# Definitions - Toxicology

| | | |
|---|---|---|
| Toxicology | - entry of toxicants into organism<br>- elimination from organism<br>- effects on organism | quantitative |
| Industrial hygiene | prevention or reduction of entry | |
| Toxicant | - chemical agents<br>- physical agents: particulates < 5 μm, noise, radiation | |
| Toxicity | property related to effect on organism | |
| Toxic hazard | likelihood of damage based on exposure<br>reduction by appropriate techniques | |

# Entry Ways for 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 |

* industrially most significant

# Response to Toxicants

**When a set of organisms is exposed to a toxicant at a fixed concentration, a variety or responses is obtained, depending on a number of factors:**

**Age of organism**

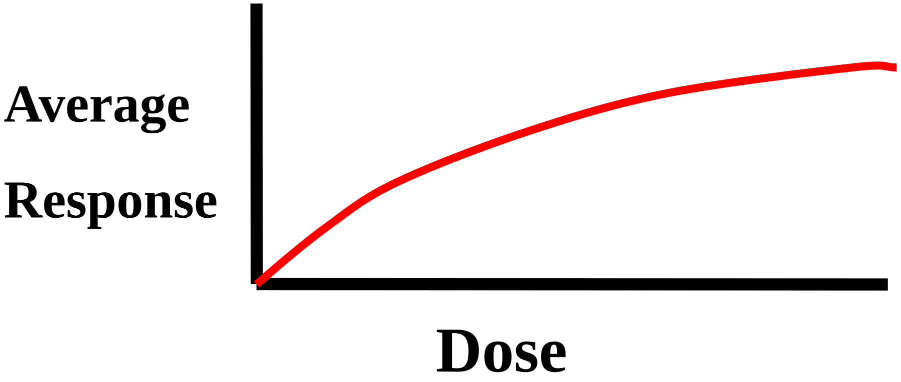
**Sex of organism**

**Health of organism**

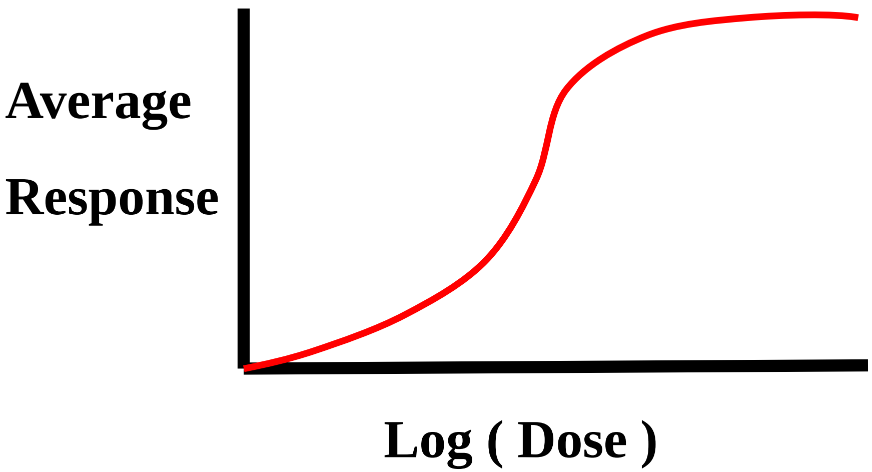
**Etc.**

**Need a statistical way to represent response.**

# Response vs. Dose




**Not very useful**




**Better at low doses, much more useful**

**Can also use a probit transformation to change s-shaped curve into a straight line.**

# Threshold Limits

## THRESHOLD DOSE: NO DETECTABLE EFFECT

**Threshold Limit Value TLV: worker's lifetime**

**8 hours per day 40 hours per week**

| | |
|---|---|
| TLV - TWA * | time weighed average |
| TLV - STEL | short term exposure limit |
| TLV - C | ceiling limit |

*** ≈ PEL Permissible Exposure Level**

➡ some toxicants have zero threshold ⬅

# Threshold Limits Values

| | TLV-TWA (ppm) |
|---|---|
| **Carbon Monoxide:** | **50** |
| **Chlorine:** | **0.5** |
| **Formaldehyde:** | **1** |
| **Methyl Alcohol:** | **200** |
| **Methyl Ethyl Ketone:** | **200** |
| **Phosgene:** | **0.1** |
| **Turpentine:** | **100** |

ppm:  parts per million by volume

# Industrial hygiene

**Concerns conditions related to workplace injury and sickness**
**e.g: exposures to toxic vapors, dust, noise, heat, cold, radiation, physical factors, etc.**

| | |
|---|---|
| **ANTICIPATION** | expectation of hazard existence |
| **IDENTIFICATION** | presence of workplace exposure |
| **EVALUATION** | magnitude exposure |
| **CONTROL** | reduction to acceptable levels |

**Chemical Plants & Labs: requires co-operation from industrial hygiene, safety & plant operations people**

# Identification

Requires study of :

- CHEMICAL PROCESS
- OPERATING CONDITIONS
- OPERATING PROCEDURES

• process design
• operating instructions
• safety reviews
• equipment description
• chemicals description MSDS's

**SOME POTENTIAL HAZARDS:**

• volatile liquids
• vapors
• dusts
• noise
• radiation
• temperature
• mechanical

**HAZARD DATA:**

• physical state / vapor pressure
• TLV's
• temperature sensitivity
• rate and heat of reaction
• by-products
• reactivity with other chemicals
• explosion limits

**RISK ASSESMENT: potential for hazard to result in an accident**

# Evaluation Volatiles

**monitoring air concentrations** ⟷ **variation in time and place**

**Time Weighted Average**

**Continuous:**

$$TWA = \frac{1}{8}\int_0^{t_w} C(t)dt$$

**ppm or mg/m³**

**Intermittent:**

$$TWA = \frac{1}{8}\sum_1^i C_i T_i$$

**Additive effect multiple toxicants:**

$$\sum_1^i \frac{C_i}{(TLV - TWA)_i} < 1$$

**Equivalent**

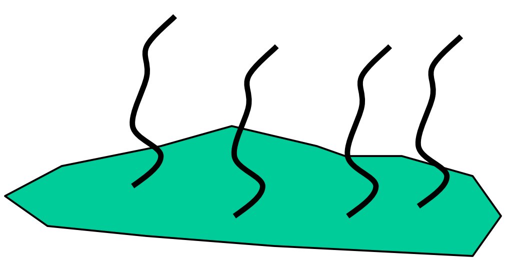
**Mixture:**

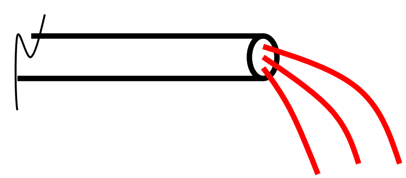
$$(TLV - TWA)_{mix} = \frac{\sum_1^i C_i}{\sum_1^i \left( \frac{C_i}{TLV - TWA} \right)_i}$$

# Source Models

- What:  Describe how material escapes from a process
- Why:  Required to determine potential consequences of and accident

**Risk = f( Probability, Consequences )**

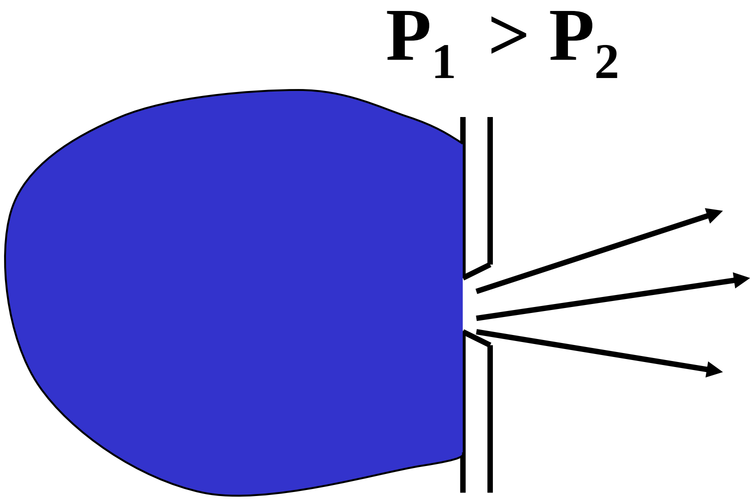




# What do Source Models Provide?

- Release rate, mass/time
- Total amount released
- State of material:  liquid, solid, gas, combination

# Source Model: Liquid thru a hole




1. Pressure drives liquid thru hole
2. Pressure energy converted to KE as liquid escapes
3. Frictional losses

## Orifice Discharge Equation

$$Q_m = C_o A \sqrt{2 \rho g_c \Delta P}$$

# Dispersion Models

**What? Describe how vapors are transported downwind of a release.**

**> 100 m**

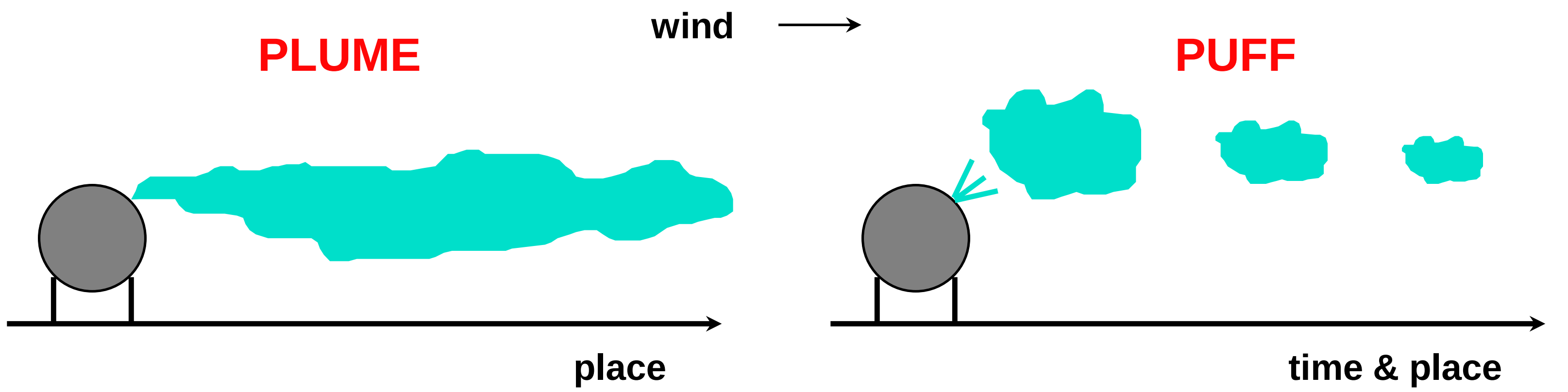
**Why? To determine the consequences**

**Results: Downwind concentrations (x,y,z)**

**Area affected**

**Downwind distances**

# Dispersion




continuous release

instantaneous release

**DOWNWIND DILUTION BY MIXING WITH FRESH AIR**

## ATMOSPHERIC DISPERSION

- wind speed
- atmospheric stability: vertical temp. profile
- roughness ground: buildings, structures, trees, water
- height release above ground level
- momentum and buoyancy: effective height

difficult

# Fires and Explosions

**FIRE:** Rapid exothermic, oxidation, with flame

**EXPLOSION:** Higher energy release rate (mixture) pressure or shock wave

} may trigger each other

**EFFECTS**

Injuries / casualties
Property losses
Process interruption

} Thermal radiation, blast wave, fragments, asphyxiation, toxic products.

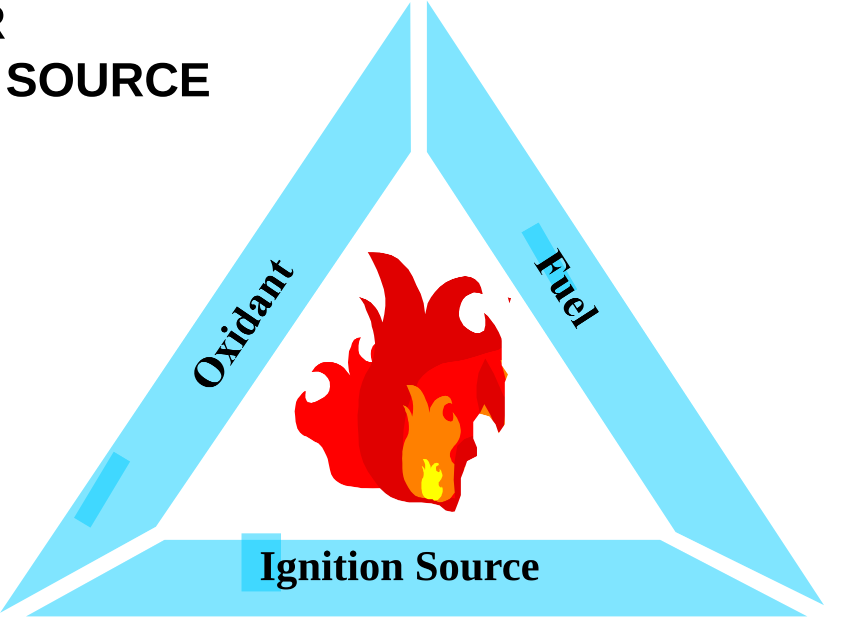
**REQUIRED KNOWLEDGE FOR PREVENTION**

Material properties
Nature of fire and explosion process
Procedures to reduce hazards

# Fire Triangle

**FIRE TRIANGLE**

**FUEL**
**OXIDIZER**
**IGNITION SOURCE**

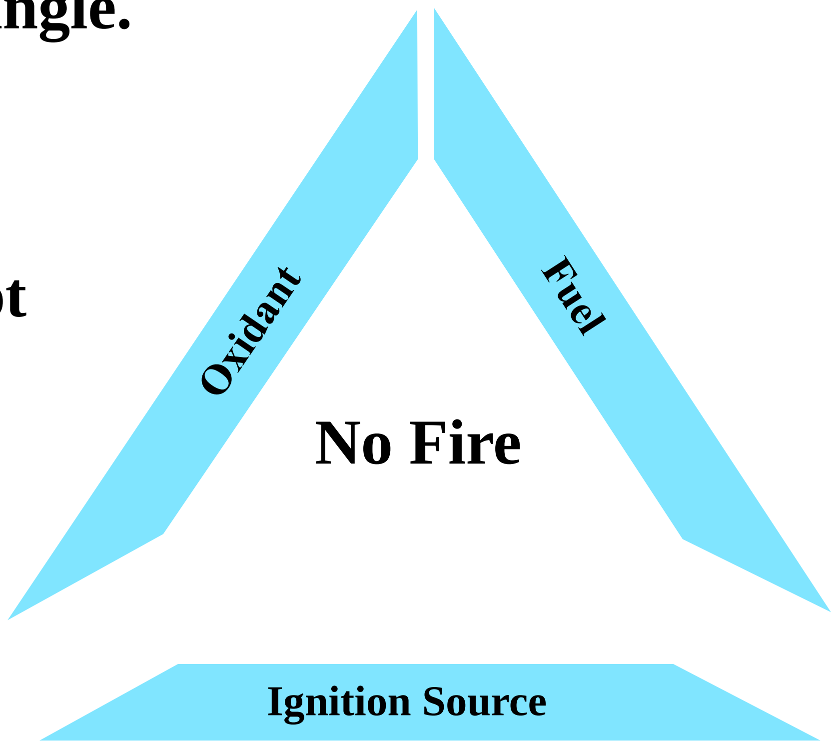



**Oxidant may not be oxygen! For example, chlorine can oxidize.**

# 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.**

# 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.

**Auto-Ignition Temperature (AIT):** Temperature above which energy can be extracted from the environment to provide an ignition source.

# Definitions - 3

**Minimum Oxygen Concentration (MOC): Oxygen concentration below which combustion is not possible.**

**Expressed as volume % oxygen.**

**Also called: Limiting Oxygen Concentration (LOC)**

**Max. Safe Oxygen Conc. (MSOC)**

**Others**

# Typical Values - 1

| | LFL | UFL |
|---|---|---|
| **Methane:** | **5%** | **15%** |
| **Propane:** | **2.1%** | **9.5%** |
| **Butane:** | **1.6%** | **8.4%** |
| **Hydrogen:** | **4.0%** | **75%** |

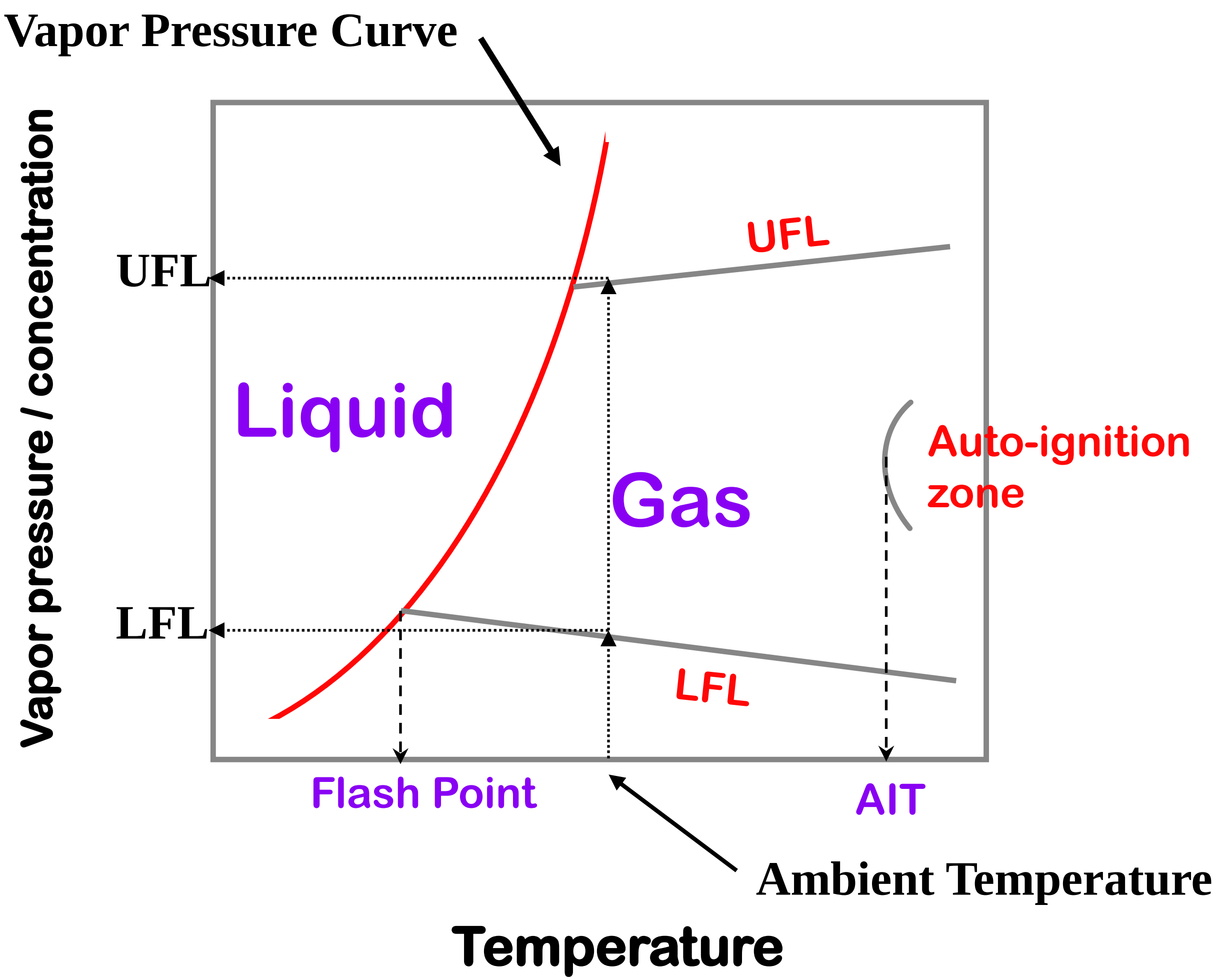
| | Flash Point Temp. (deg F) |
|---|---|
| **Methanol:** | **54** |
| **Benzene:** | **12** |
| **Gasoline:** | **-40** |

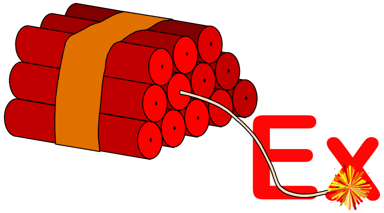
# Typical Values - 2

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

| | MOC (Vol. % Oxygen) |
|---|---|
| **Methane:** | **12%** |
| **Ethane:** | **11%** |
| **Hydrogen:** | **5%** |

# Flammability Relationships





# Explosions - Definitions

**Explosion:** **A very sudden release of energy resulting in a shock or pressure wave.**

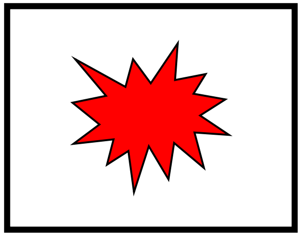
**Shock, Blast or pressure wave:** **Pressure wave that causes damage.**

**Deflagration:** **Reaction wave speed < speed of sound.**

**Detonation:** **Reaction wave speed > speed of sound.**

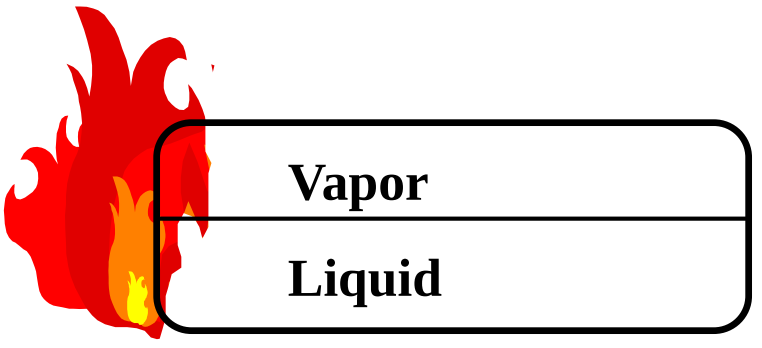
**Speed of sound: 344 m/s, 1129 ft/s at ambient T, P.**

**Deflagrations are the usual case with explosions involving flammable materials.**



# BLEVE

**BLEVE: Boiling Liquid Expanding Vapor Explosion**




**Vessel with liquid stored below its normal boiling point**

**Below liquid level - liquid keeps metal walls cool.**

**Above liquid level - metal walls overheat and lose strength.**

**After vessel failure, a large amount of superheated liquid is released, which will flash explosively into vapor. If the liquid is flammable, a fireball may result.**

# Most Important Concept

**Chemicals have hazardous properties that can be well characterized and are well-understood.**

- **Toxicity**
- **Flammability**
- **Reactivity**
- **Others**