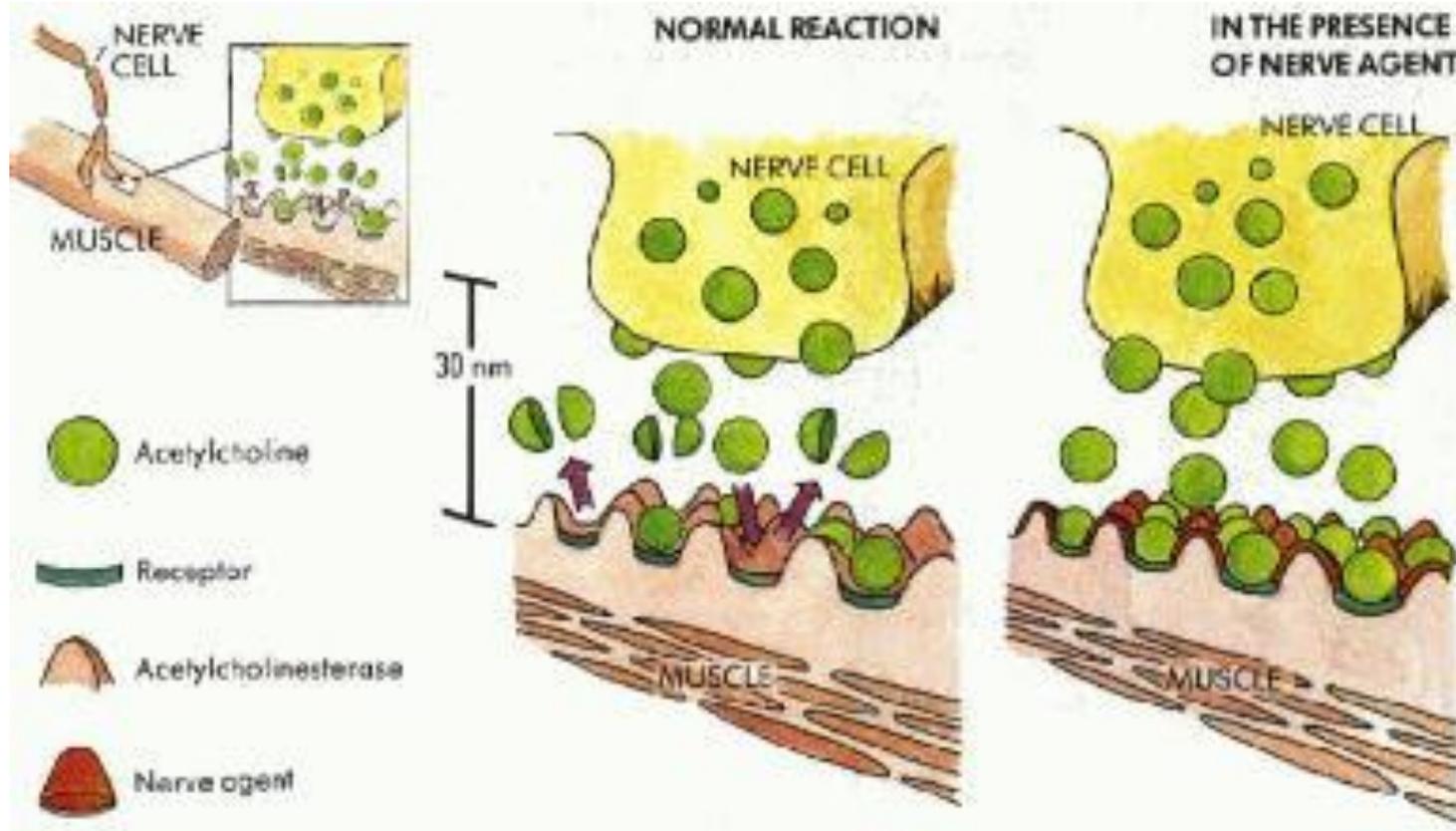
Health Effects: Pesticides

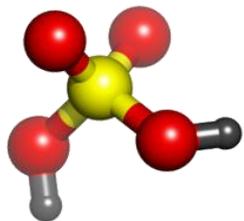
- ▶ Organochlorines
 - ▶ Animals: Estrogenic
 - ▶ Animals: Suppression of immune system
 - ▶ Humans: dizziness, nausea, vomiting, skin rash

- ▶ Carbamates and Organophosphates
 - ▶ Neurotoxicity is the principal toxicity
 - Affect skeletal muscle, smooth muscle and central nervous system (brain)
 - ▶ Used in suicide attempts

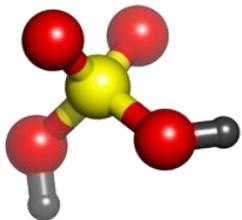


Inhibition of Acetylcholinesterase in Carbamate/Organophosphate Insecticide Exposure





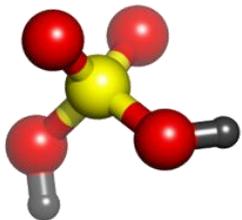
Occupational Exposure Limits: Evaluating Exposure



Occupational Exposure Limits (OELs)

- Government regulation or professional standard organizations set OELs
- OELs apply to workers only, NOT the general public
- Primarily limits for inhalation exposure
- Expressed in milligrams/cubic meter (mg/m^3) or parts per million (ppm)
- Exposure must be measurable for comparison with the OEL
- Some publish exposure standards for noise, lasers, non-ionizing radiation, heat & cold stress, as well as chemicals



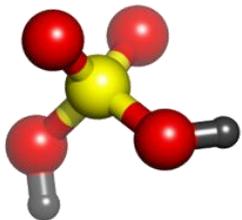


International Occupational Exposure Limits

- ▶ **Indicative OEL Values (IOELVs)**
 - Specified by the Council of the European Union
 - Based on advice from Scientific Committee on Occupational Exposure Limits (SCOEL)
 - 2009 –Third list of IOELVs published
 - Member states have until 12/2011 to implement legislation

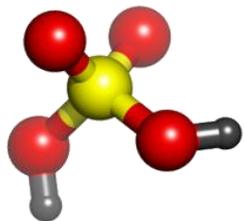
- ▶ **European Union Reach**
 - Worker derived no-effect levels (DNELs)
 - Must be calculated for quantities >10 tons/year
 - Safety margins higher than the IOELVs

- ▶ **German Exposure Limits**
 - DFG MAK – Maximum Workplace Concentrations



U.S. Exposure Limits

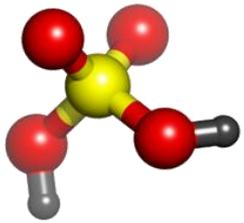
- ▶ PEL – Permissible Exposure Limits
 - Occupational Safety and Health Administration (OSHA)
 - USA legal limits
- ▶ REL – Recommended Exposure Limits
 - National Institute of Occupational Safety & Health (NIOSH)
 - Recommended, not legal limits
- ▶ ACGIH TLV[®] – Threshold Limit Values[®]
 - American Conference of Governmental Industrial Hygienists
 - Recommended, not legal limits
- ▶ AIHA WEEL – Workplace Environmental Exposure Limits
American Industrial Hygiene Association (AIHA)
 - Recommended, not legal limits



Exposure Limits

Permissible Exposure Limit (PEL)

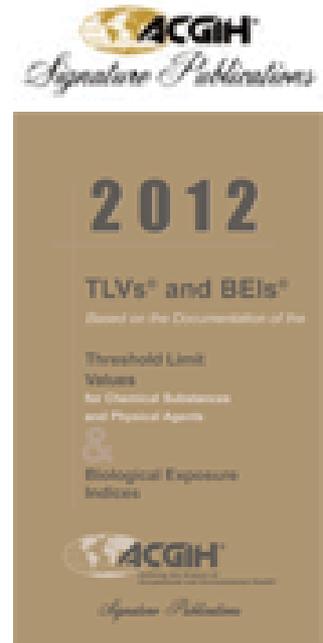
- ▶ Exposure limits are published by the U.S Occupational Safety and Health Administration (OSHA)
- ▶ Intended to control health effects from exposures to “air contaminants”
- ▶ Applies only to workplaces covered by OSHA
- ▶ Action Levels published for highly toxic chemicals
 - ½ the PEL
 - Benzene, asbestos, vinyl chloride, formaldehyde

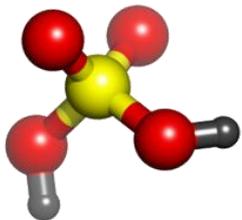


Exposure Limits

ACGIH TLVs®:

- ▶ ACGIH is a private, non-governmental corporation
- ▶ ACGIH TLVs are published as guidelines
- ▶ Not legal standards
- ▶ ACGIH TLVs are usually lower than PELs
- ▶ Reviewed and revised annually





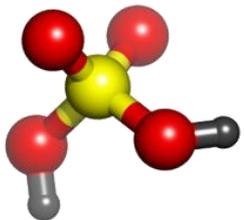
Exposure Limits

ACGIH TLVS®:

- 8 Hour time-weighted average (TWA)
- 15 minute short-term exposure limit (STEL)
- Ceiling value (C)

ACGIH TLV® Examples:

- Carbon dioxide = 5000 ppm TWA
- Osmium tetroxide = 0.0002 ppm TWA
- Hydrogen chloride = 2 ppm ceiling
- Ammonia = 35 ppm STEL



Time Weighted Average (TWA)

Average exposure for an individual over a working period of time, determined by taking one or more samples during the working period:

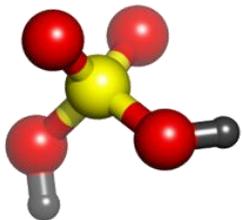
$$\text{TLV - TWA}^* = \frac{C_1T_1 + C_2T_2 + \dots + C_NT_N}{T_1 + T_2 + \dots + T_N}$$

Where:

C = airborne concentration

T = time

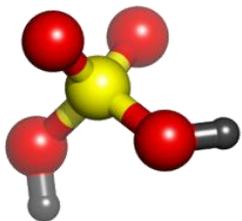
* A TLV expressed as a TWA



8-Hr Time Weighted Average

Average exposure for an individual over an 8-hr working period of time, determined by taking one or more samples during the 8-hr working period:

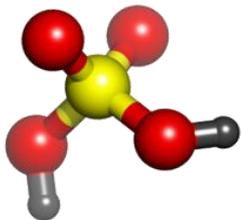
$$\text{TLV} - \text{TWA}_8 = \frac{C_1T_1 + C_2T_2 + \dots + C_NT_N}{8 \text{ hrs}}$$



Example, 8-hour Time-Weighted Average

A degreaser operator is monitored for exposure to Stoddard solvent. The monitoring data is:

<i>TIME PERIOD (NUMBER)</i>	<i>CONCENTRATION (PPM)</i>	<i>TIME (HOUR)</i>
1	80	2
2	110	4
3	55	2



Solution

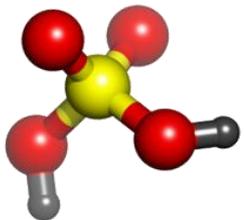
$$\text{TLV - TWA}_8 = \frac{C_1 T_1 + C_2 T_2 + \dots + C_N T_N}{8 \text{ hrs}}$$

$$\text{TLV - TWA}_8 = \frac{(80 \times 2) + (110 \times 4) + (55 \times 2)}{8 \text{ hrs}}$$

EIGHT HOUR TLV-TWA = 89 ppm

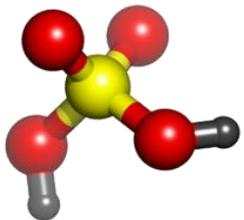
Over exposed?

(TLV-TWA = 100 ppm)



Other ACGIH TLV Notations ...

- “Skin” potential exposure by the dermal route, including mucous membranes and the eyes
 - **Examples: some solvents, phenol, pesticides**
- “SEN” potential to produce sensitization
 - **Example: toluene diisocyanate**



Evaluating Exposure

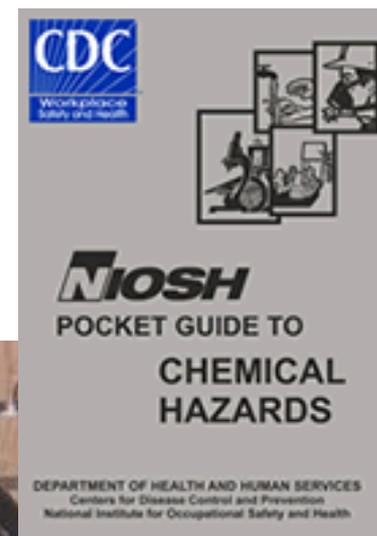
▶ Qualitative assessment

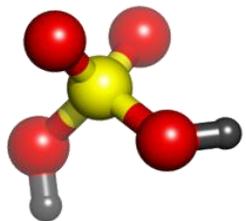
- **Observe task**
 - Airborne contaminants ?
 - Skin immersion ?
- **Evaluate toxicity**
 - Safety data sheets
 - NIOSH Pocket Guide

<http://www.cdc.gov/niosh/npg/>

▶ Quantitative

- **Model exposure**
- **Perform air sampling**





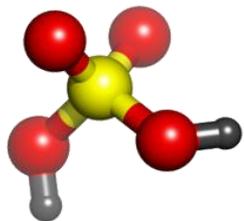
Evaluating Exposure

Quantitative

- Model the contaminant concentration in the room
- Example: What concentration, in mg/m^3 would be produced by the release of 1 gram (g) of benzene in a 125 cubic meter room (m^3)?

Mass of contaminant/volume of room

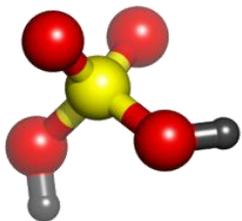
$$1 \text{ g}/125 \text{ m}^3 = 1000 \text{ milligrams}/125 \text{ m}^3 = 8\text{mg}/\text{m}^3$$



Calculation for PPM Concentration

$$\frac{(8 \text{ mg/m}^3) \quad (24.45)}{78.11 \text{ (Molecular Weight)}} = 2.5 \text{ ppm}$$

**ACGIH STEL for benzene is 2.5 ppm
(15 minute short term exposure)**

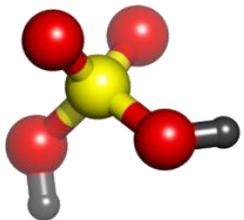


Evaluating Exposure

Air monitoring:

- ▶ Results must be analyzed
- ▶ Results are compared against a standard OEL
- ▶ Methods:
 - Air sampling pump and media or badges
 - Filters-for metals, particulates
 - Charcoal tubes-for solvents
 - Silica gel tubes-for acids





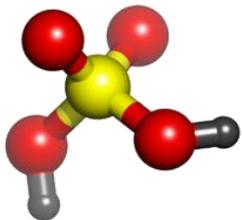
Evaluating Exposure

Other air monitoring methods:

▶ Direct reading instruments

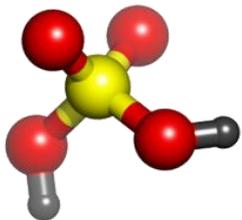
- Photoionization detectors—solvent...
- Particle counters—dusts
- Portable gas detection
 - Operate with hand pump
 - Color coded detector tubes
 - Detect 500 gases and vapors





Evaluating Exposure: Control Banding

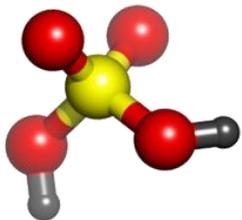
- ▶ Initiatives:
 - World Health Organization (WHO)
 - International Labor Organization (ILO)
- ▶ Over 17 million organic and inorganic substances
- ▶ 170,000 chemicals may require registration under EU REACH regulations
- ▶ Shift in traditional industrial hygiene approach towards exposure



Evaluating Exposure: Control Banding

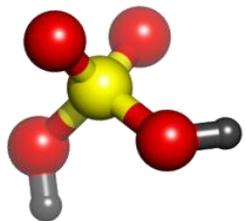
What is control banding?

- ▶ A complementary approach to traditional industrial hygiene
- ▶ Focuses resources on exposure controls rather than exposure assessment
- ▶ Provides technical expertise to chemical users through simplified guidance



Evaluating Exposure: Control Banding

- ▶ Web Page: National Institute of Occupational Safety and Health (NIOSH)
 - www.cdc.gov/niosh/topics/ctrlbanding/
- ▶ Publications:
- ▶ AIHA (2007)
 - *Guidance for Conducting Control Banding Analysis*
- ▶ ACGIH (2008)
 - *Control Banding: Issues and Opportunities*
- ▶ NIOSH (2009)
 - *Qualitative Risk Characterization and Management of Occupational Hazards*
<http://www.cdc.gov/niosh/docs/2009-152/>



Summary of Presentation

- ▶ Provided definitions of dose/exposure
- ▶ Explained the dose response relationship
- ▶ Summarized exposure and health effects of metals and solvents
- ▶ Summarized international exposure limits
- ▶ Described methods for evaluating exposure
- ▶ Described control banding