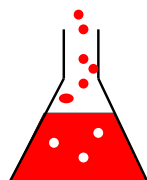
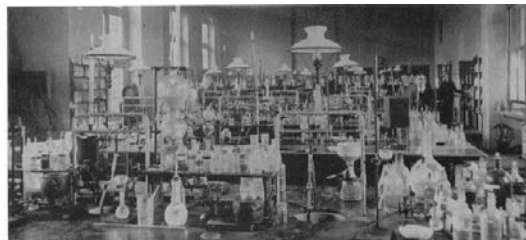


CM5310: Laboratory Safety



Legacy of the Past



Potential in the Present



Hazardous Properties of Chemicals

- Toxic
- Reactive
- Flammable
- Explosive



Each major group has many sub-groups, i.e. under toxic is carcinogenic

Definitions - 1

Accident: The occurrence of a sequence of events that produce unintended injury, death or property damage.

Hazard: A chemical or physical condition that has the potential for causing damage to people, property or the environment. Hazards from chemicals are always present. Hazards can be created by procedures or equipment.

Incident: The loss of containment of material or energy.

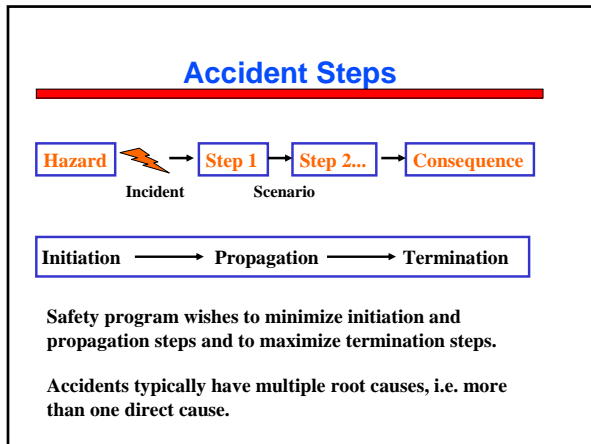
Definitions - 2

Consequence: A measure of the expected effects of an incident. Examples: burns, asphyxiation, cancer, lung failure, etc.

Scenario: A description of the events that result in an accident or scenario.

Risk: A measure of human injury, environmental damage, or economic loss in terms of both the incident likelihood (probability) and the magnitude of the injury or loss (consequence).

$$\text{Risk} = f(\text{probability, consequence})$$



Accident Cause

Most accidents are due to the **loss of control of material or energy.**

Examples:

- Chemical spilling from an overturned beaker. (loss of material control)
- Unexpected reaction of a chemical resulting in gas evolution and rupture of container. (loss of energy control)
- Sudden disconnection of a hose containing high pressure nitrogen. (loss of material control)
- Fire in a beaker. (loss of energy control)

Toxicology

Considers worker exposures

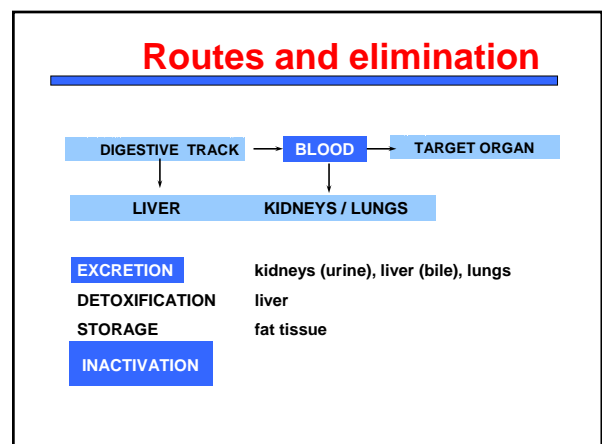
Definitions

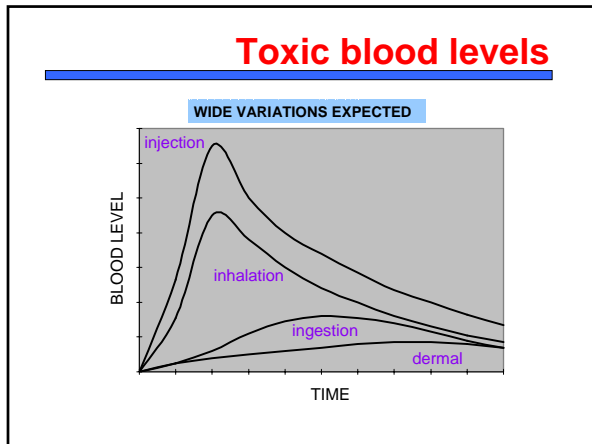
- Toxicology:**
 - entry of toxicants into organism
 - elimination from organism
 - effects on organismQuantitative
- Industrial hygiene:** prevention or reduction of entry
- Toxicant**
 - chemical agents
 - physical agents: particulates < 5 µm, noise, radiation
- Toxicity:** property related to effect on organism
Problem: organisms respond via a distribution of effects
- Toxic hazard:** likelihood of damage based on exposure
reduction by appropriate techniques

Entry toxicants

ROUTE	ENTRY	CONTROL
Ingestion	mouth, stomach	rules on eating, drinking, smoking
* Inhalation	mouth, nose	ventilation, hoods, protection equipment
Injection	cuts in skin	protective clothing
* Dermal Absorption	skin	protective clothing

* most significant





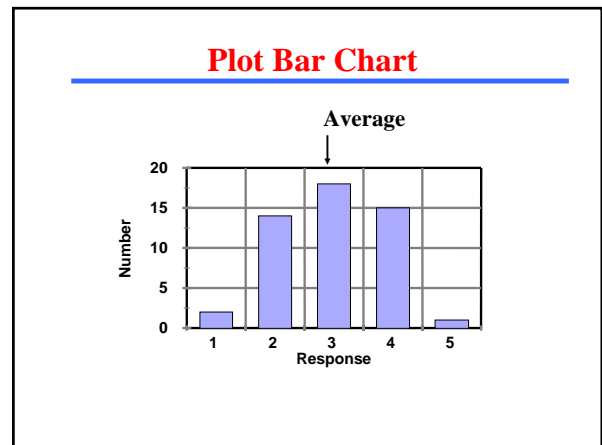
Toxicology Experiment with Rabbits!

Start with 50 rabbits.
Expose each to a fixed concentration.
Get a variety of responses.

Determine Response Curve

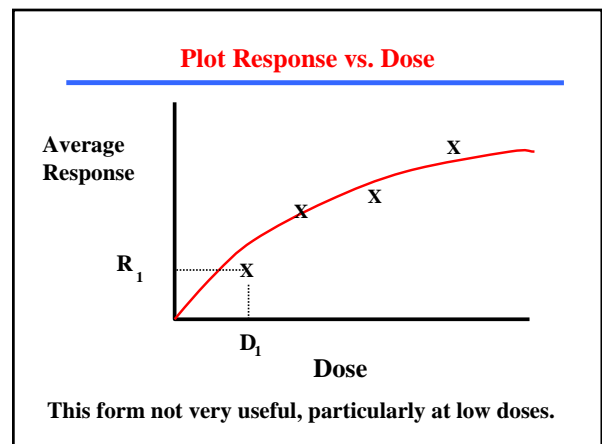
Response	Number	Fraction
Least	1	2
	2	14
	3	18
Worst	4	15
	5	1
	50	1.00

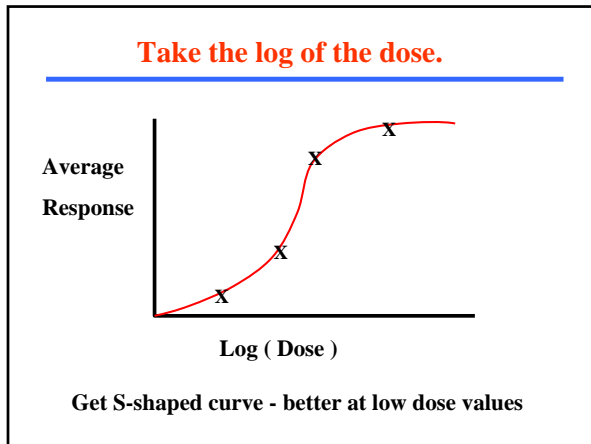
Average = $(1 \times 2 + 2 \times 14 + 3 \times 18 + 4 \times 15 + 5 \times 1) / 50 = 149 / 50$
 = 2.98



Repeat experiment at different doses.

Dose	Average Response
D_1	$R_1 = 2.98$
D_2	R_2
D_3	R_3
D_4	R_4





Threshold Limit Values - 1

THRESHOLD DOSE: NO DETECTABLE EFFECT

Threshold Limit Value TLV: worker's lifetime
8 hours per day 40 hours per week

TLV - TWA *	Time weighted average
TLV - STEL	Short term exposure limit
TLV - C	Ceiling limit

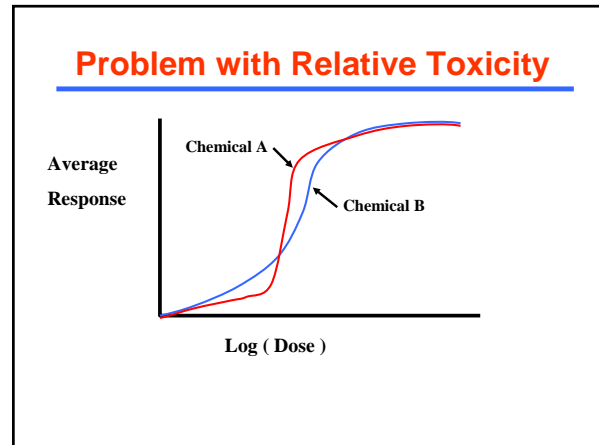
Threshold Limit Values - 2

Published by ACGIH: American Conference of Governmental Industrial Hygienists, a professional organization without legal authority.

Cannot be used as indication of relative toxicity.

Cannot be used for air pollution exposures.

➡ Some toxicants have zero thresholds ⬅



Three Types of TLVs

TLV-TWA - Time weighted average for normal 8-hour workday, to which nearly all workers can be exposed, day after day, without adverse effects.

TLV-STEL - Short-term exposure limit. The max. concentration to which workers can be exposed for a period of up to 15 minutes continuously without suffering (1) intolerable irritation, (2) chronic or irreversible tissue damage, (3) narcosis of sufficient degree to increase accident proneness, impair self rescue, or materially reduce worker efficiency, provided that no more than 4 excursions per day are permitted, with at least 60 minutes between exposure periods, and provided that the daily TLV-TWA is not exceeded

Three Types of TLVs

TLV-C - Ceiling limit. The concentration that should not be exceeded, even instantaneously.

Several hundred TLV-TWA values are available for common materials. Less values are available for STEL and C.

TLV – Example Values

Acetone	750 ppm
Ammonia	25 ppm
CO	25 ppm
Chlorine	0.5 ppm
Gasoline	300 ppm
Hexane	50 ppm
Phosgene	0.1 ppm

For flammables, TLV is ¼ of lower flammable limit.

Conversion from mg/m³ to ppm

$$\text{ppm} = \left(\frac{22.4}{M}\right) \left(\frac{T}{273}\right) \left(\frac{1}{P}\right) (\text{mg/m}^3) = 0.08205 \left(\frac{T}{PM}\right) (\text{mg/m}^3)$$

T in K, *P* in atm.

For liquid mixtures ppm = mg/m³, but this is not true for vapors!

PEL - Permissible Exposure Level

Published by OSHA, and have legal authority.

Defined the same as TLV.

Most PELs are same as TLVs.

Not updated as regularly as TLVs.

Most companies use lowest of the two values.

For some chemicals, i.e. benzene, vinyl chloride, a specific OSHA regulation has been published. Each regulation is unique, but most require EXPLICIT data that workers are not exposed.

See OSHA.gov web site for regulations.

IDLH

IDLH – Immediately Dangerous to Life and Health

Defined as a condition “that poses a threat of exposure to airborne contaminants when that exposure is likely to cause death or immediate or delayed permanent adverse health effects or prevent escape from such an environment.”

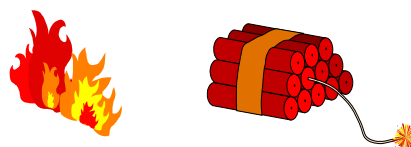
Published by NIOSH for about 380 chemicals.

See NIOSH Pocket Guide on CD.

IDLH – Example Values

Acetone	2,500 ppm
Ammonia	300 ppm
CO	1,200 ppm
Chlorine	10 ppm
Hexane	1,100 ppm
Phosgene	2 ppm

Fires & Explosions



Introduction

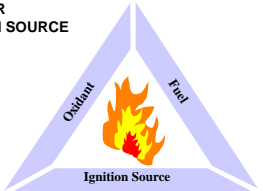
FIRE rapid exothermic, oxidation, with flame } may trigger each other
EXPLOSION higher energy release rate (mixture) }
 pressure or shock wave

EFFECTS injuries / casualties } Thermal radiation, asphyxiation, toxic products, process interruption } blast, fragments
 property losses }
 process interruption }

REQUIRED KNOWLEDGE FOR PREVENTION
 material properties
 nature of fire and explosion process
 procedures to reduce hazards

Fire Triangle

FIRE TRIANGLE FUEL
 OXIDIZER
 IGNITION SOURCE



Oxidant may not be oxygen, i.e. chlorine.

Fire Triangle

FUELS	Gases: Acetylene, Propane, CO, H ₂ Liquids * Gasoline, Organic Solvents Solids * Plastics, Wood Dust, Fibers, Metal Particles
OXIDIZERS	Gases: O ₂ , F ₂ , Cl ₂ Liquids: H ₂ O ₂ , HNO ₃ , HClO Solids: Peroxides, NH ₄ , NO ₂
IGNITION SOURCE	Sparks, Flames, Static Electricity, Heat

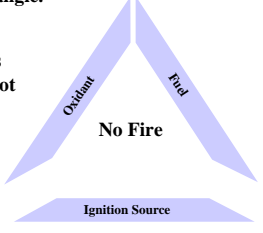
* Liquids are volatilized and solids decomposed prior to their combustion in the vapor phase

Sufficient quantity / energy required.

Application of the Fire Triangle


Fires and explosions can be prevented by removing any single leg from the fire triangle.

Problem: Ignition sources are so plentiful that it is not a reliable control method.




Robust Control: Prevent existence of flammable mixtures.

Combustion Behavior – Most Hydrocarbons



Smoke and fire are very visible!

Combustion Behavior – Carbon Disulfide



No smoke and fire, but heat release rate just as high.

Definitions - 1

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.

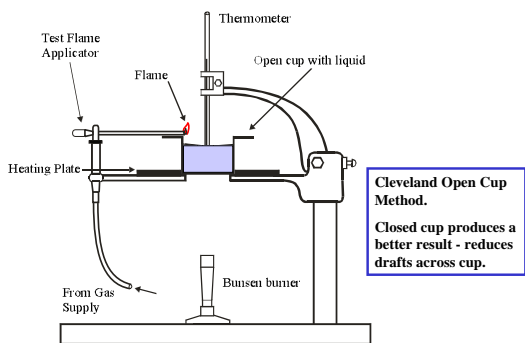
Defined only for gas mixtures in air.
 Both UFL and LFL defined as volume % fuel in air.

Definitions - 2

Flash Point: Temperature above which a liquid produces enough vapor to form an ignitable mixture with air.
 Defined only for liquids at atm. Pressure.

Auto-Ignition Temperature (AIT): Temperature above which adequate energy is available in the environment to provide an ignition source.

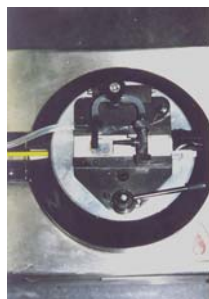
Experimental Determination - Flashpoint



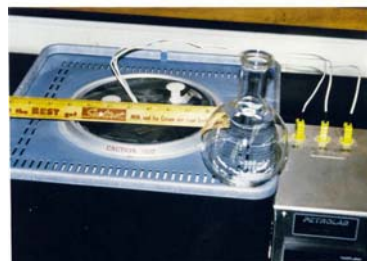
Setaflash Flashpoint Device



Setaflash Flashpoint Device – Close-up



Auto-Ignition Temperature (AIT) Device



Typical Values - 1

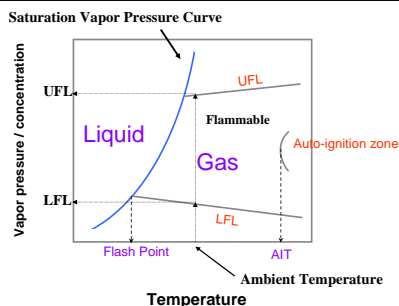
	LFL	UFL
Methane:	5%	15%
Propane:	2.1%	9.5%
Butane:	1.6%	8.4%
Hydrogen:	4.0%	75%
Flash Point Temp. (deg F)		
Methanol:	54	
Benzene:	12	
Gasoline:	-40	

Typical Values - 2

	AIT (deg. F)
Methane:	1000
Methanol:	867
Toluene:	997

Great variability in reported AIT values!
Use lowest value.

Flammability Relationships



Chemical Reactivity

Very difficult to characterize!

Can have: Decompositions, reactivity with other chemicals (normal and emergency situations), catalyst effects, contamination of reactants, changes in raw material concentrations, accumulation of unreacted materials, equipment malfunctions (stirrer, cooling, vessel), improper mixing, unintended reactions, reactions occurring elsewhere,

Can use calorimeters (DSC, ARC, others) to study and characterize.

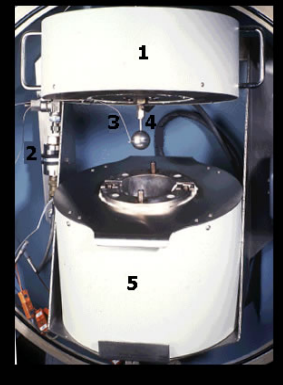
ARC – Accelerating Rate Calorimeter

Used to characterize the reactive behavior of chemicals.



CALORIMETER

1. Calorimeter Top
2. Pressure Transducer
3. Bomb Thermocouple
4. Bomb (Sample Container)
5. Calorimeter Bottom



ARC Test Cell – About 10 ml



Determining Self Heat Rate

Heat sample at constant rate.

Measure temperature and temperature rate.

$(dT/dt)_{max}$ is self heat rate.

