



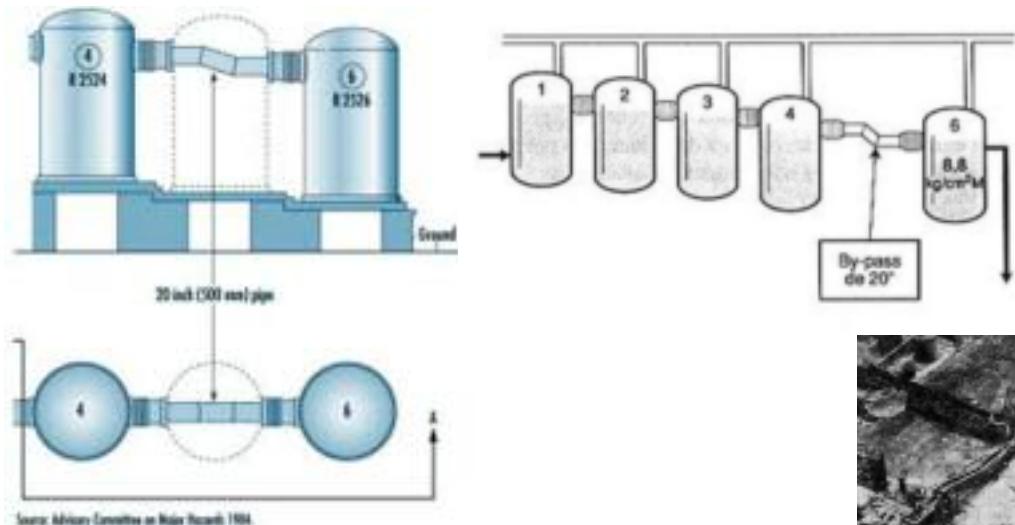
Process Safety Engineering: Introduction & Overview

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The Rising Case for Change

■ Flixborough, England (1974)



- Cyclohexane explosion
- 29 Fatalities and offsite effects



HAZARD: poorly designed modification

The Rising Case for Change

- 1984 – Bhopal, India – Toxic Material Released

- 2,500 immediate fatalities;
20,000+ total
- Many other offsite injuries



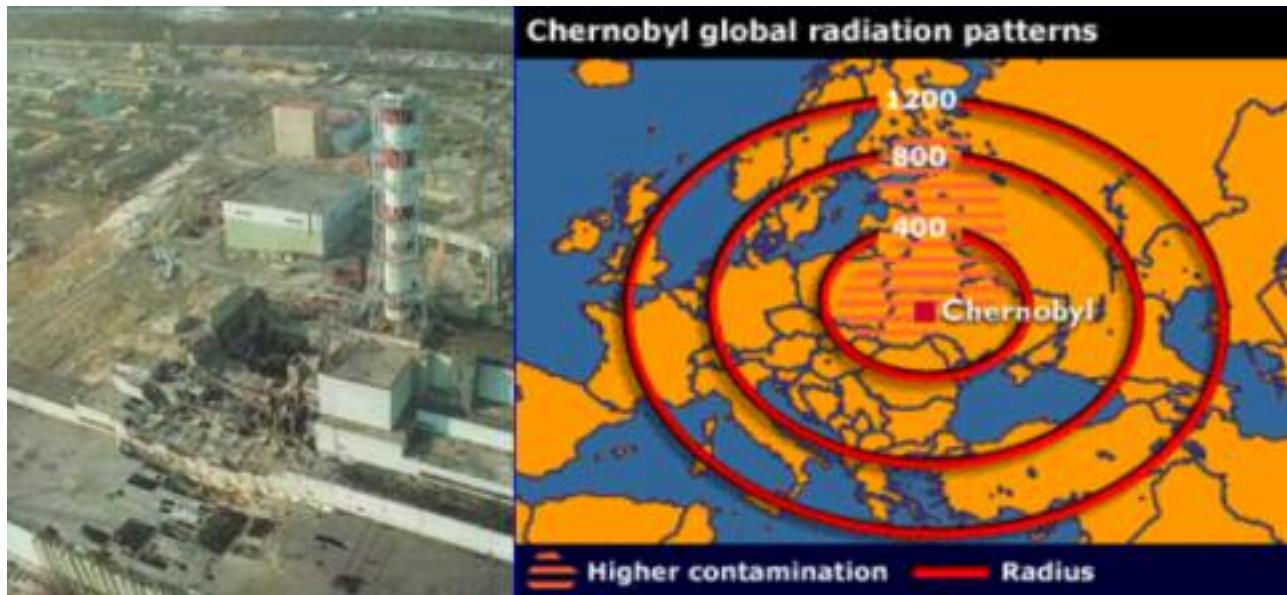
- 1984 – Mexico City, Mexico –Explosion

- 300 -650 fatalities
(mostly offsite)
- \$20M damages



LPG explosion caused by a leak at a marketing terminal pipeline that ignited and started a fire at the terminal.

■ 1986 – Chernobyl



- Large area of Russia, Ukraine and Belarus evacuated, 336,000 people resettled.
- Fewer than 50 direct death but, thousands of cancer related cases
- Severe damage to the environment

- 1988 – Norco, LA – Explosion
 - 7 onsite fatalities, 42 injured
 - \$400M+ damages



- Henderson, Nevada, (1988)



- 1989 – Pasadena, TX – Explosion and Fire
 - 23 fatalities, 130 injured; damage \$800M+



A seal blew out on an ethylene loop reactor, releasing ethylene-isobutane vapor cloud, a compound used in making plastics

Some Recent Incidents



T2 Laboratories Inc –Jacksonville, FL, 2007

4 Killed and 13 Wounded in reactor explosion in manufacture of gasoline additive.



BP America Refinery –Texas City, TX, 2005

15 Killed and 180 Wounded in isomerization unit explosion and fire.



West Pharmaceutical Services –Kinston, NC, 2003

6 Killed and Dozens Wounded in dust cloud explosion and fire from release of fine plastic powder.

Safety & Loss Prevention

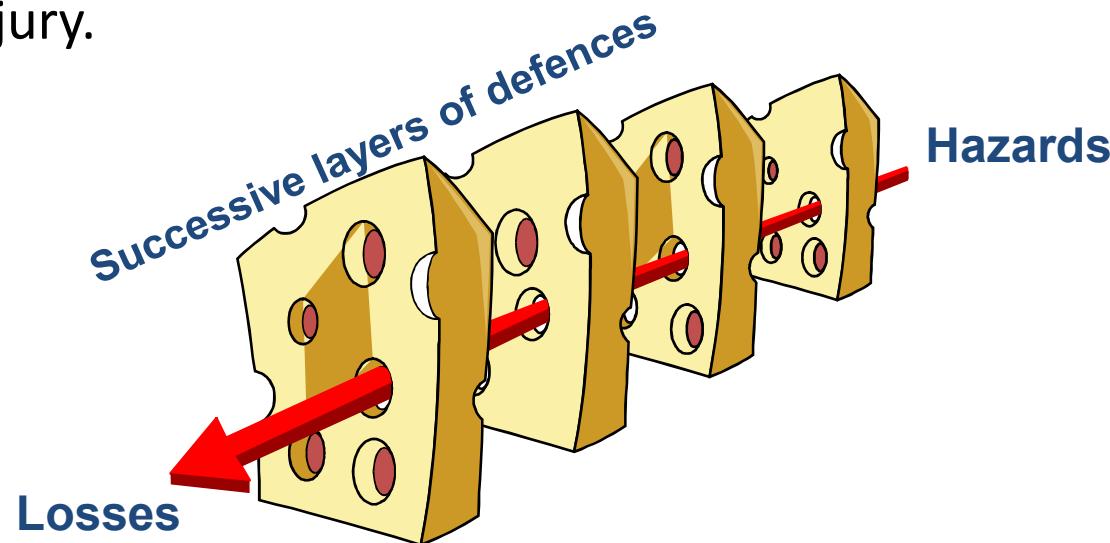
"To know is to survive and to ignore fundamentals is to court disaster."

H. H. Fawcett

- The word "**safety**" : the older strategy of accident prevention through the use of hard hats, safety shoes, and a variety of rules and regulations.
- Recently, "**safety**" has been replaced by "**loss prevention**". This term includes hazard identification, technical evaluation, and the design of new engineering features to prevent loss.

Safety, hazard, and risk

- ***Safety or loss prevention:*** the prevention of accidents through the use of appropriate technologies to identify the hazards of a chemical plant and eliminate them before an accident occurs.
- ***Hazard:*** a chemical or physical condition that has the potential to cause damage to people, property, or the environment.
- ***Risk:*** a measure of human injury, environmental damage, or economic loss in terms of both the incident likelihood and the magnitude of the loss or injury.



Hazards in Chemical plants

- Mechanical hazards that cause worker injuries from tripping, falling, or moving equipment.
- Chemical hazards. These include fire and explosion hazards, reactivity hazards, and toxic hazards.

➤ Active hazard

- Immediately adverse effect
- Similar to “unsafe act”

➤ Latent hazard

- Effect may not be noticeable for some time.
- Unforeseen trigger conditions could activate the risk.



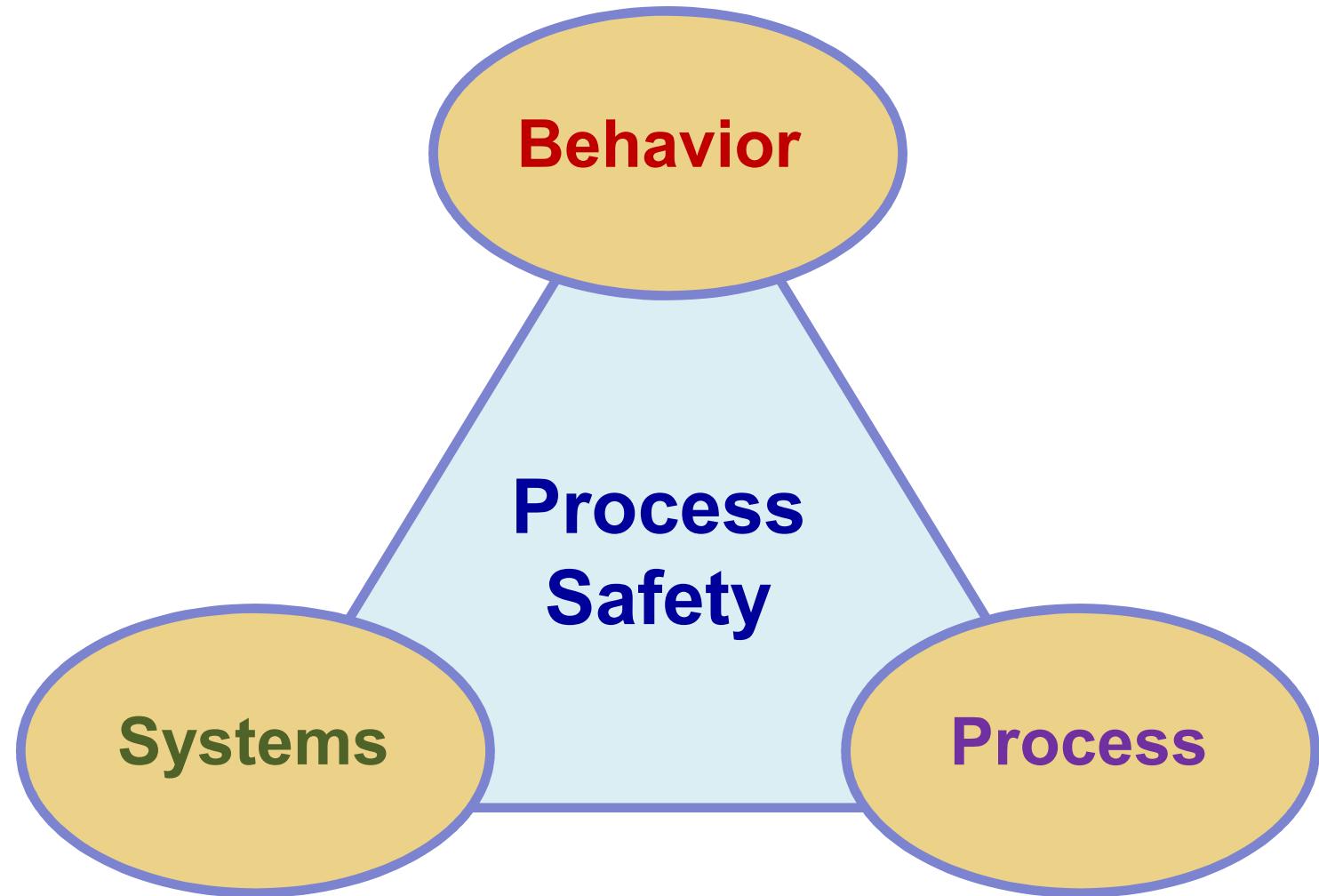
S-A-F-E-T-Y

- **S** - Management **S**ystems
- **A** - Proper **A**ttitude
- **F** - Understand **F**undamentals
- **E** - **E**xperience
- **T** - **T**ime to do things safely
- **Y** - **Y**our Participation

✓ **Safety Program:** identifies and eliminates existing safety hazards.

✓ **Safety Management Systems:** prevent the existence of safety hazards.

Three Elements of Process Safety



Process Safety Milestone Practices

Pre-1930's

Identify who caused the loss and
punish the guilty

Behavior

Pre-1970's

Find breakdown in, and fix man-
machine interface

Process

1970's, 80's

Development of risk assessment
techniques and systematic
approaches

Mgmt Systems

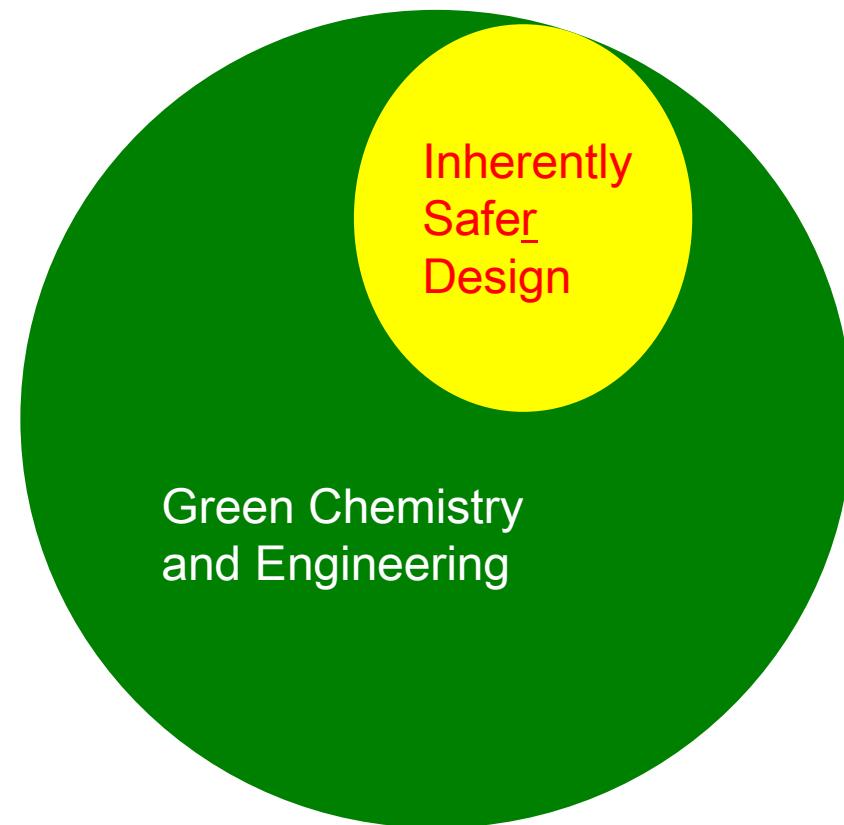
1980's +

Performance-, risk-based
standards, regulations; 'green' and
'inherent' designs

Comprehensive

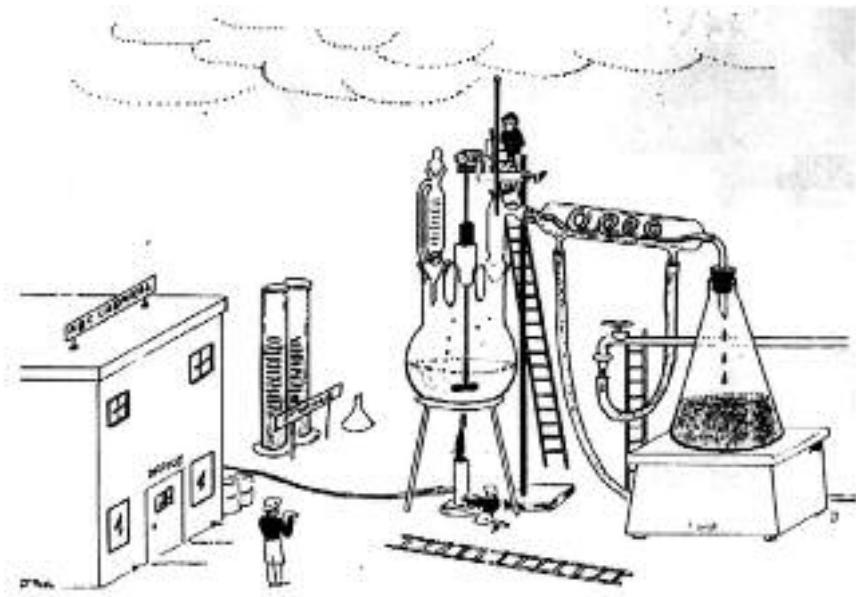
Inherently Safer Design

- **Definition:** *The design of chemical processes and products with specific attention to eliminating hazards from the manufacturing process rather than relying on the control of these hazards.*



Inherently Safer Design Strategies

- ✓ Minimize
- ✓ Moderate
- ✓ Substitute
- ✓ Simplify



Strategy	Examples
Substitute	Replace material with a less hazardous substance.
Minimize	Use smaller quantities; eliminate unnecessary equipment; reduce size of equipment or volumes processed.
Moderate	Use less hazardous conditions, a less hazardous form of material or facilities which minimize the impact of a release.
Simplify	Design facilities which eliminate unnecessary complexity and make operating errors less likely.

Accidents and Loss Statistics

Statistical methods:

- OSHA incidence rate,
- fatal accident rate (FAR), and
- fatality rate, or deaths per person per year.

OSHA incidence rate

- OSHA stands for the **Occupational Safety and Health Administration** of the US govt.

OSHA incidence rate based on Injury & Illness :

OSHA Injury & Illness Rate = (# of Injuries & Illness*200,000)/(Total hrs all employees)

Based on 100 worker-years

$$WorkYear = \left(\frac{40\text{hrs}}{\text{wk}} \right) \left(\frac{50\text{wk}}{\text{yr}} \right) = 2000 \text{hr/yr}$$

OSHA incidence rate based on lost workdays:

- **Lost Workdays** are those days which the employee would have worked but could not because of occupational injury or illness. Also need to account for diminished long term performance.
- Same bases, but use lost workdays

OSHA Incidence Rate (lost WD) = (# lost workdays * 200,000)/ (Total hrs worked)

Fatal accident rate (FAR)

FAR= (# of Fatalities X 10⁸)/(Total hrs worked by all employees)

- Based on 1000 workers' career

$$WCareer = \left(\frac{40hr}{wk} \right) \left(\frac{50wk}{yr} \right) \left(\frac{50yr}{career} \right) = 10^5 \text{ hr/career}$$

Remark: refer to Table 1.3 & 1.4 lists several FARs

Fatality Rate

$$FatalityRate = \left(\frac{\# Fatalities / yr}{Total \# People Exposed} \right)$$

In Class Assignment

- The FAR for travel by car is reported as 57 while that for travel by air is 240

1. If the average speed of travel is 50 mph by car and 250 mph by air, determine the deaths per million miles travel by car or air.
2. If you are required to make a round trip from Aqaba to Amman, which is the safer mode of transportation as indicated by the statistics?

Assignment Solution

1) Calculations

$$Car - > \left(\frac{57 \text{ deaths}}{10^8 \text{ hr}} \right) \left(\frac{1 \text{ hr}}{50 \text{ miles}} \right) \left(\frac{10^6}{\text{MillionMiles}} \right) = 0.0114 \text{ deaths/MillionMiles}$$

$$Air - > \left(\frac{240 \text{ deaths}}{10^8 \text{ hr}} \right) \left(\frac{1 \text{ hr}}{250 \text{ miles}} \right) \left(\frac{10^6}{\text{MillionMiles}} \right) = 0.0096 \text{ deaths/MillionMiles}$$

2) For a fixed distance, air travel is the safest mode

HW

1.1 1.2

1.3 1.4

1.5 1.6

1.8 1.9

1.25

1.26

Toxicology

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Overview

- **Toxin:** any of a group of poisonous, usually unstable compounds generated by microorganisms, plants or animals.
- **Toxicant:** -chemical agents
 - physical agents: particulates < 5 μm , noise, radiation
- **Toxicity:** The effect a specific quantity or dosage of a specific toxin has on a living microorganism.
- **Toxicology:** the study of poison.

“ALL THINGS ARE POISONS, OR THERE IS NOTHING WITHOUT POISONOUS QUALITIES. IT IS ONLY THE DOSE WHICH MAKES A THING POISON.”

PARACELSUS (1493 - 1541)

General Concepts of Toxicology

EXPOSURE TERMINOLOGY

Hazardous Material. A Material That Falls Into One or More Of the Following Categories. Hazardous Materials Can Have One or Many Characteristics That Can Add to the Intensity of the Toxic Action of a Particular Solid, Liquid, or Gas.

- Ignitability** Is Flammable or Combustible.
- Reactivity** Can React With Itself or Other Materials.
- Corrosivity** Can Deteriorate Another Substance.
- Toxicity** In Its Normal State Is Harmful to Living Things.

EVERYTHING IS TOXIC;

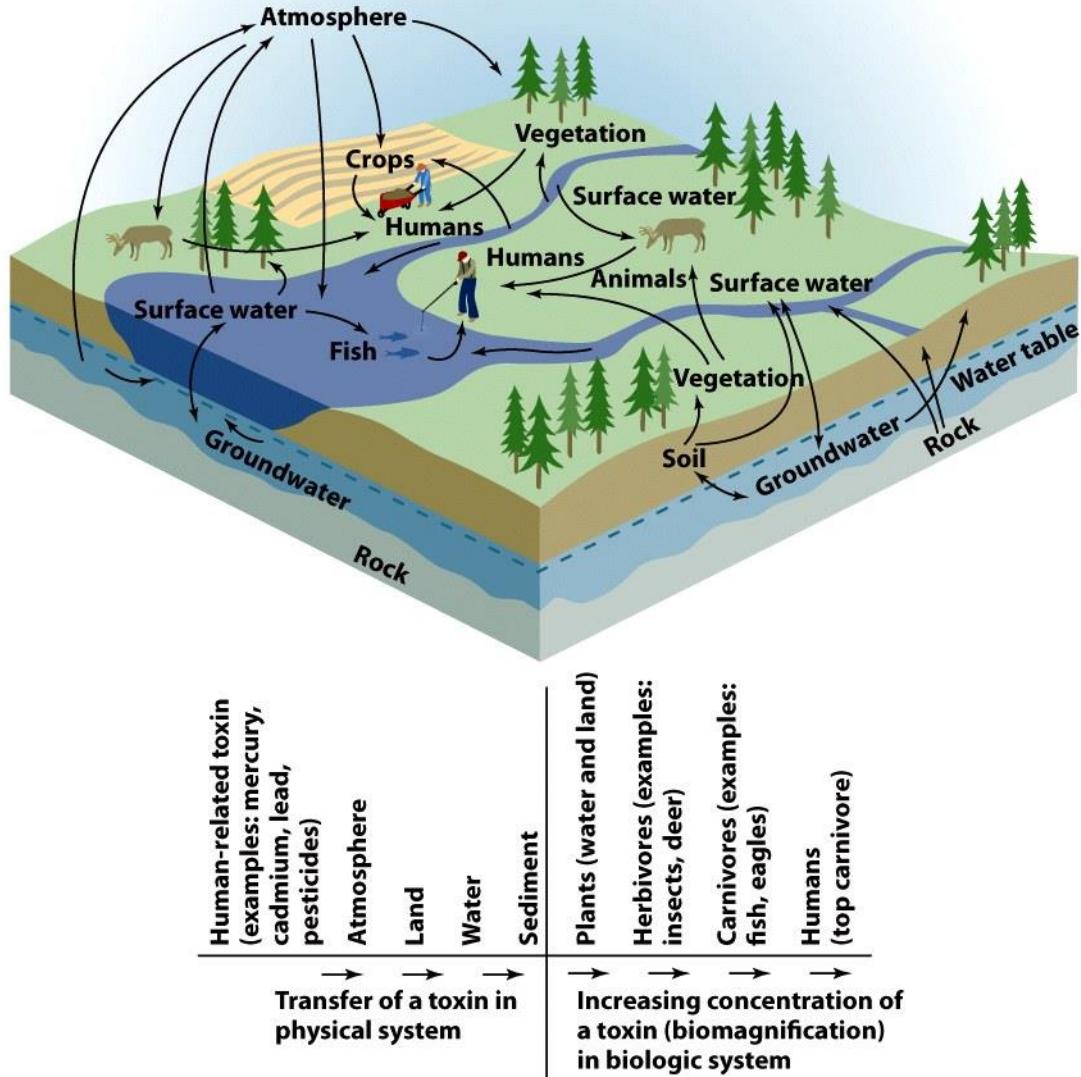
IT ALL DEPENDS ON THE DOSE

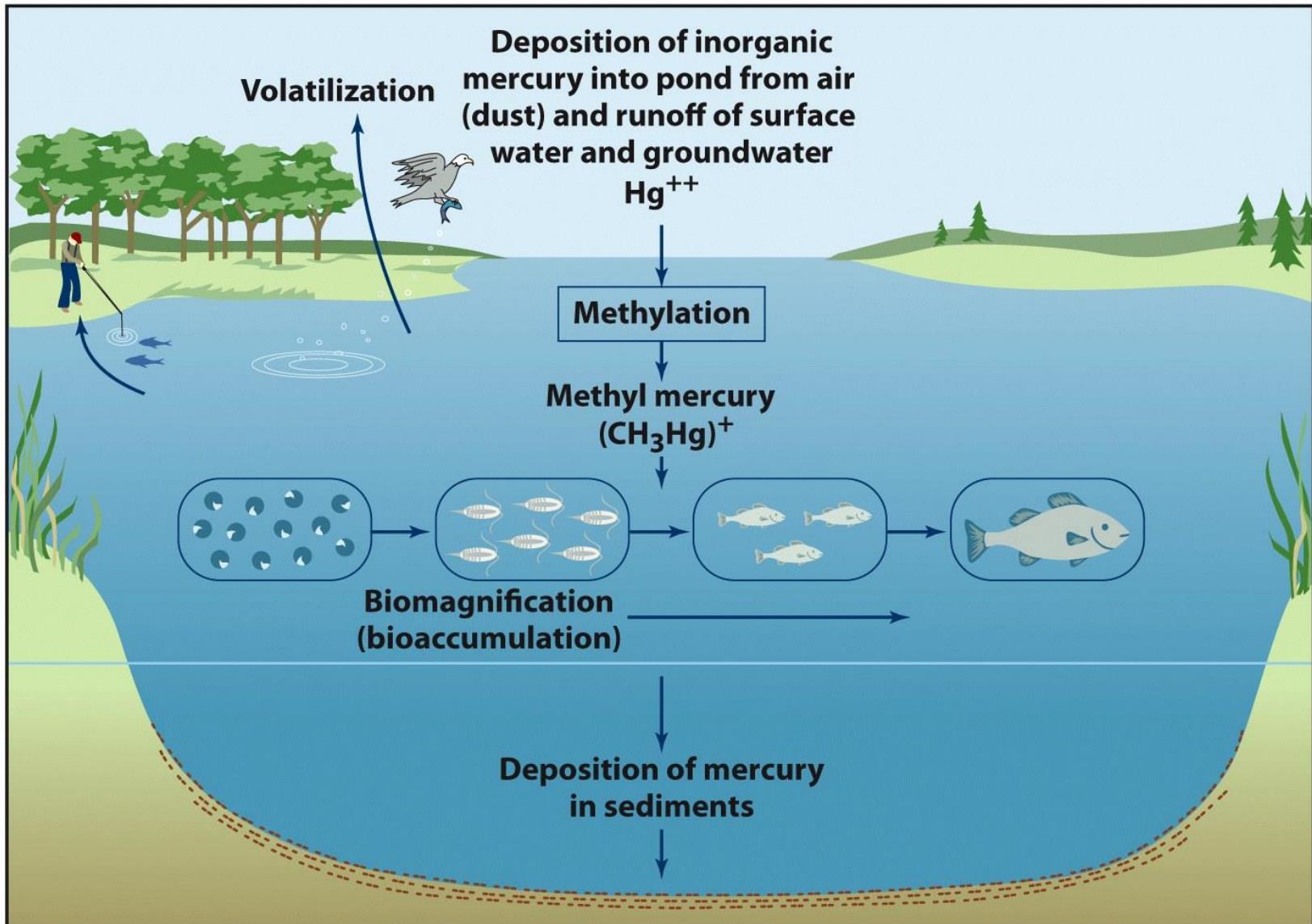
How Well the Body Accepts a Substance Depends on:

- The Type of Substance.**
- The Amount (Dose) Absorbed.**
- The Period of Time Over Which It Is Absorbed.**
- The Susceptibility/Sensitivity of the Person Exposed.**

Toxic Pathways

- Chemical elements can become concentrated
- **Biomagnification-** the accumulation or increase in concentration of a substance in living tissue as it moves through the food chain.
E.g. Cadmium, mercury





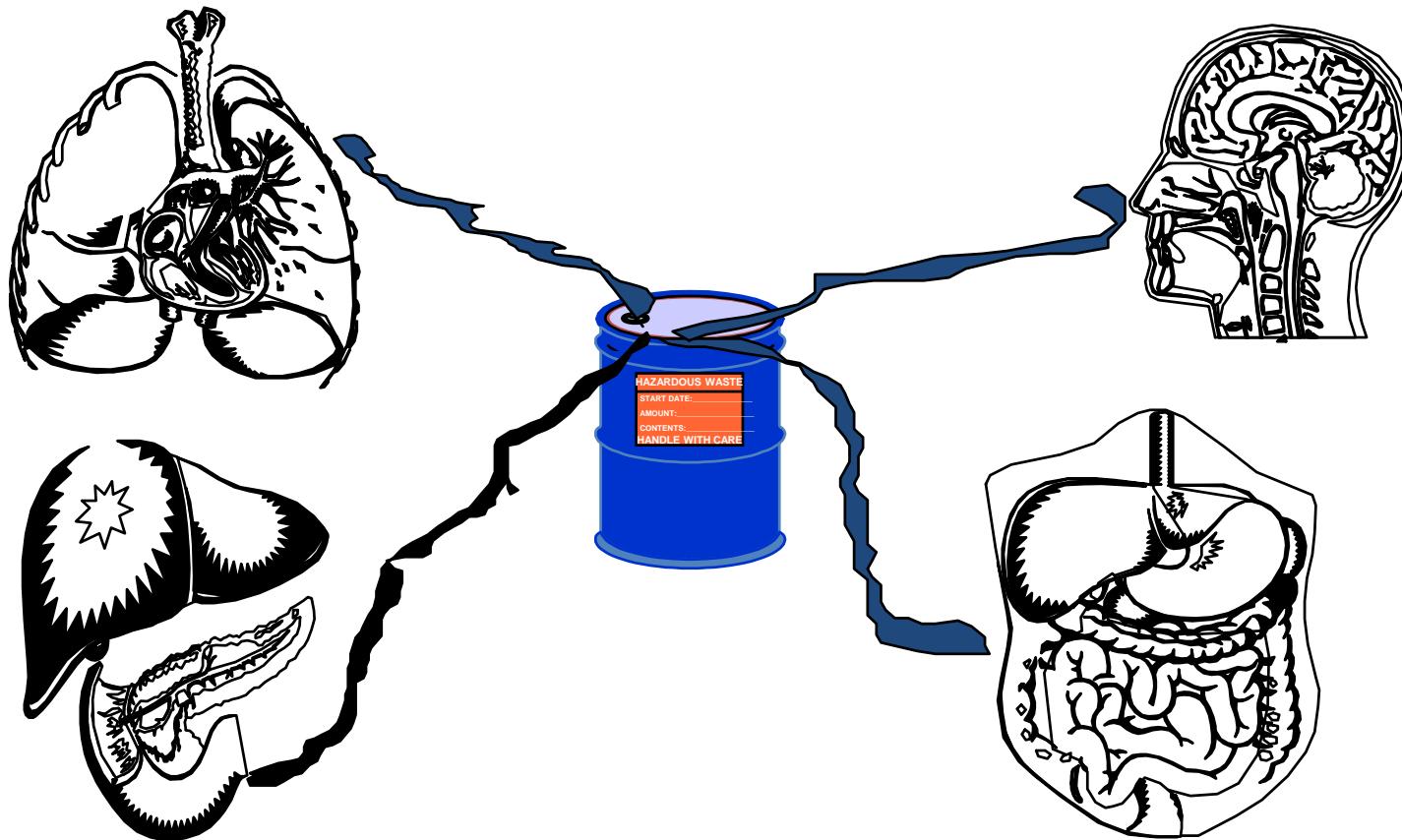
Toxicants routes into biological organisms

INHALATION

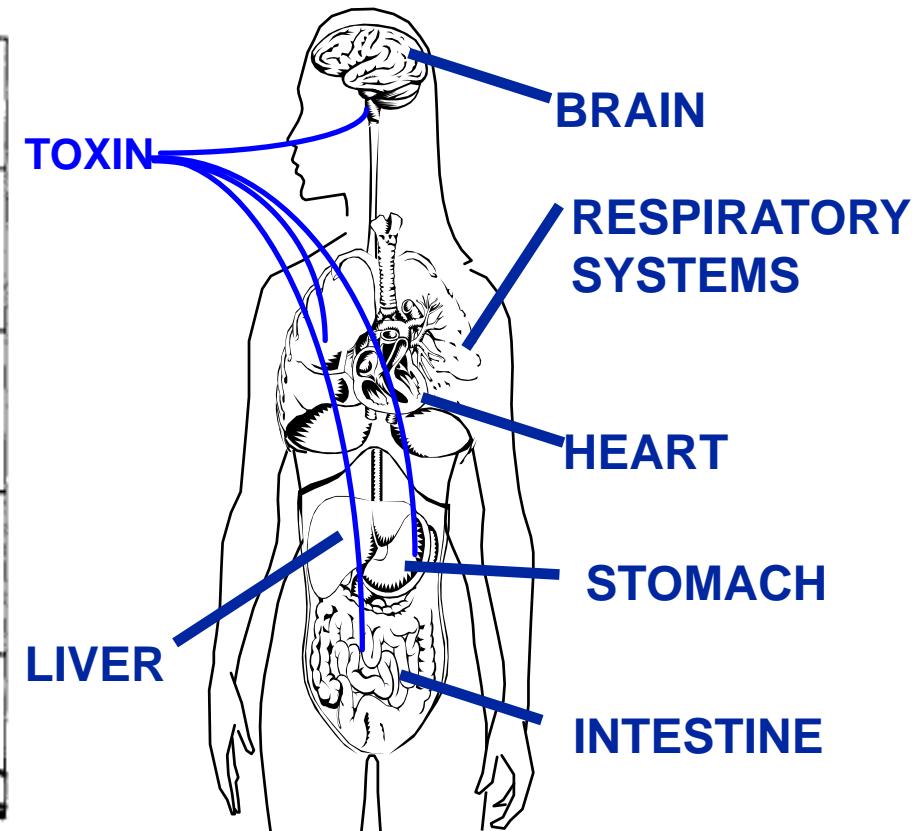
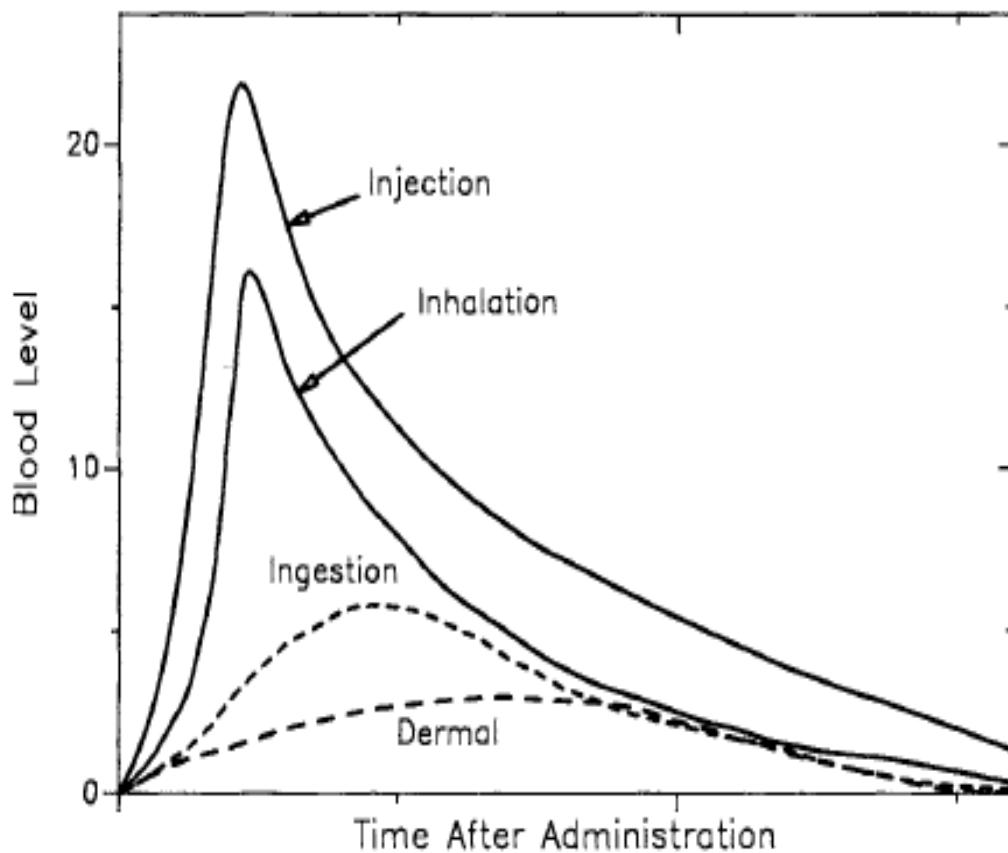
INGESTION

ABSORPTION

INJECTION

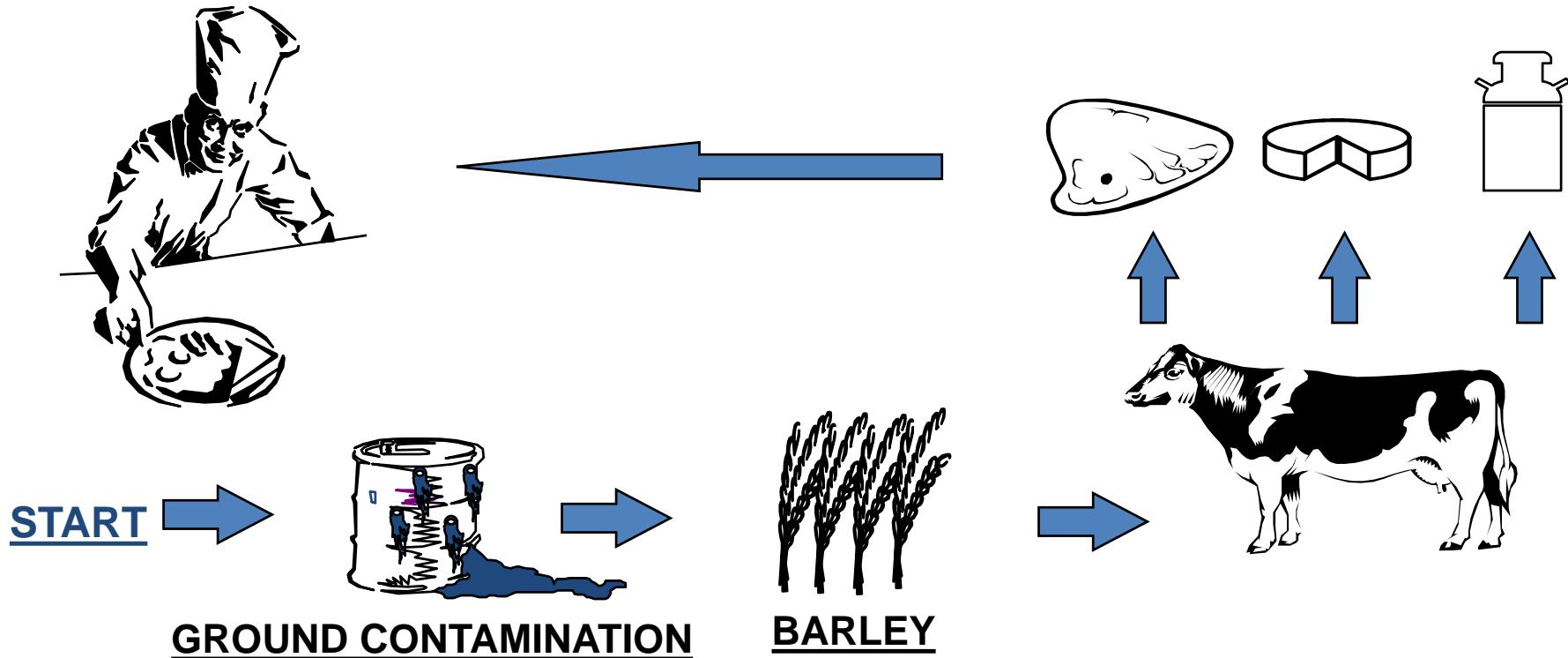


Toxic Blood Level: Route of Exposure



Food chain exposure

We Could Potentially Eat Toxic Food



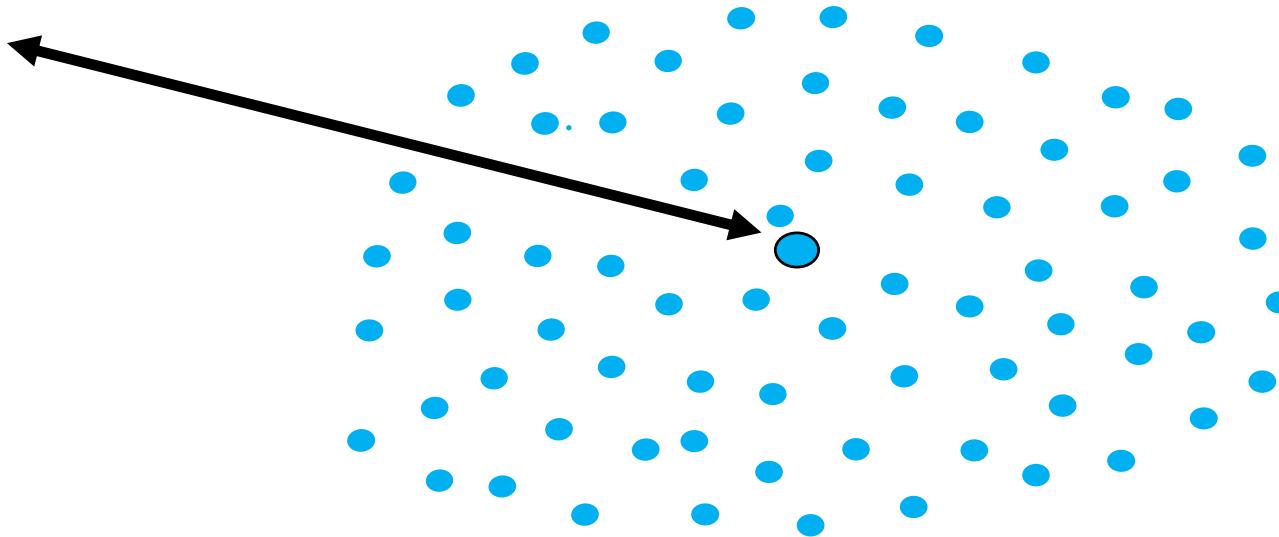
Measurement of Toxicity

- ✓ **PARTS PER MILLION - ppm**
- ✓ **PARTS PER BILLION - ppb**
- ✓ **PARTS PER TRILLION - ppt**
- ✓ **LETHAL DOSE - LD₅₀**
- ✓ **LETHAL CONCENTRATION - LC₅₀**
- ✓ **THRESHOLD LIMIT VALUE - TLV**

ppm



PARTS PER MILLION - ppm

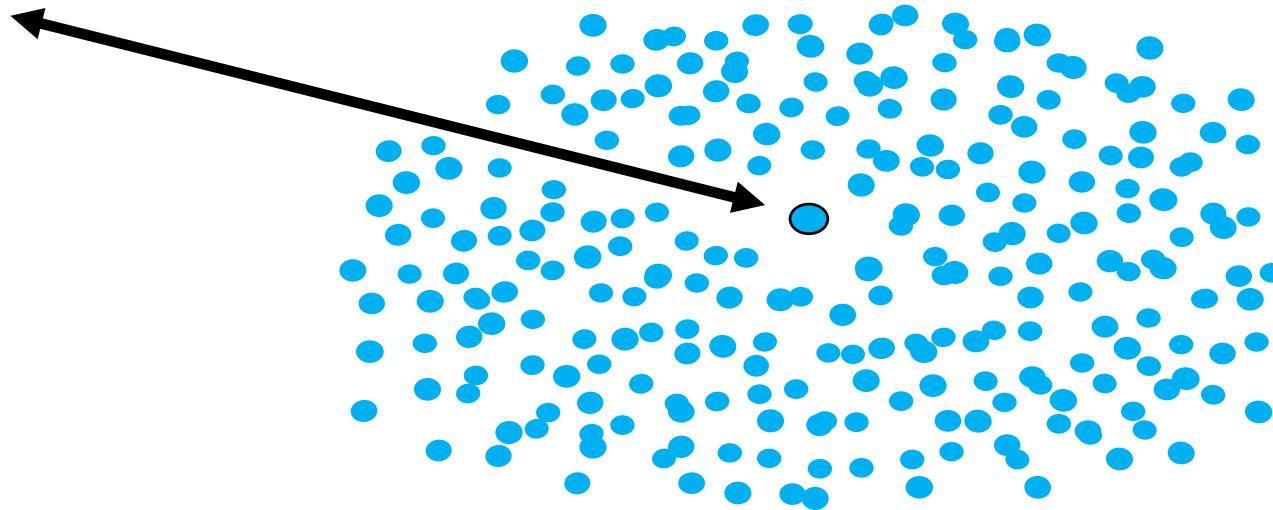


ONE PART IN ONE MILLION PARTS

ppb



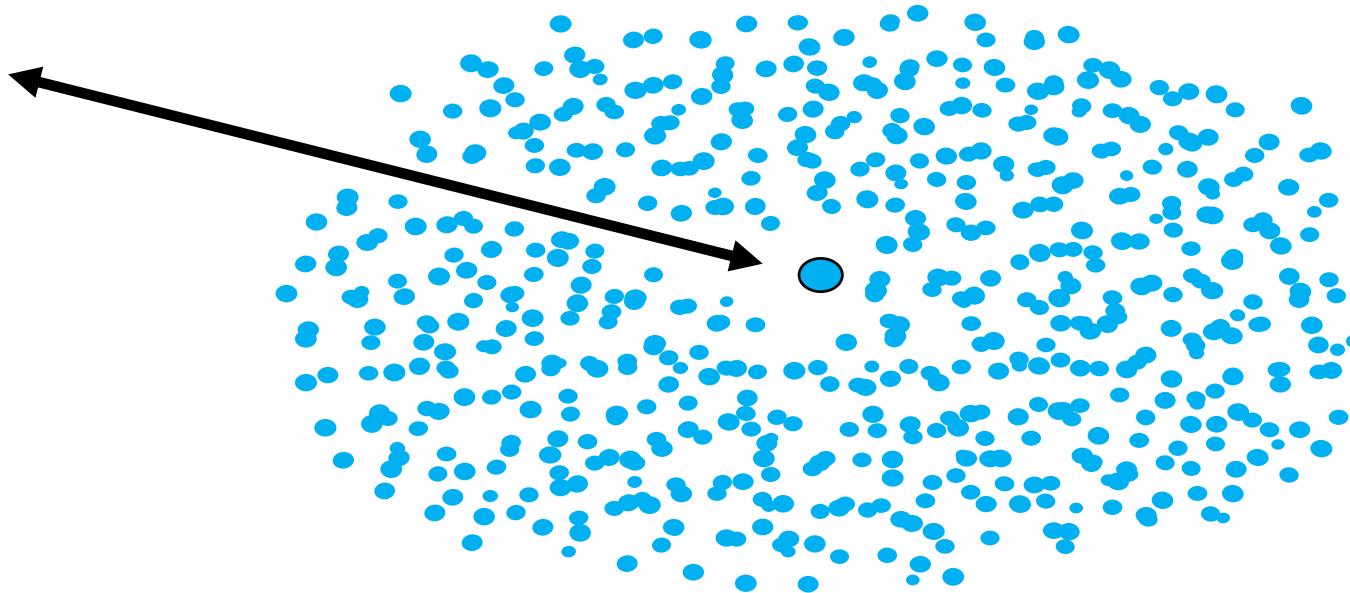
PARTS PER BILLION - ppb



ONE PART IN ONE BILLION PARTS



PARTS PER TRILLION - ppt



ONE PART IN ONE TRILLION PARTS

Lethal Dose - LD_{50}

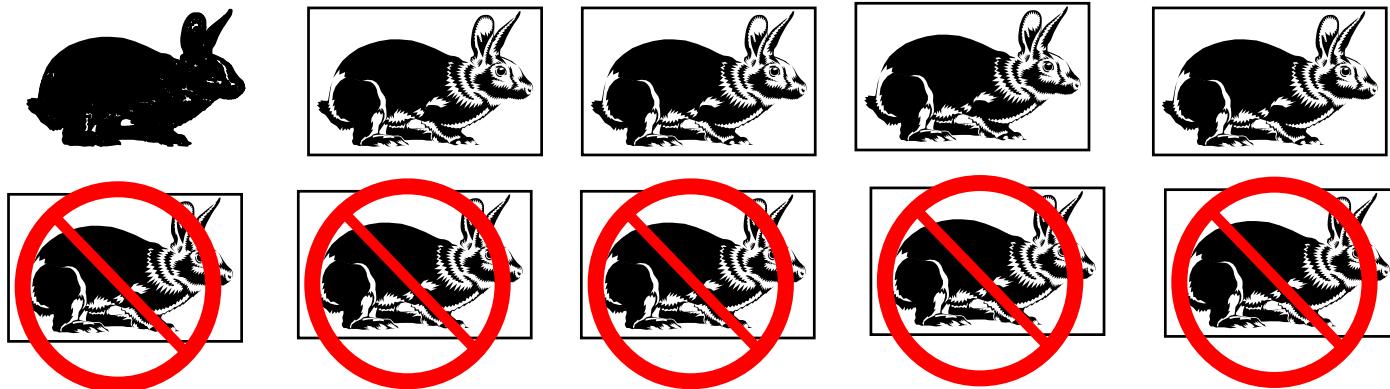
The LD_{50} is the dosage, when administrated to laboratory animals, results in 50% fatalities. The expression is made in milligrams of the substance administered per body weight of the animal expressed in kilograms (mg/kg). LD_{50} typically refers to dermal dosages.

When extrapolated to humans, the lethal dose of an average person who weighs w kilograms is $LD_{50} \times w$.



Lethal Concentration - LC₅₀

The LC₅₀ is the concentration of a material that, normally express as parts per million (ppm) by volume, that when administrated to laboratory animals, kill half of them during the period of exposure. LC₅₀ typically refers to airborne dosages.



Threshold Limit Value - TLV

The TLV is the upper limit of a toxin concentration to which an average healthy person may be repeatedly exposed on an all-day, everyday basis (8hrs/5days) without suffering adverse health effects. TLV is Typically used for workplace exposure determinations.

- Gaseous substances in air, are usually express in: parts per million (ppm).
- Fumes or mists in air, are expressed in: milligrams per cubic meter (mg/m³).
- TLV values are set by the American Conference of Governmental Industrial Hygienist (ACGIH).

TLV Types

- **TLV-TWA:** Time Weighted Average time weighted average concentration for a normal eight-hour work day
- **TLV-STEL:** Short Term Exposure Limit 15 minute time weighted average exposure repeated exposure no more than four times per 8 hour work shift.
- **TLV-C:** Ceiling Concentration that should not be exceeded, even instantaneously.

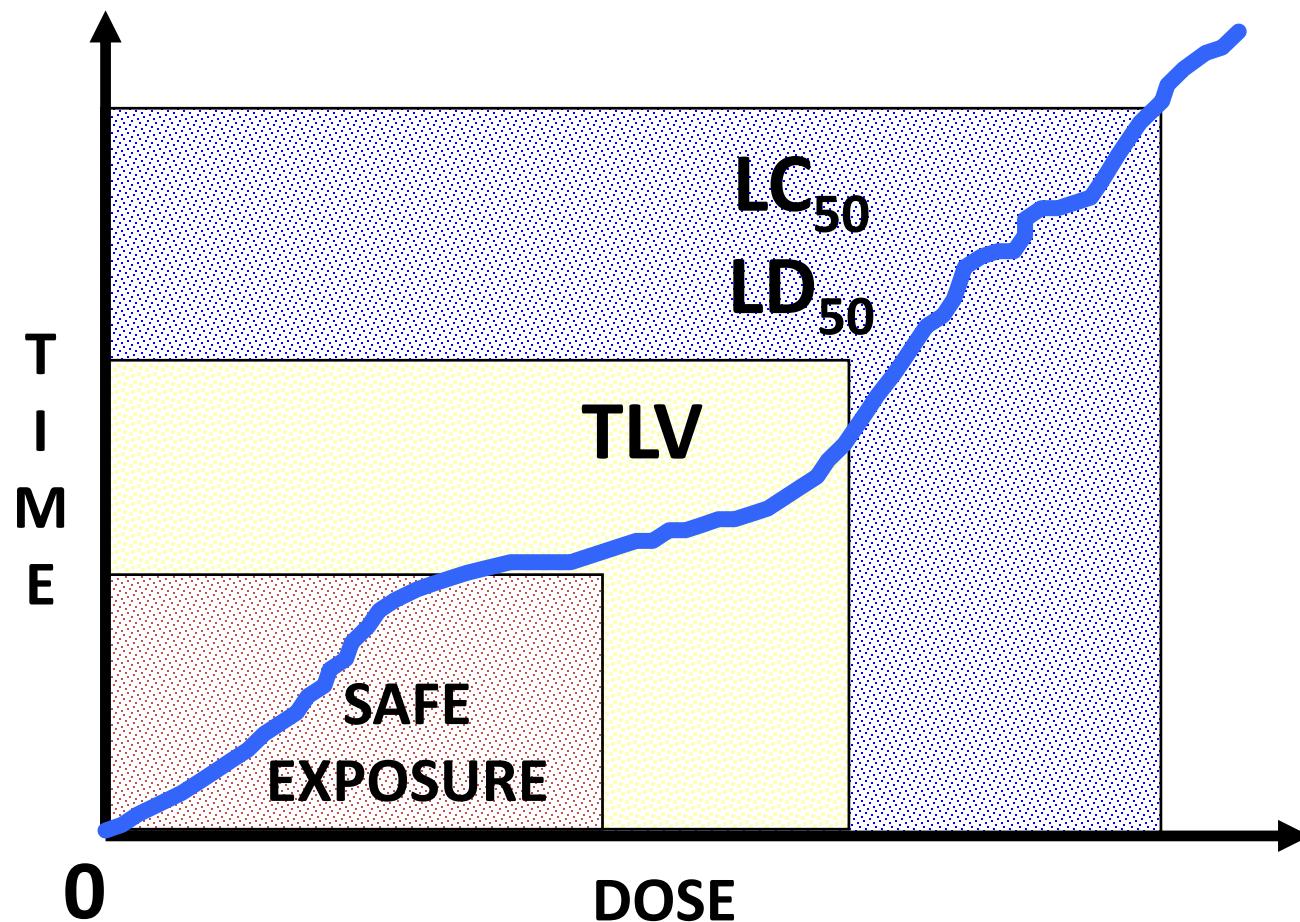
TLV – Example Values

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 $\frac{1}{4}$ of lower flammable limit.

Some toxicants have zero thresholds

Exposure Model



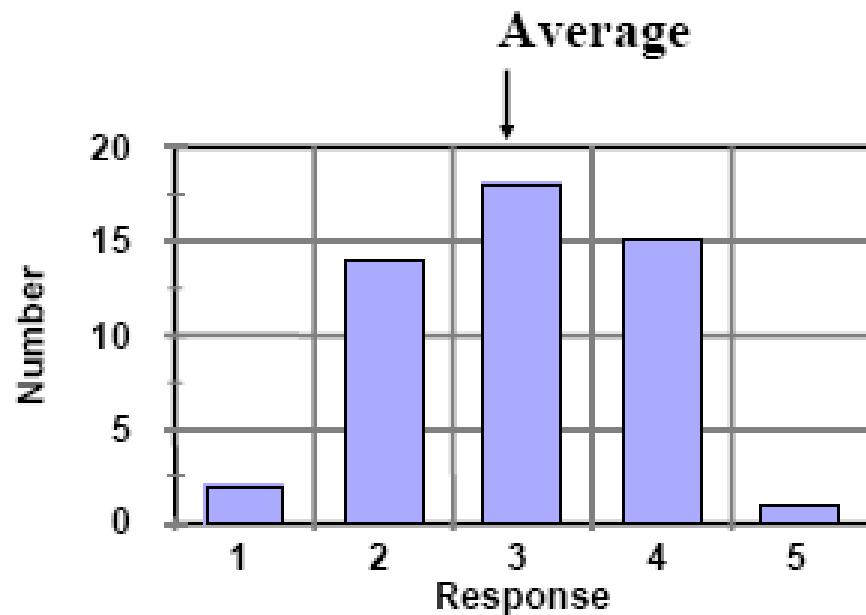
Toxicology Experiment with Rabbits!

- Start with 50 rabbits,
- Expose each to ***a fixed concentration***,
- Get a variety of responses,
- Determine response curve:

	Response	Number	Fraction
Least	1	2	0.04
	2	14	0.28
	3	18	0.36
	4	15	0.30
	5	1	0.02
		50	1.00

$$\begin{aligned}\text{Average} &= (1 \times 2 + 2 \times 14 + 3 \times 18 + 4 \times 15 + 5 \times 1) / 50 = 149 / 50 \\ &= 2.98\end{aligned}$$

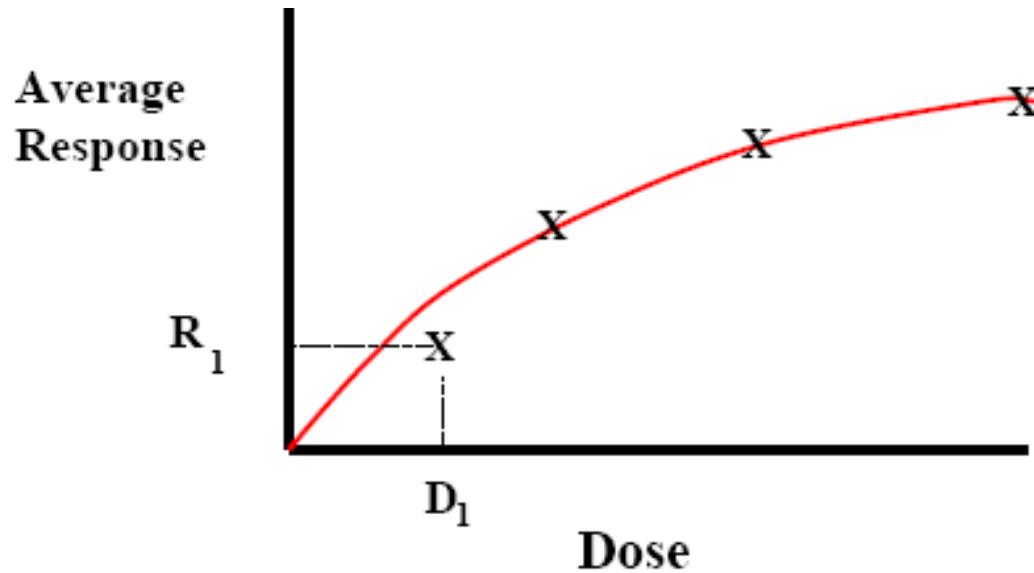
➤ Plot Bar Chart



➤ Repeat experiment at different doses

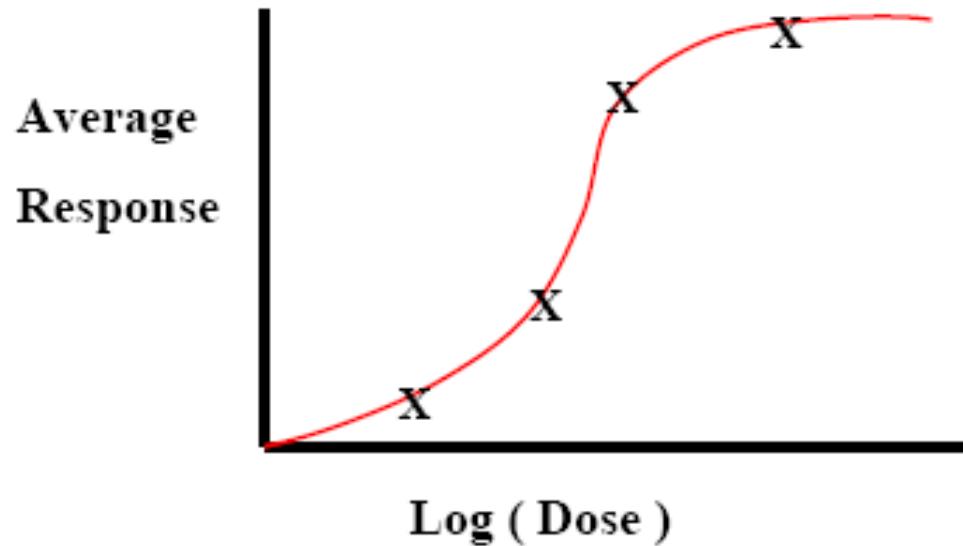
Dose	Average Response
D ₁	R ₁ = 2.98
D ₂	R ₂
D ₃	R ₃
D ₄	R ₄

➤ Plot Response vs. Dose



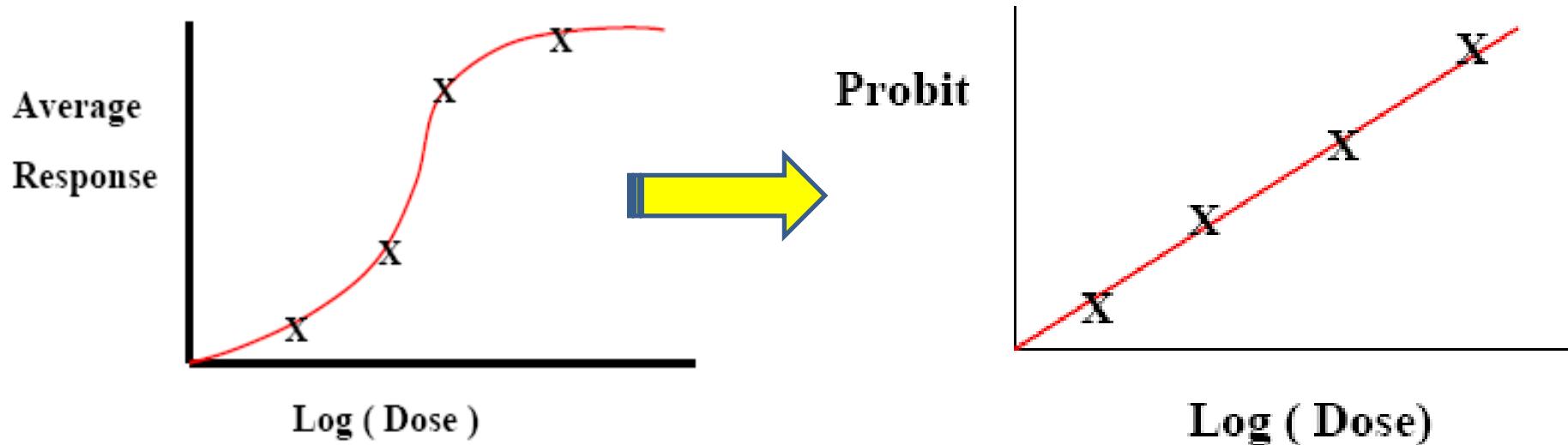
This form not very useful, particularly at low doses.

- Take the log of the dose.



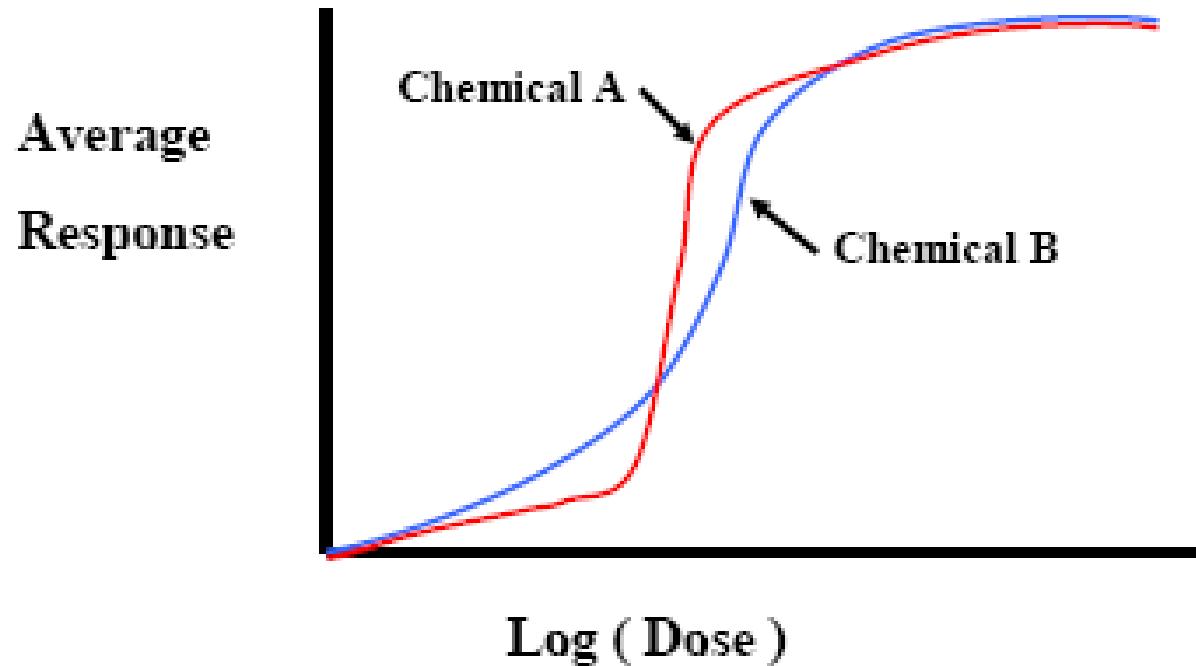
Get S-shaped curve - better at low dose values

➤ Transform into Probit (Probability Unit)



Change **S-shape** into straight line using a mathematical transformation called a **probit**.
See Table 2-4 in text for numerical conversion.

Relative Toxicity



The causative factor

$$Y = k_1 + k_2 \ln V.$$

Type of injury or damage	Causative variable	Probit parameters	
		k_1	k_2
Toxic release ²			
Ammonia deaths	$\Sigma C^{2.0}T$	-35.9	1.85
Carbon monoxide deaths	$\Sigma C^{1.0}T$	-37.98	3.7
Chlorine deaths	$\Sigma C^{2.0}T$	-8.29	0.92
Ethylene oxide deaths ³	$\Sigma C^{1.0}T$	-6.19	1.0
Hydrogen chloride deaths	$\Sigma C^{1.0}T$	-16.85	2.0
Nitrogen dioxide deaths	$\Sigma C^{2.0}T$	-13.79	1.4
Phosgene deaths	$\Sigma C^{1.0}T$	-19.27	3.69
Propylene oxide deaths	$\Sigma C^{2.0}T$	-7.42	0.51
Sulfur dioxide deaths	$\Sigma C^{1.0}T$	-15.67	1.0
Toluene	$\Sigma C^{2.5}T$	-6.79	0.41

%	0	1	2	3	4	5	6	7	8	9
0	—	2.67	2.95	3.12	3.25	3.36	3.45	3.52	3.59	3.66
10	3.72	3.77	3.82	3.87	3.92	3.96	4.01	4.05	4.08	4.12
20	4.16	4.19	4.23	4.26	4.29	4.33	4.36	4.39	4.42	4.45
30	4.48	4.50	4.53	4.56	4.59	4.61	4.64	4.67	4.69	4.72
40	4.75	4.77	4.80	4.82	4.85	4.87	4.90	4.92	4.95	4.97
50	5.00	5.03	5.05	5.08	5.10	5.13	5.15	5.18	5.20	5.23
60	5.25	5.28	5.31	5.33	5.36	5.39	5.41	5.44	5.47	5.50
70	5.52	5.55	5.58	5.61	5.64	5.67	5.71	5.74	5.77	5.81
80	5.84	5.88	5.92	5.95	5.99	6.04	6.08	6.13	6.18	6.23
90	6.28	6.34	6.41	6.48	6.55	6.64	6.75	6.88	7.05	7.33
%	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
99	7.33	7.37	7.41	7.46	7.51	7.58	7.65	7.75	7.88	8.09

¹D. J. Finney, *Probit Analysis*, (Cambridge: Cambridge University Press, 1971), p. 25. Reprinted by permission.

Example

Determine the concentration of ethylene oxide that will cause a 50% fatality rate if the exposure occurs for 30 min.

HW

2.2 2.8 2.18 2.19 2.24

2.25 2.26 2.27

Process Safety Engineering:

HAZOP- Introduction

Dr. Motasem Saidan

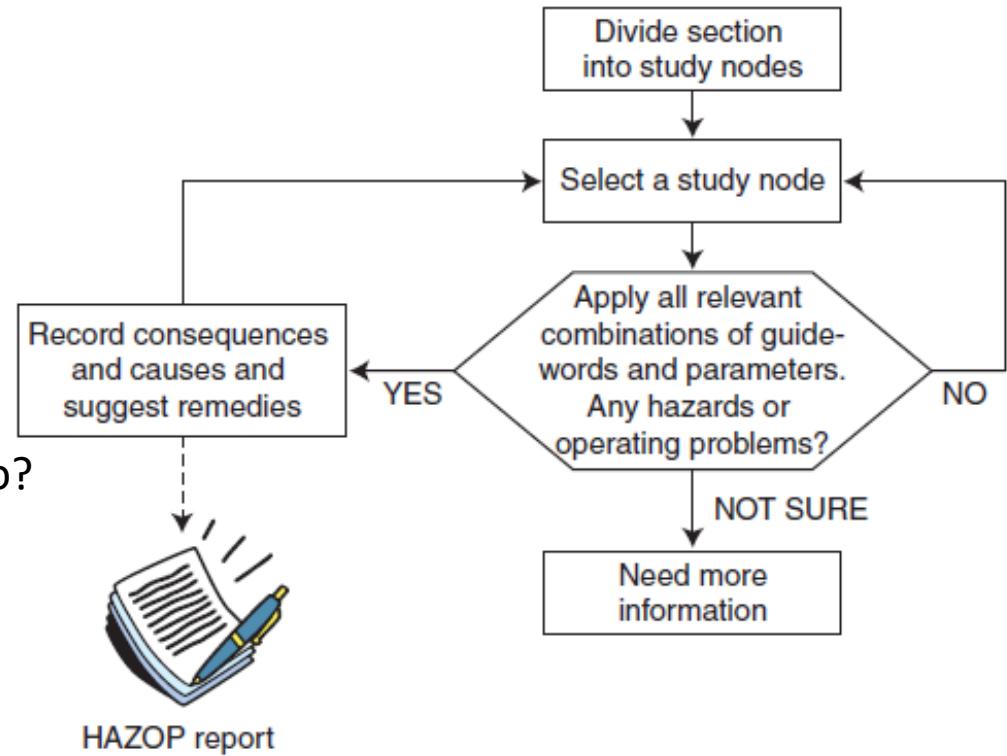
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HAZOP: Definitions

- A Hazard and Operability (HAZOP) study is a structured and systematic examination of a planned or existing process or operation in order to identify and evaluate problems that may represent risks to personnel or equipment, or prevent efficient operation.
- The HAZOP technique was initially developed to analyze chemical process systems, but has later been extended to other types of systems and also to complex operations and to software systems.
- A HAZOP is a qualitative technique based on guide-words and is carried out by a multi-disciplinary team (HAZOP team) during a set of meetings.

HAZOP procedure

1. Divide the system into sections (i.e., reactor, storage)
2. Choose a study node (i.e., line, vessel, pump, operating instruction)
3. Describe the design intent
4. Select a process parameter
5. Apply a guide-word
6. Determine cause(s)
7. Evaluate consequences/problems
8. Recommend action: What? When? Who?
9. Record information
10. Repeat procedure (from step 2)



- **Node**

A node is a specific location in the process in which (the deviations of) the design/process intent are evaluated. Examples might be: separators, heat exchangers, scrubbers, pumps, compressors, and interconnecting pipes with equipment.

- **Design Intent**

The design intent is a description of how the process is expected to behave at the node; this is qualitatively described as an activity (e.g., feed, reaction, sedimentation) and/or quantitatively in the process parameters, like temperature, flow rate, pressure, composition, etc.

- **Deviation**

A deviation is a way in which the process conditions may depart from their design/process intent.

- **Parameter**

The relevant parameter for the condition(s) of the process e.g. pressure, temperature, composition).

- **Guideword**

A short word to create the imagination of a deviation of the design/process intent. The most commonly used set of guide-words is: no, more, less, as well as, part of, other than, and reverse. In addition, guidewords like too early, too late, instead of, are used; the latter mainly for batch-like processes. The guidewords are applied, in turn, to all the parameters, in order to identify unexpected and yet credible deviations from the design/process intent.

Guide-word + Parameter → Deviation

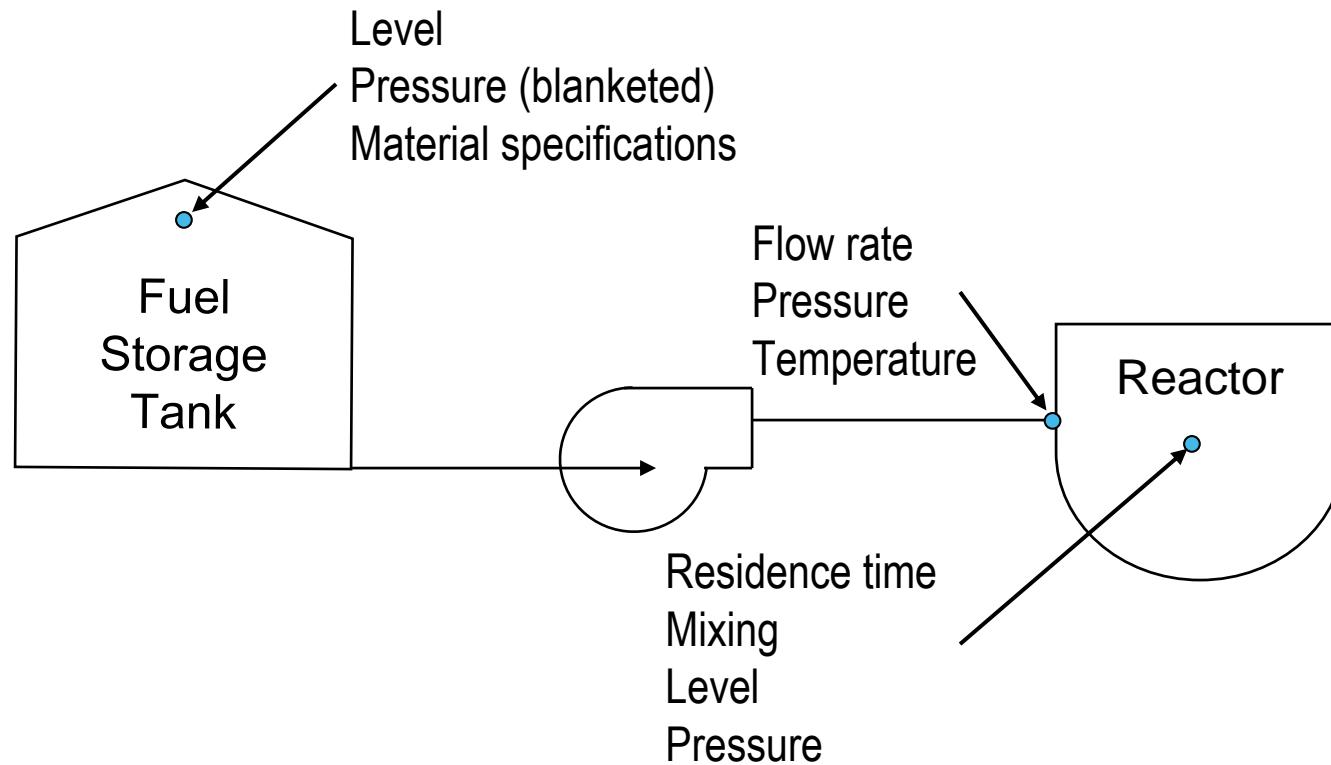
The basic HAZOP guide-words are:

Guide-word	Meaning	Example
No (not, none)	None of the design intent is achieved	No flow when production is expected
More (more of, higher)	Quantitative increase in a parameter	Higher temperature than designed
Less (less of, lower)	Quantitative decrease in a parameter	Lower pressure than normal
As well as (more than)	An additional activity occurs	Other valves closed at the same time (logic fault or human error)
Part of	Only some of the design intention is achieved	Only part of the system is shut down
Reverse	Logical opposite of the design intention occurs	Back-flow when the system shuts down
Other than (other)	Complete substitution - another activity takes place	Liquids in the gas piping

HAZOP Deviations Guide

Design Intent Example	NO / NONE	MORE OF	LESS OF
“Contain the working inventory of liquid RM-12”	Containment lost Procedure step skipped No [function] No transfer No agitation No reaction	Procedure started too late Procedure done too long Too much [function] Too much transferred Too much agitation High [controlled variable] High reaction rate High flow rate High pressure High temperature	Procedure started too soon Procedure stopped too soon Not enough [function] Not enough transferred Not enough agitation Low [controlled variable] Low reaction rate Low flow rate Low pressure Low temperature
PART OF	AS WELL AS	REVERSE	OTHER THAN
Part of procedure step skipped	Extra step performed		Wrong procedure performed
Part of [function] achieved	Extra [function] Transfer from more than one source Transfer to more than one destination	Steps done in wrong order Reverse [function] Reverse flow Reverse mixing	Wrong [function] achieved Transfer from wrong source Transfer to wrong destination
Part of [composition] Component missing Phase missing Catalyst deactivated	Extra [composition] Extra phase present Impurities; dilution		Maintenance/test/sampling at wrong time/location

HAZOP Focus



HAZOP Prerequisites

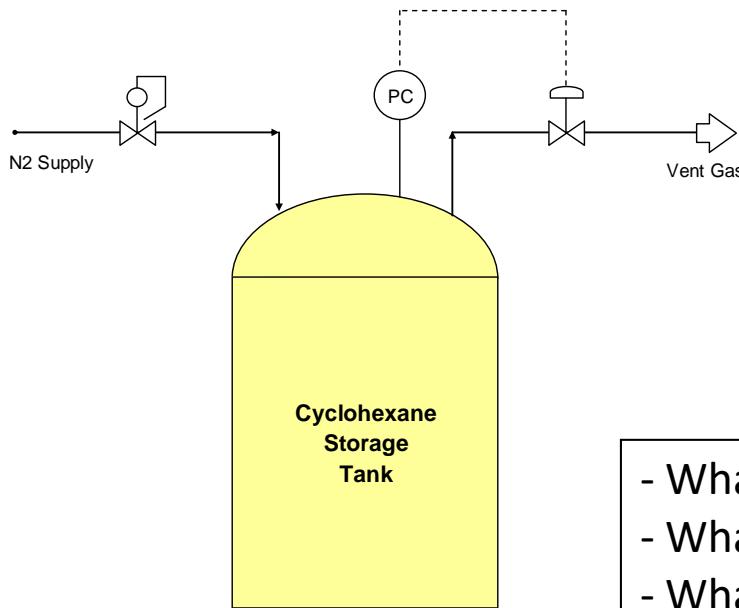
As a basis for the HAZOP study the following information should be available:

- ✓ Process flow diagrams
- ✓ Piping and instrumentation diagrams (P&IDs)
- ✓ Layout diagrams
- ✓ Material safety data sheets
- ✓ Provisional operating instructions
- ✓ Heat and material balances
- ✓ Equipment data sheets Start-up and emergency shut-down procedures

Process Hazard Analysis

- Process Hazard Analysis (PHA) is a technique for determining the RISK of operating a process or unit operation.
- PHAs are required by law for process handling threshold quantities for certain listed Highly Hazardous Chemicals (HHC) or flammables.
- Approved techniques for conducting PHAs:
 - HAZOP (Hazard and Operability)
 - What If?
 - FMEA (Failure Mode and Effects Analysis)
- In general, a PHA is conducted as a series of facilitated, team brainstorming sessions to systematically analyze the process.

Risk Assessment Example

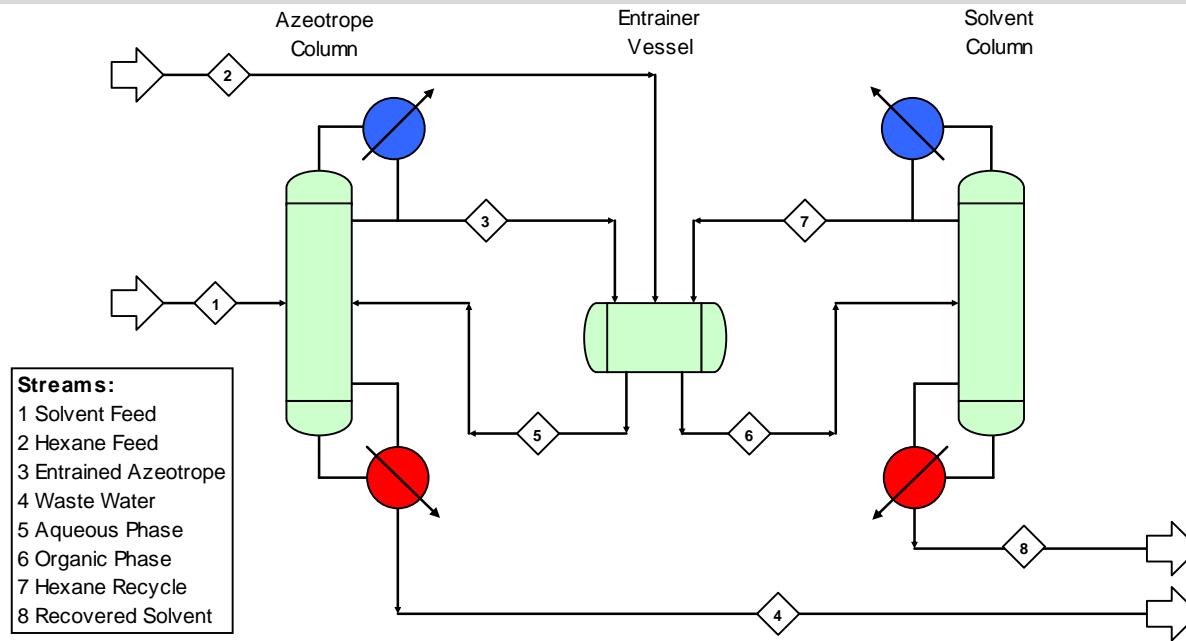


- Consider a low design pressure API storage tank filled with cyclohexane.
- Assume that the storage tank is equipped with a “pad/de-pad” vent system to control pressure.

- What hazard scenarios might occur from this system?
- What are the consequences of these scenarios?
- What Safeguards might we choose to mitigate the risk?

What If...?	Initiating Cause	Consequence	Safeguards
1. There is High Pressure in the Cyclohexane Storage Tank?	1.1 Failure of the pressure regulator on nitrogen supply line.	1.1 Potential for pressure in tank to rise due to influx of nitrogen through failed regulator. Potential to exceed design pressure of storage tank. Potential tank leak or rupture leading to spill of a flammable liquid. Potential fire should an ignition source be present. Potential personnel injury should exposure occur.	1. Pressure relief vent (PRV) sized to relieve overpressure due to this scenario. 2. Pressure transmitter with high alarm set to indicate high pressure in Cyclohexane Storage Tank.

Example



What If...?	Initiating Cause	Consequence
1. There is higher pressure in the Entrainment Vessel?	1.1 External fire in the process area.	1.1 Potential increased temperature and pressure leading to possible vessel leak or rupture. Potential release of flammable material to the atmosphere. Potential personnel injury due to exposure.
	1.2 Pressure regulator for inert gas pad fails open.	1.2 Potential for vessel pressure to increase up to the inert gas supply pressure. Potential vessel leak or rupture leading to release of flammable material to the atmosphere. Potential personnel injury due to exposure.
2. There is higher level in the Entrainor Vessel?	2.1 Vessel level transmitter fails and indicates lower than actual volume.	2.1 Potential to overfill vessel with cyclohexane. Potential to flood vent line with liquid leading to flammable liquid reaching the vent gas incinerator. Potential to overwhelm incinerator leading to possible explosion. Potential personnel injury due to exposure.

Consider what types of safeguards would be required to mitigate the Process Risk due to these scenarios.

Prevention of Fires & Explosions

Dr. Motasem Saidan

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Design Criteria

1. Prevent flammable mixtures.
2. Reduce ignition sources.

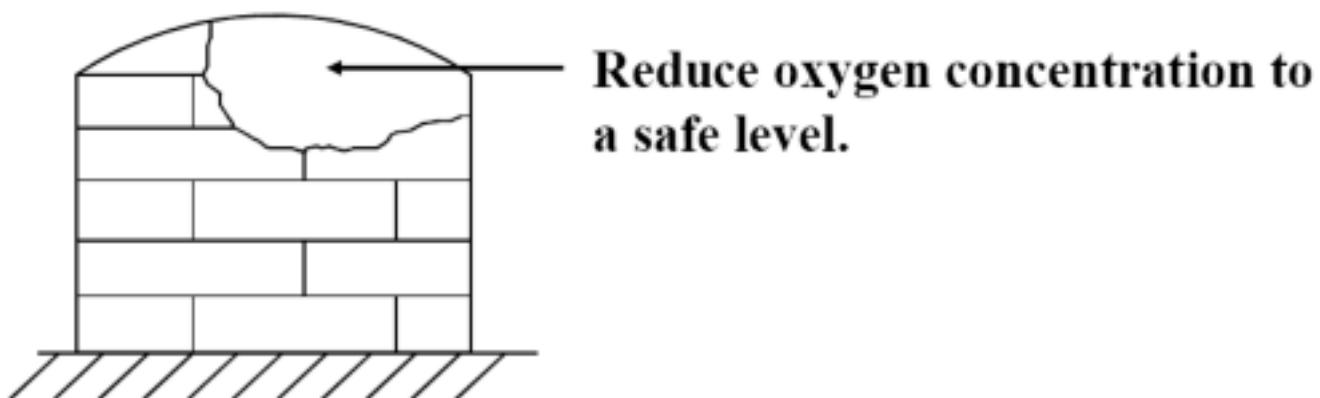
- Need to remember inherently safer design, that is, to reduce inventories, substitute with less dangerous materials, and reduce operating T and P.

Inerting and Purgning

- Inerting is the process of adding an inert gas to a combustible mixture to reduce the concentration of oxygen below the limiting oxygen concentration (LOC).

Purpose:

To reduce the oxygen or fuel concentration to below a target value using an inert gas. Can use nitrogen, carbon dioxide, others. Nitrogen is the most common.



Inerting Procedures

1. Vacuum Purge - evacuate and replace with inert.
2. Pressure Purge - pressurize with inert, then relieve pressure.
3. Sweep Purge - continuous flow of inert.
4. Siphon Purge - fill with liquid, then drain and replace liquid with inert.
5. Combined: pressure and vacuum purge, others.

Vacuum Purge

Inerting – Vacuum Purging

Most common procedure for inerting reactors Steps

1. Draw a vacuum
2. Relieve the vacuum with an inert gas
3. Repeat Steps 1 and 2 until the desired oxidant level is

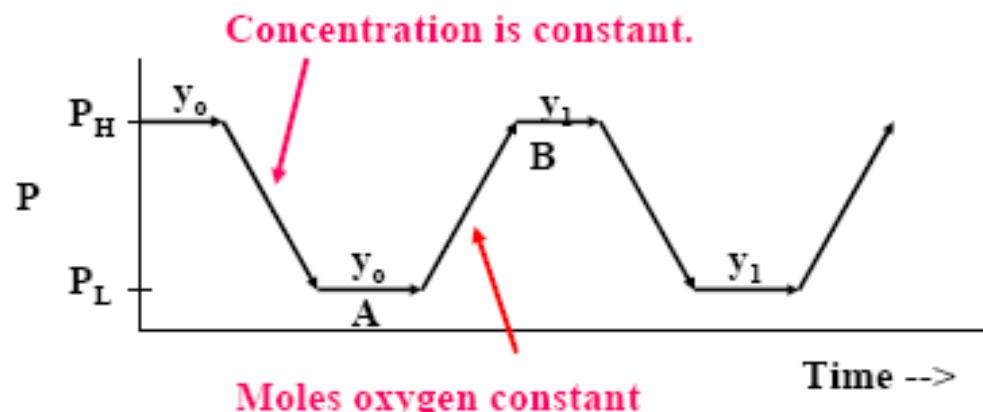
$$\text{At A: } n_{O_2} = y_o \left(\frac{P_L V}{R_T T} \right)$$

$$\text{At B: } n_{TOT} = \frac{P_H V}{R_T T}$$

$$y_1 = \frac{n_{O_2}}{n_{TOT}} = \frac{y_o \left(\frac{P_L V}{R_T T} \right)}{\frac{P_H V}{R_T T}} = y_o \left(\frac{P_L}{P_H} \right)$$

$$\text{At end of jth cycle: } y_j = y_o \left(\frac{P_L}{P_H} \right)^j \quad \text{Eq. (7-6)}$$

$$\text{Total nitrogen used: } \Delta n_{N_2} = j(P_H - P_L) \frac{V}{R_T T} \quad \text{Eq. (7-7)}$$



1. Pure nitrogen used.
2. Vessel is well mixed (not a bad assumption for gases).
3. Ideal gas law.

Example 7-1

Use a vacuum purging technique to reduce the oxygen concentration within a 1000-gal vessel to 1 ppm. Determine the number of purges required and the total nitrogen used. The temperature is 75°F, and the vessel is originally charged with air under ambient conditions. A vacuum pump is used that reaches 20 mm Hg absolute, and the vacuum is subsequently relieved with pure nitrogen until the pressure returns to 1 atm absolute.

Solution

The concentration of oxygen at the initial and final states is

$$y_o = 0.21 \text{ lb-mol O}_2/\text{total mol},$$

$$y_f = 1 \text{ ppm} = 1 \times 10^{-6} \text{ lb-mol O}_2/\text{total mol}.$$

The required number of cycles is computed using Equation 7-6:

$$y_j = y_o \left(\frac{P_L}{P_H} \right)^j,$$

$$\ln \left(\frac{y_j}{y_o} \right) = j \ln \left(\frac{P_L}{P_H} \right),$$

$$j = \frac{\ln(10^{-6}/0.21)}{\ln(20 \text{ mm Hg}/760 \text{ mm Hg})} = 3.37.$$

The total nitrogen used is determined from Equation 7-7. The low pressure P_L is

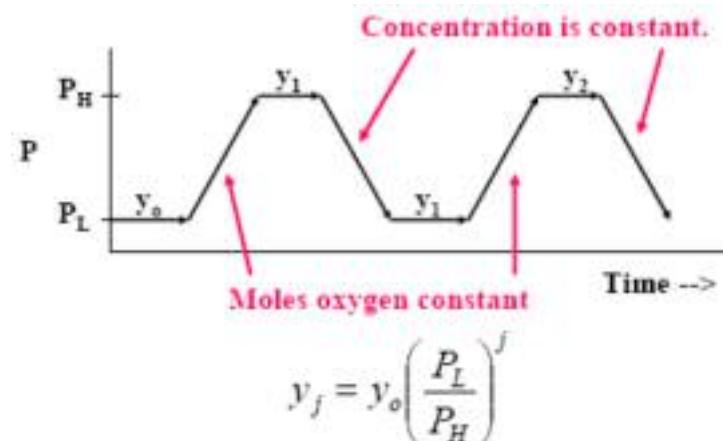
$$P_L = \left(\frac{20 \text{ mm Hg}}{760 \text{ mm Hg}} \right) (14.7 \text{ psia}) = 0.387 \text{ psia},$$

$$\begin{aligned} \Delta n_{N_2} &= j(P_H - P_L) \frac{V}{R_g T} \\ &= 4(14.7 - 0.387) \text{ psia} \frac{(1000 \text{ gal})(1 \text{ ft}^3/7.48 \text{ gal})}{(10.73 \text{ psia ft}^3/\text{lb-mol}^\circ\text{R})(75 + 460)^\circ\text{R}} \\ &= 1.33 \text{ lb-mol} = 37.2 \text{ lb of nitrogen.} \end{aligned}$$

Inerting – Pressure Purging

Most common procedure for inerting reactors Steps

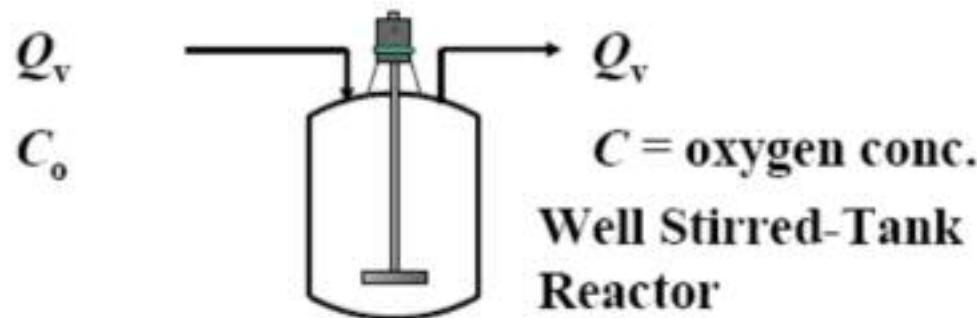
1. Add inert gas under pressure
2. Vent down to atmospheric pressure
3. Repeat Steps 1 and 2 until the desired oxidant level is reached



✓ Faster than vacuum purge, but uses more nitrogen.

Sweep Purging

- ‘In one end, and out the other’
- For equipment not rated for pressure, vacuum
- Requires large quantities of inert gas



Mass Balance on Oxygen: $V \frac{dC}{dt} = C_o Q_v - C Q_v$

Solution is: $Q_v t = V \ln \left[\frac{C_1 - C_o}{C_2 - C_o} \right] = \text{Total Nitrogen Volume}$

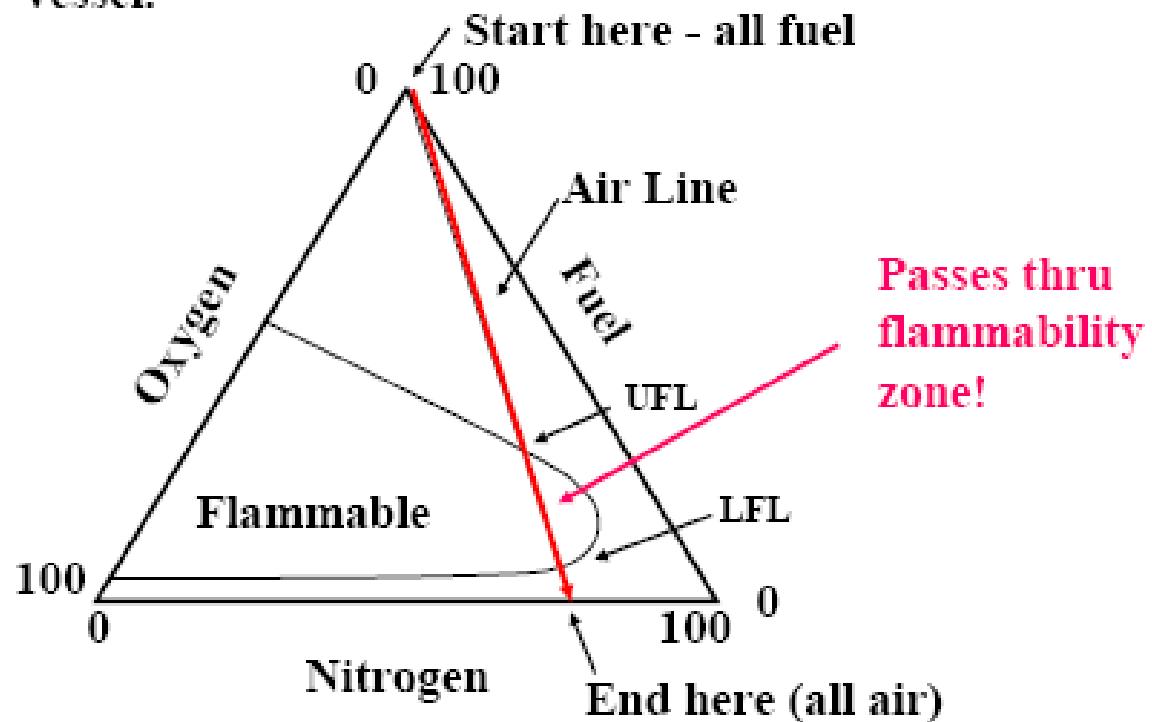
If $C_o = 0$: $Q_v t = V \ln \left[\frac{C_1}{C_2} \right]$ **Uses lots of inert!!**
 Assumes well-stirred

Using the Flammability Diagram

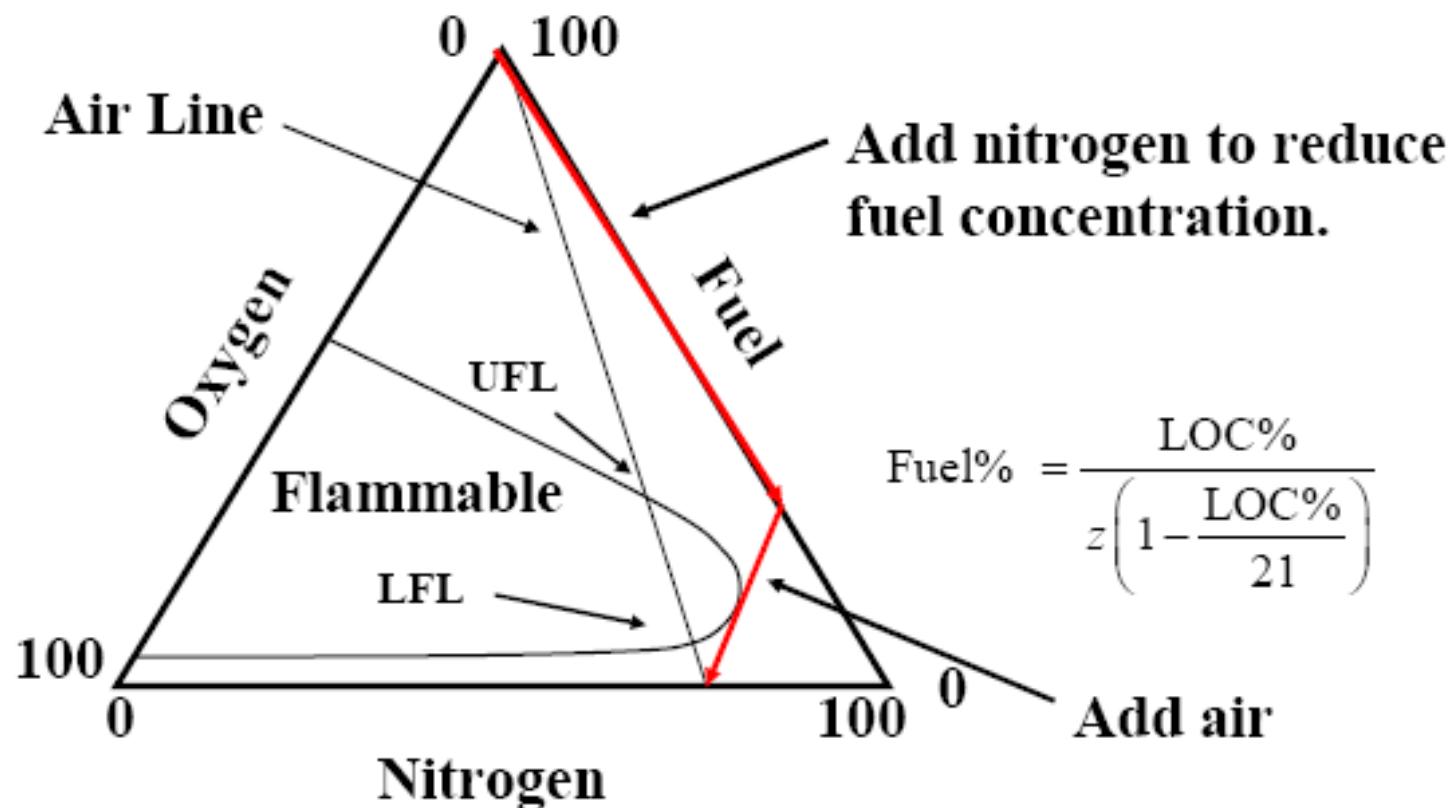
Taking a Vessel Out of Service

- Out-Of-Service Fuel Concentrations (OSFCs)

Depressurize vessel to atmospheric, then blow air into vessel.



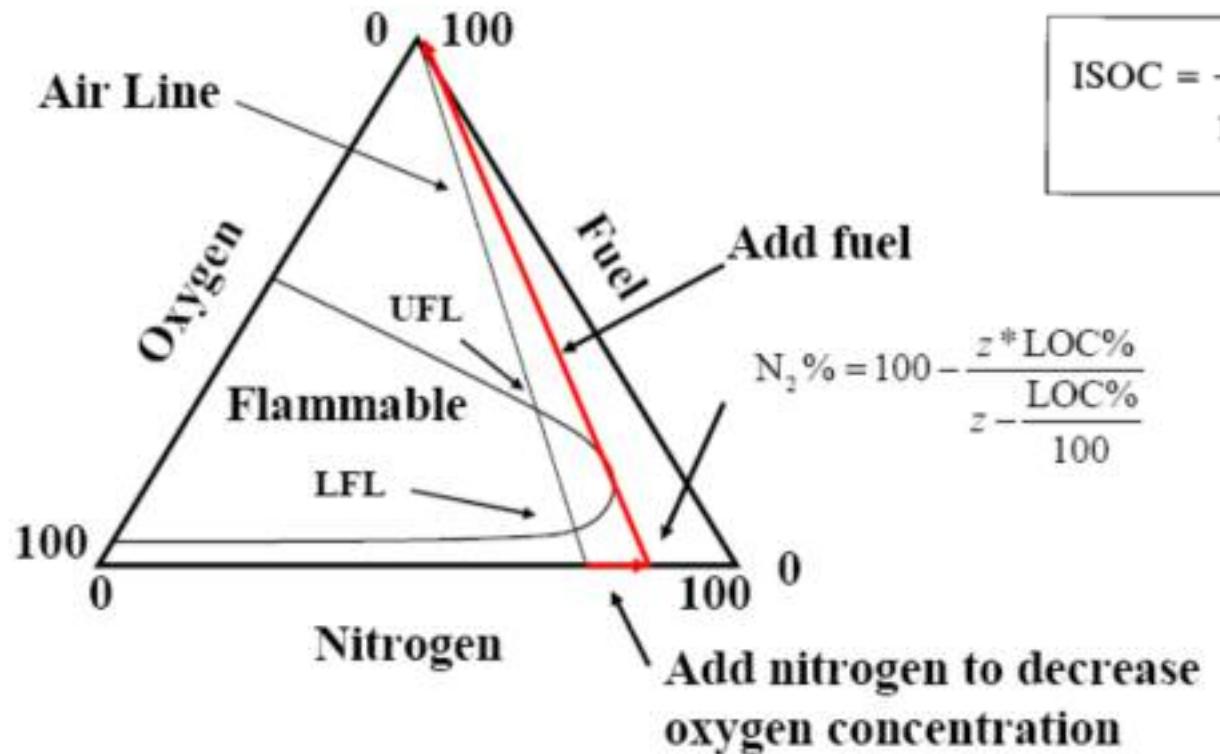
(1) Fuel + (z) Oxygen \rightarrow Products



Placing a vessel into service

The in-service oxygen concentration (ISOC) represents the maximum oxygen concentration that just avoids the flammability zone, with a small margin of safety.

(1) Fuel + (z) Oxygen \rightarrow Products



HW

7.5

7.7



Process Safety Engineering: Fires & Explosions

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Fires & Explosions

Accident Statistics



Evaluation of the largest chemical plant accidents:

- Most of the large accidents are due to fires and explosions.

Introduction

The distinction between *fires* and *explosions* is the rate of energy release

FIRE: release energy slowly, rapid exothermic, oxidation, with flame

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

Fires can also result from explosions, and explosions can result from fires

EFFECTS

- injuries / casualties
- property losses
- process interruption

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

REQUIRED KNOWLEDGE FOR PREVENTION

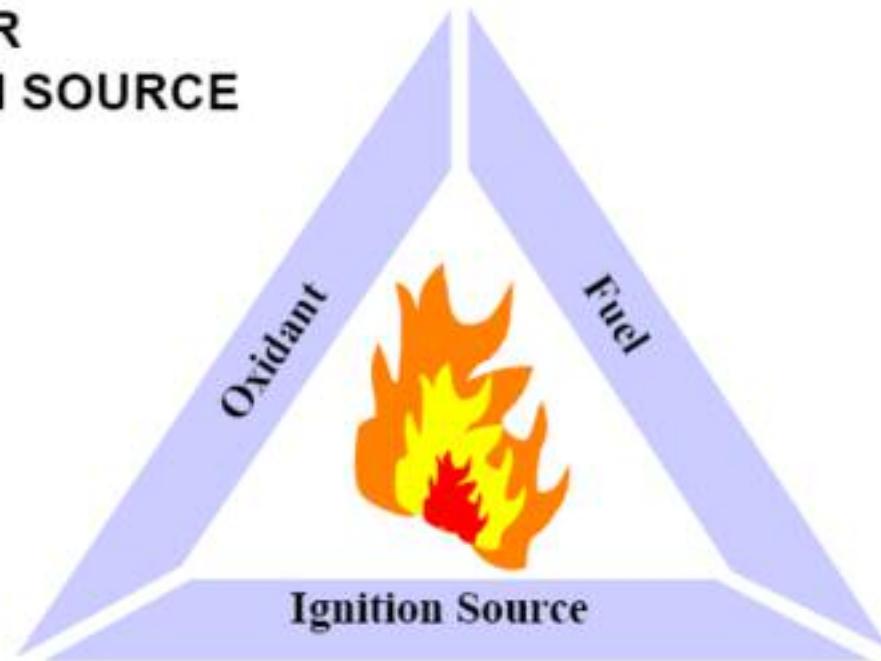
- material properties
- nature of fire and explosion process
- procedures to reduce hazards (Ch. 7)

Fire Triangle

- *Combustion or fire*: Combustion or fire is a chemical reaction.

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 , HCl ₃ O
Solids:	Peroxides, NH ₄ , NO ₂

IGNITION SOURCE

Sparks, Flames, Static Electricity, Heat
--

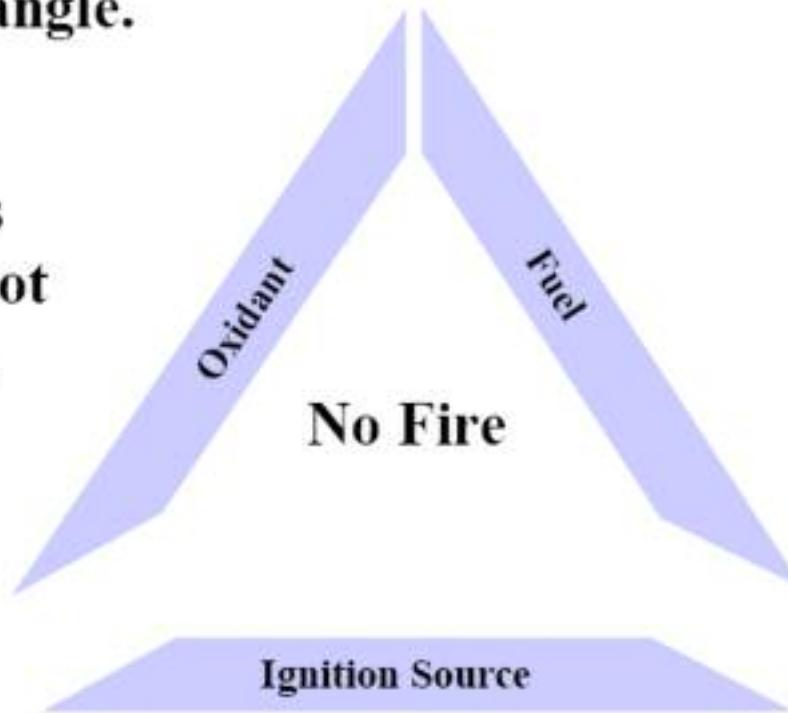
- * Liquids are volatized and solids decomposed prior to their combustion in the vapor phase

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.

Texas Fertilizer Plant Blast

"So this is what has happened, that the fire has got out of control and basically heated up the vessel. What seems to me to be wrong about this whole incident is that instead of evacuating the plant, when the fire establishment could not control it, there seemed to be brought up more and more fire people and they were putting them at risk. I don't know, it sounds as if there have been a lot of deaths among fire people"

Waco, Texas early April 18, 2013



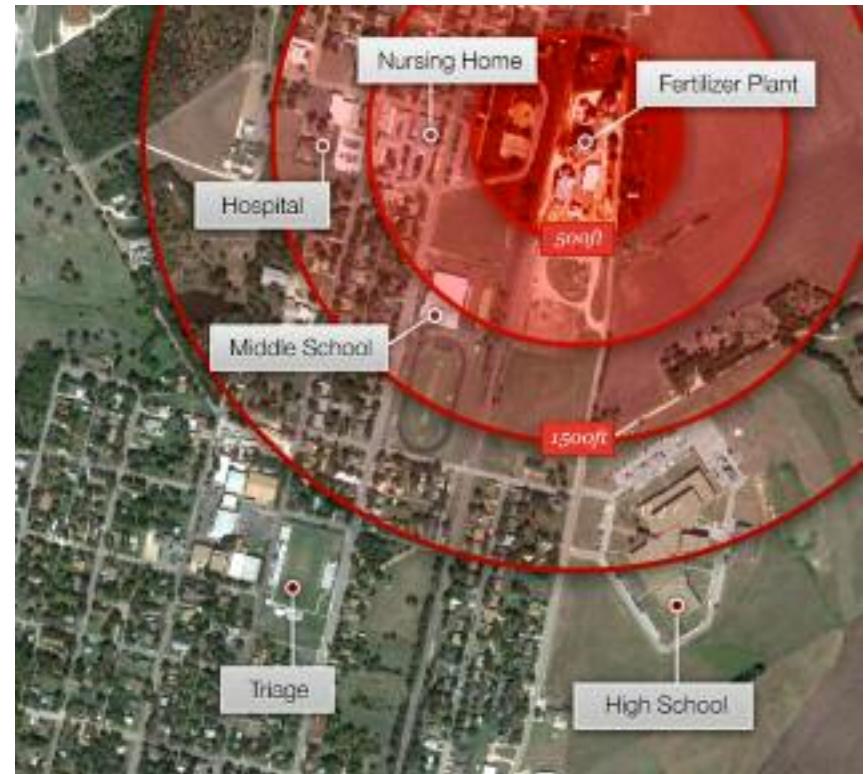
The fertilizer plant indicated the worst case scenario would be a 10-minute release of ammonia gas that would not harm anyone.

West Fertilizer told the Environmental Protection Agency that it presented no risk of fire or explosion, despite having 54,000 pounds of anhydrous ammonia

The chief safety expert at the Russia's Nitrogen Industry Institute, Igor Solovyev, reminded that there haven't been any serious accidents at fertilizer plants in half a century and that serious violations of safety arrangements must have led to the Texas explosion.

Texas Fertilizer Plant Blast

West Chemical and Fertilizer was fined \$2,300 in March 2006 for failing to update a risk management plan and for having poor employee-training records and no formal written maintenance program, according to the EPA. The company later certified it had corrected the deficiencies, the EPA said





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.

Combustion Behavior – Methane



Methane burns mostly within vessel, flame shoots out of vessel.

Combustion Behavior – Dusts



Much of the dust burns outside of the chamber

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.

Flammability limits: Vapor-air mixtures will ignite and burn only over a well-specified range of compositions.

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.
 - The flash point generally increases with increasing pressure.
- **Auto-Ignition Temperature (AIT):** Temperature above which adequate energy is available in the environment to provide an ignition source.

Definitions - 3

- **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 Conc. (MSOC) Others

! Read the definitions at both page 227 and 228

Typical Values - 1

	LFL	UFL	
Methane:	5.3%	15%	
Propane:	2.2%	9.5%	See Appendix B
Butane:	1.9%	8.5%	
Hydrogen:	4.0%	75%	

Flash Point Temp. (deg C)

Methanol:	12.2
Benzene:	-11.1
Gasoline:	-43

Typical Values - 2

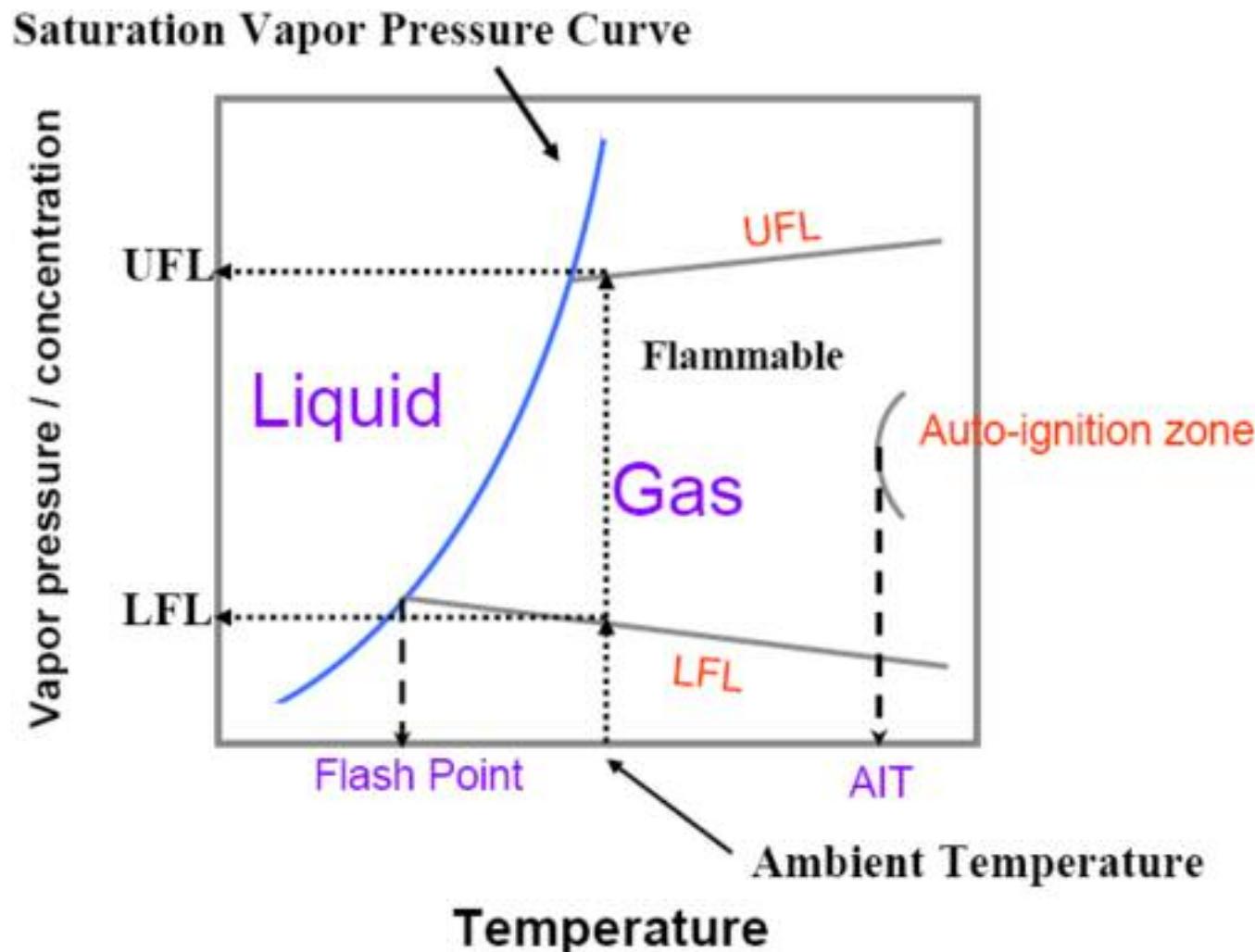
	<u>AIT (deg. C)</u>	
Methane:	632	
Methanol:	574	Great variability in reported AIT values!
Toluene:	810	Use lowest value.

	<u>LOC (Vol. % Oxygen)</u>
Methane:	12%
Ethane:	11%
Hydrogen:	5%

Appendix B

Table 6-2

Flammability Relationships



Minimum Ignition Energies

What: Energy required to ignite a flammable mixture.

Typical Values: (wide variation expected)

Vapors: 0.25 mJ

Dusts: about 10 mJ

➤ Static spark that you can feel:

about 20 mJ

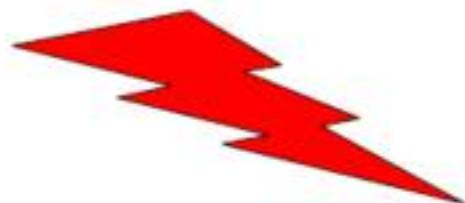
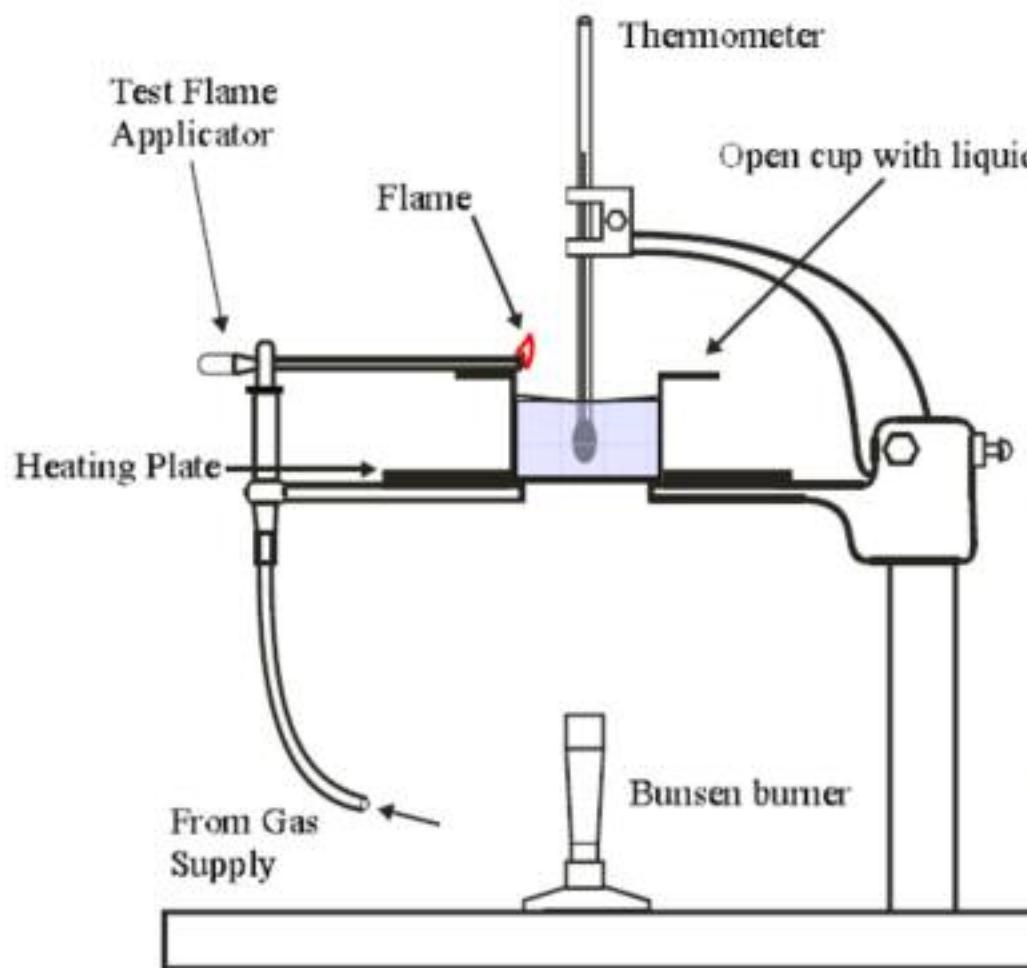


TABLE 6-3 IGNITION SOURCES OF MAJOR FIRES¹

Electrical (wiring of motors)	23%
Smoking	18%
Friction (bearings or broken parts)	10%
Overheated materials (abnormally high temperatures)	8%
Hot surfaces (heat from boilers, lamps, etc.)	7%
Burner flames (improper use of torches, etc.)	7%
Combustion sparks (sparks and embers)	5%
Spontaneous ignition (rubbish, etc.)	4%
Cutting and welding (sparks, arcs, heat, etc.)	4%
Exposure (fires jumping into new areas)	3%
Incendiaryism (fires maliciously set)	3%
Mechanical sparks (grinders, crushers, etc.)	2%
Molten substances (hot spills)	2%
Chemical action (processes not in control)	1%
Static sparks (release of accumulated energy)	1%
Lightning (where lightning rods are not used)	1%
Miscellaneous	1%

¹Accident Prevention Manual for Industrial Operations (Chicago: National Safety Council, 1974).

Experimental Determination - Flashpoint



Cleveland Open Cup Method.

Closed cup produces a better result - reduces drafts across cup.

Flash point temperatures for pure materials

$$T_f = a + \frac{b(c/T_b)^2 e^{-c/T_b}}{(1 - e^{-c/T_b})^2},$$

where

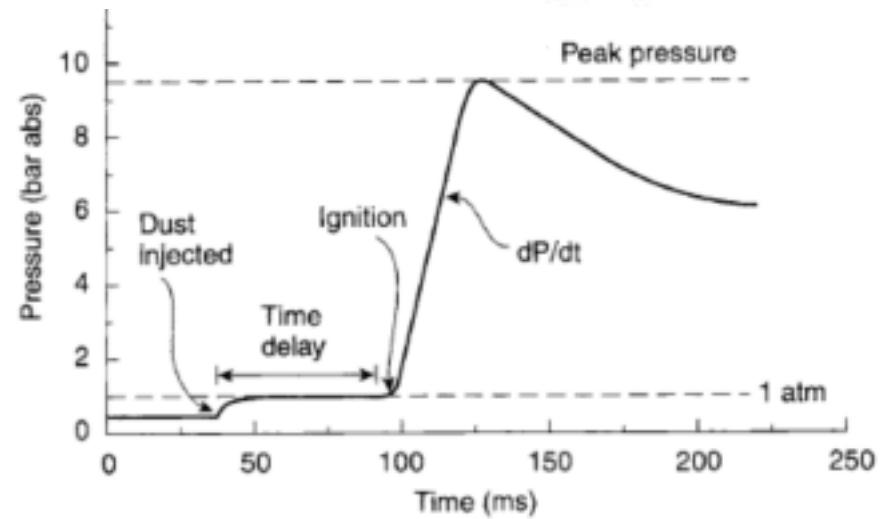
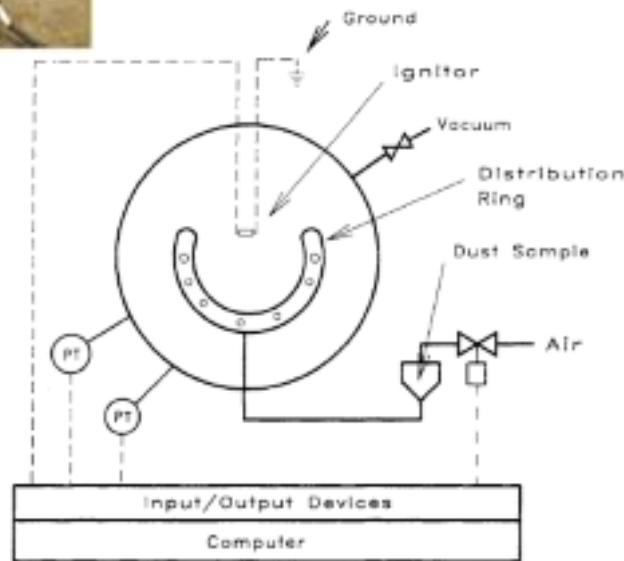
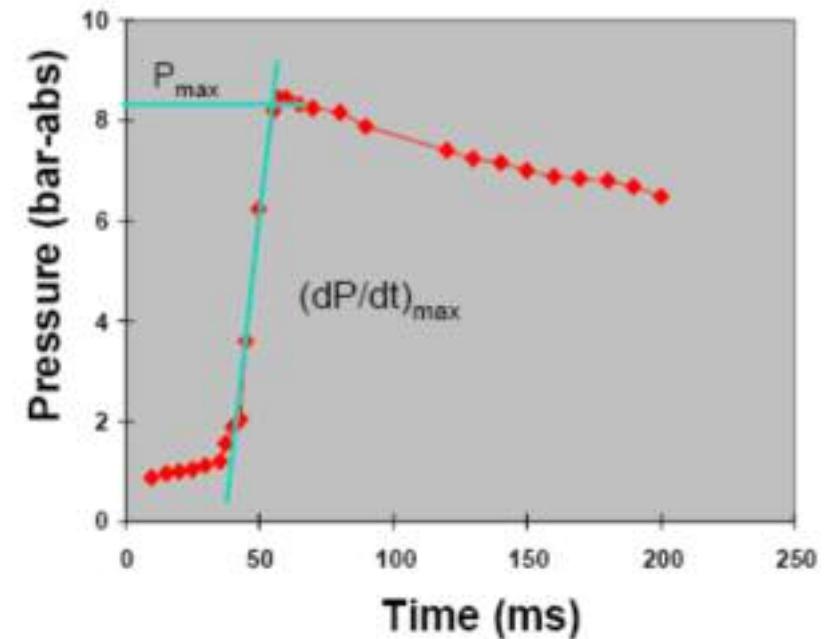
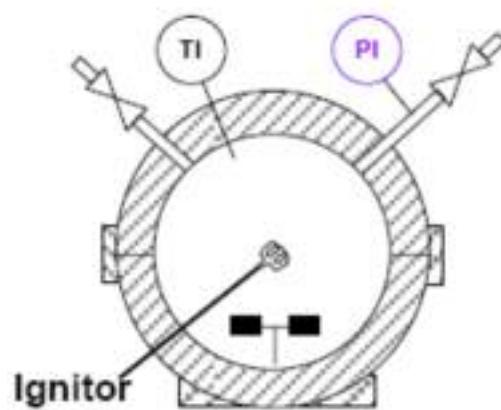
T_f is the flash point temperature (K),
 a , b , and c are constants provided in Table 6-1 (K), and
 T_b is the boiling point temperature of the material (K).

Table 6-1 Constants Used in Equation 6-1 for Predicting the Flash Point¹

Chemical group	<i>a</i>	<i>b</i>	<i>c</i>
Hydrocarbons	225.1	537.6	2217
Alcohols	230.8	390.5	1780
Amines	222.4	416.6	1900
Acids	323.2	600.1	2970
Ethers	275.9	700.0	2879
Sulfur	238.0	577.9	2297
Esters	260.8	449.2	2217
Ketones	260.5	296.0	1908
Halogens	262.1	414.0	2154
Aldehydes	264.5	293.0	1970
Phosphorus-containing	201.7	416.1	1666
Nitrogen-containing	185.7	432.0	1645
Petroleum fractions	237.9	334.4	1807

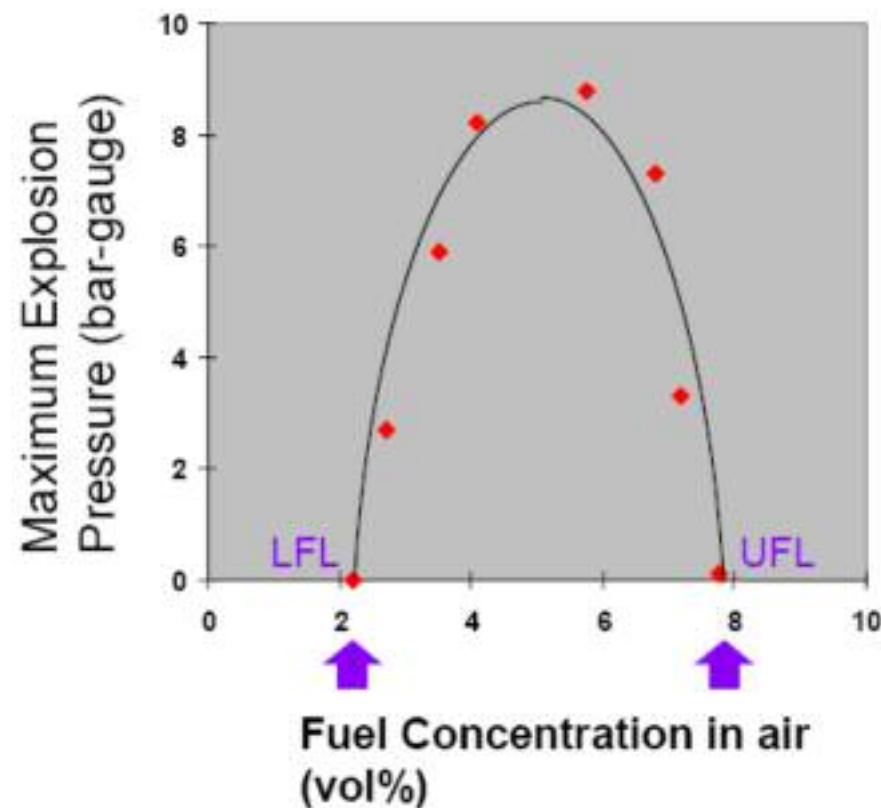
¹K. Satyanarayana and P. G. Rao, *Journal of Hazardous Materials* (1992), 32: 81–85.

Experimental Determination: P versus t



Experimental Determination - LFL, UFL

Run experiment at different fuel compositions with air:



Need a criteria to define limit - use 1 psia pressure increase. Other criteria are used - with different results!

Flammability limits are an empirical artifact of experiment!

Flammability Limits of Mixtures

Le Chatelier Rule (1891)

$$LFL_{mix} = \frac{1}{\sum_{i=1}^n \frac{y_i}{LFL_i}}$$

$$UFL_{mix} = \frac{1}{\sum_{i=1}^n \frac{y_i}{UFL_i}}$$

y_i is the mole fraction of component i on a combustible basis, and n is the number of combustible species.

Assumptions:

- 1) Product heat capacities constant
- 2) No. of moles of gas constant
- 3) Combustion kinetics of pure species unchanged
- 4) Adiabatic temperature rise the same for all species

Example 6-2

What are the LFL and UFL of a gas mixture composed of 0.8% hexane, 2.0% methane, and 0.5% ethylene by volume?

Solution

The mole fractions on a fuel-only basis are calculated in the following table. The LFL and UFL data are obtained from appendix B.

	Volume %	Mole fraction on combustible basis	LFL, (vol. %)	UFL, (vol. %)
Hexane	0.8	0.24	1.2	7.5
Methane	2.0	0.61	5.3	15
Ethylene	0.5	0.15	3.1	32.0
Total combustibles	3.3			
Air	96.7			

Equation 6-2 is used to determine the LFL of the mixture:

$$\begin{aligned} \text{LFL}_{\text{mix}} &= \frac{1}{\sum_{i=1}^n \frac{y_i}{\text{LFL}_i}} \\ &= \frac{1}{\frac{0.24}{1.2} + \frac{0.61}{5.3} + \frac{0.15}{3.1}} \\ &= 1/0.363 = 2.75\% \text{ by volume total combustibles.} \end{aligned}$$

Equation 6-3 is used to determine the UFL of the mixture:

$$\begin{aligned} \text{UFL}_{\text{mix}} &= \frac{1}{\sum_{i=1}^n \frac{y_i}{\text{UFL}_i}} \\ &= \frac{1}{\frac{0.24}{7.5} + \frac{0.61}{15} + \frac{0.15}{32.0}} \\ &= 12.9\% \text{ by volume total combustibles.} \end{aligned}$$

Because the mixture contains 3.3% total combustibles, it is flammable.

Flammability Limit Dependence on Temperature

As temperature increases:

UFL increases, LFL decreases
--> Flammability range increases

$$LFL_T = LFL_{25} - \frac{0.75}{\Delta H_c} (T - 25) = LFL_{25} - \frac{100C_p}{\Delta H_c} (T - 25)$$

$$UFL_T = UFL_{25} + \frac{0.75}{\Delta H_c} (T - 25)$$

$T : {}^\circ C$

Approx. for many
hydrocarbons

ΔH_c : kcal/mole, heat of combustion

Flammability Limit Dependence on Pressure

As pressure increases:

UFL increases (broadening the flammability range)
LFL mostly unaffected

$$UFL_p = UFL + 20.6 * (\log P + 1)$$

P is pressure in mega-Pascals, absolute

No theoretical basis for this yet!

Example 6-3

If the UFL for a substance is 11.0% by volume at 0.0 MPa gauge, what is the UFL at 6.2 MPa gauge?

Solution

The absolute pressure is $P = 6.2 + 0.101 = 6.301$ MPa. The UFL is determined using Equation 6-6:

$$\begin{aligned}UFL_p &= UFL + 20.6(\log P + 1) \\&= 11.0 + 20.6(\log 6.301 + 1) \\&= 48 \text{ vol. \% fuel in air.}\end{aligned}$$

In Class Problem

What is the UFL of a gas mixture composed of 1% methane, 2% ethane and 3% propane by volume at 50°C and 2 atmospheres:

Data:

Component	MW	Heat of Combustion (kcal/mol)
Methane	16.04	212.79
Ethane	30.07	372.81
Propane	44.09	526.74

Solution Procedure:

1. Correct for temperature
2. Correct for pressure (only for UFL)
3. Find for mixture.

Correction for Temperature : UFL from Table 6-1

$$\text{Eq. 6-4} \rightarrow UFL_T = UFL_{25} \left(1 + 0.75(T - 25) / \Delta H_c \right)$$

$$\text{Methane } UFL_{50} = 15 \left(1 + 0.75(25) / 212.79 \right) = 16.32$$

$$\text{Ethane } UFL_{50} = 12.5 \left(1 + 0.75(25) / 372.81 \right) = 13.13$$

$$\text{Propane } UFL_{50} = 9.5 \left(1 + 0.75(25) / 526.74 \right) = 9.84$$

Correction for Pressure (UFL only)

$$\text{Eq. 6-5} \rightarrow UFL_P = UFL + 20.6(\log_{10} P + 1)$$

$$P = (2\text{atm}) \left(\frac{101\text{kPa}}{\text{atm}} \right) \left(\frac{\text{MPa}}{1000\text{kPa}} \right) = 0.202\text{MPa}$$

$$UFL_{2\text{atm}} = UFL_{1\text{atm}} + 20.6(\log_{10}(0.202\text{MPa}) + 1)$$

$$UFL_{2\text{atm}} = UFL_{1\text{atm}} + 6.290$$

$$UFL_{\text{Methane}} = 22.61$$

$$UFL_{\text{Ethane}} = 19.40$$

$$UFL_{\text{Propane}} = 16.13$$

Mixture calculation

Mixture	Vol%	Mol frac	Comb
Methane	1	0.1667	
Ethane	2	0.3333	
Propane	3	0.5000	
Combustibles	6		

Equation 6-2 for mixtures

$$UFL_{mix} = \frac{1}{\sum_{i=1}^n \frac{y_i}{UFL_i}}$$

$$UFL_{Mixture} = \frac{1}{\frac{0.1667}{22.61} + \frac{0.3333}{19.40} + \frac{0.5}{16.13}} = 18.0 \text{ vol\%}$$

Since total combustibles in air $1+2+3=6 < 18$ then the system is in the combustible range (below UFL)

Estimating Flammability Limits

- For many hydrocarbon vapors the LFL and the UFL are a function of the stoichiometric concentration (C_{st}) of fuel.

$$LFL = 0.55 \cdot C_{st}$$

C_{st} stoichiometric conc. [vol%]

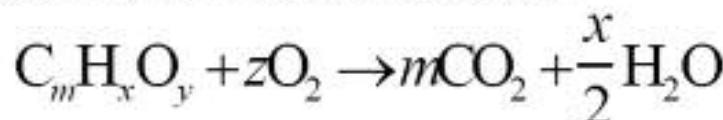
$$UFL = 3.5 \cdot C_{st}$$

Very approximate!

Not always conservative!

where C_{st} is volume % fuel in fuel plus air.

General combustion reaction:



$$z = m + \frac{1}{4}x - \frac{1}{2}y$$

$$C_{st} = \frac{100}{1 + \left(\frac{z}{0.21}\right)}$$

$$C_{st} = \frac{21\%}{0.21 + z}$$



$$LFL = \frac{0.55(100)}{4.76m + 1.19x - 2.38y + 1},$$

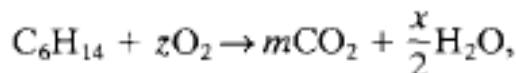
$$UFL = \frac{3.50(100)}{4.76m + 1.19x - 2.38y + 1}.$$

Example 6-4

Estimate the LFL and the UFL for hexane, and compare the calculated limits to the actual values determined experimentally.

Solution

The stoichiometry is



and z , m , x , and y are found by balancing this chemical reaction using the definitions in Equation 6-9:

$$m = 6,$$

$$x = 14,$$

$$y = 0,$$

The LFL and the UFL are determined by using Equations 6-10 and 6-11:

$$\begin{aligned}\text{LFL} &= 0.55(100)/[4.76(6) + 1.19(14) + 1] \\ &= 1.19 \text{ vol. \% versus 1.2 vol. \% actual,}\end{aligned}$$

$$\begin{aligned}\text{UFL} &= 3.5(100)/[4.76(6) + 1.19(14) + 1] \\ &= 7.57 \text{ vol. \% versus 7.5 vol. \% actual.}\end{aligned}$$

Estimating LOC

$$LOC = \left(\frac{\text{moles fuel}}{\text{total moles}} \right) \left(\frac{\text{moles O}_2}{\text{moles fuel}} \right) = LFL \left(\frac{\text{moles O}_2}{\text{moles fuel}} \right).$$

LOC limiting oxygen conc. [vol% O₂]

(1) Fuel + (z) Oxygen → Products

$$LOC \cong z \cdot LFL$$

Typically 8 - 10%

Very approximate!

Not always conservative!

Example 6-5

Estimate the LOC for butane (C_4H_{10}).

Solution

The stoichiometry for this reaction is



The LFL for butane (from appendix B) is 1.9% by volume. From the stoichiometry

$$LOC = \left(\frac{\text{moles fuel}}{\text{total moles}} \right) \left(\frac{\text{moles } O_2}{\text{moles fuel}} \right) = LFL \left(\frac{\text{moles } O_2}{\text{moles fuel}} \right).$$

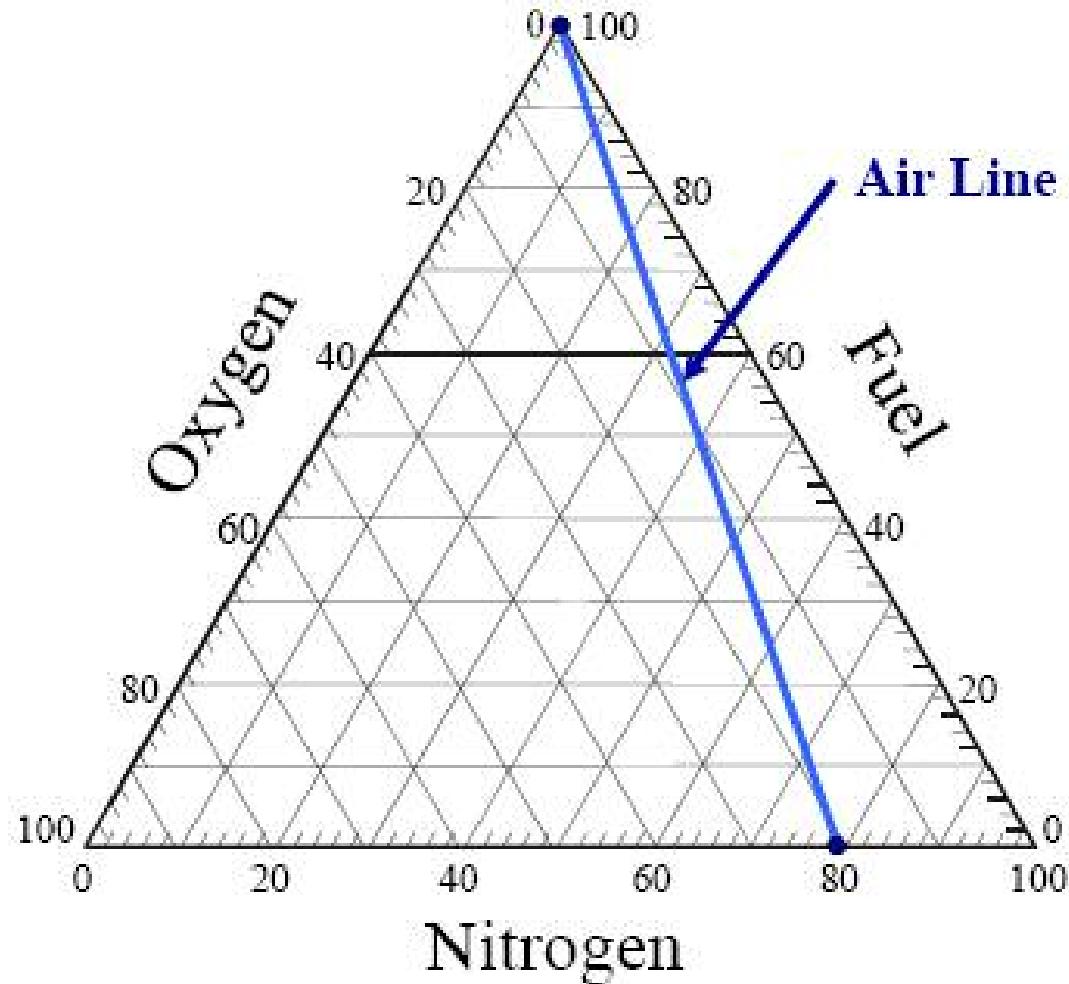
By substitution, we obtain

$$\begin{aligned} LOC &= \left(1.9 \frac{\text{moles fuel}}{\text{total moles}} \right) \left(\frac{6.5 \text{ moles } O_2}{1.0 \text{ moles fuel}} \right) \\ &= 12.4 \text{ vol. \% } O_2. \end{aligned}$$

The combustion of butane is preventable by adding nitrogen, carbon dioxide, or even water vapor until the oxygen concentration is below 12.4%. The addition of water, however, is not recommended because any condition that condenses water would move the oxygen concentration back into the flammable region.

Flammability Diagram

The Air Line is drawn as a straight line between the upper apex, representing 100% Fuel, and the point on the lower line at 79% nitrogen / 21% oxygen, Representing 100% air.

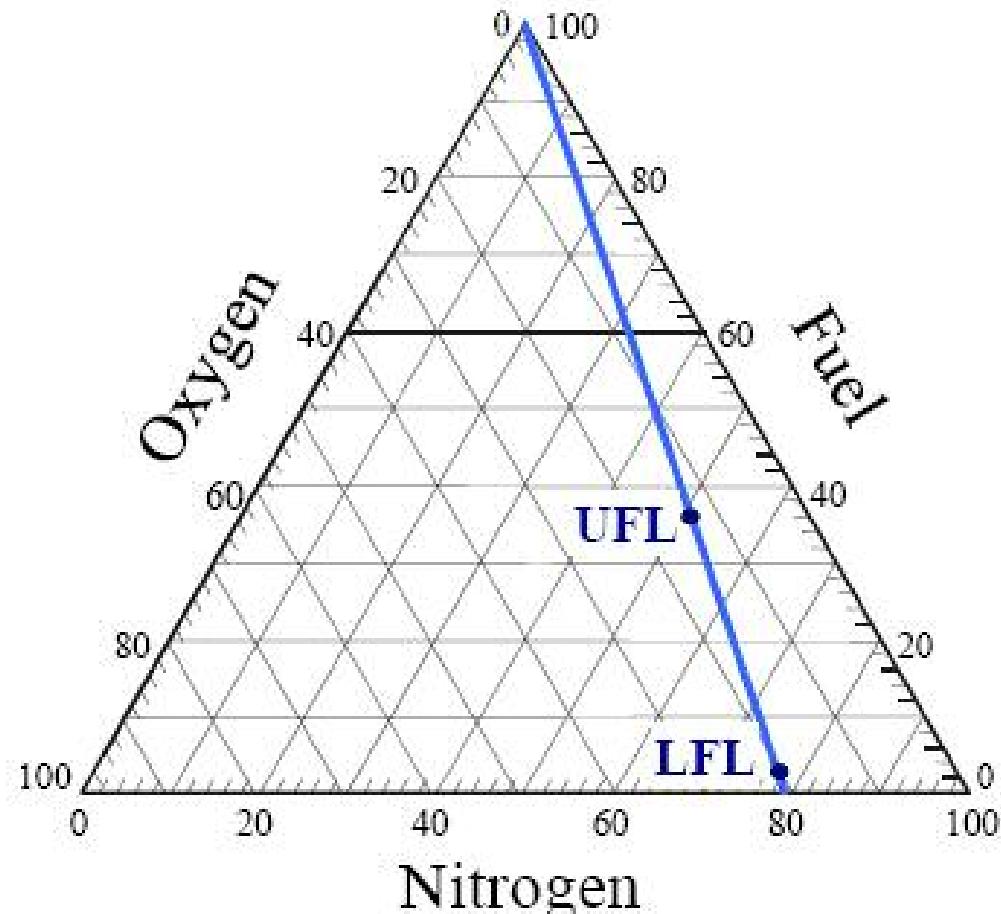


Flammability Diagram

The LFL and the UFL points

In Appendix B of the text, the LFL and UFL for ethylene are given as 2.7% and 36%, respectively.

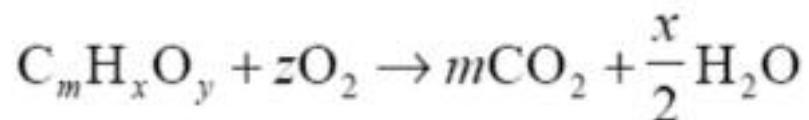
These values are plotted on the Air Line at the corresponding Fuel percentages.



Flammability Diagram

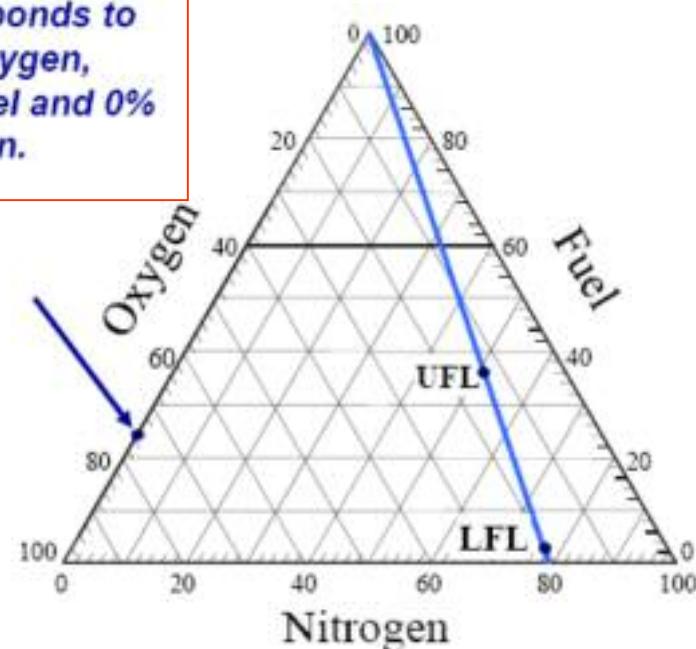
Stoichiometric concentration

The general combustion reaction is used to determine the coefficient z , corresponding to the moles of oxygen required for complete combustion of one mole of ethylene.



$$z = m + \frac{1}{4} x - \frac{1}{2} y = 2 + \frac{1}{4} (4) - \frac{1}{2} (0) = 3$$

This point corresponds to 75% oxygen, 25% fuel and 0% nitrogen.



If 3 mol O_2 is required to burn 1 mol C_2H_4 , the stoichiometric concentration C_{st} in pure oxygen is 75% O_2 , 25% C_2H_4 .

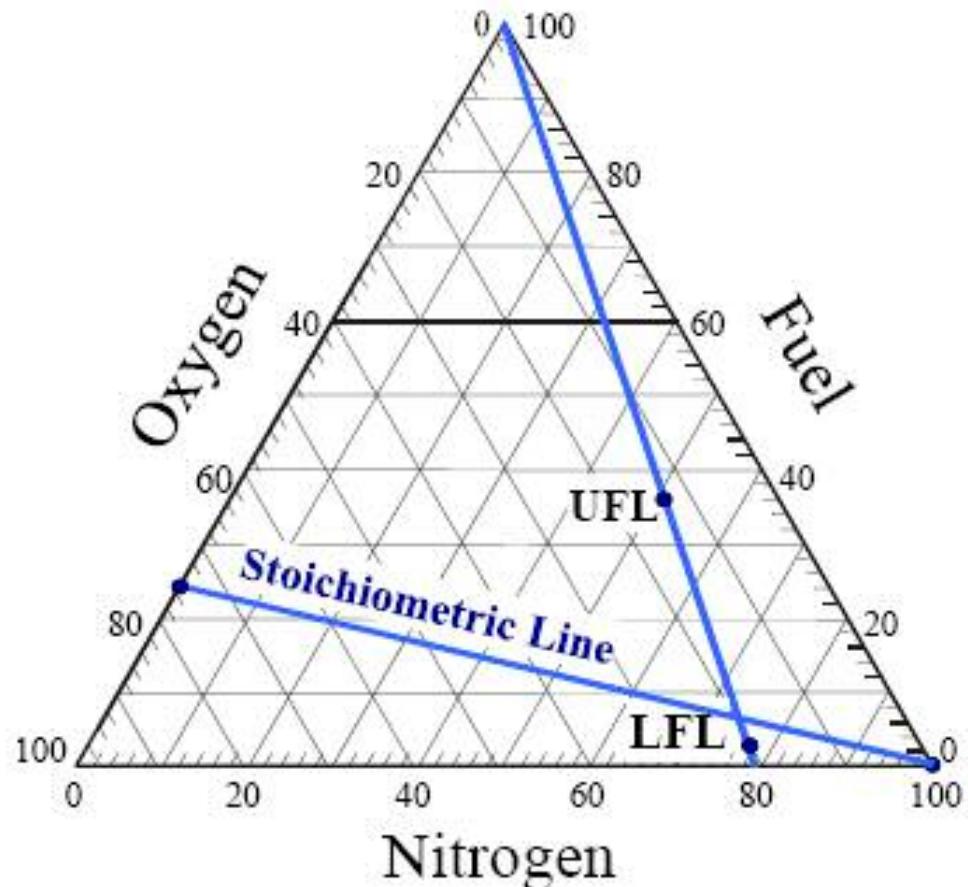
$$\left(\frac{z}{1+z} \right) * 100 = \left(\frac{3}{1+3} \right) * 100 = 75\%$$

Flammability Diagram

The Stoichiometric Line

The Stoichiometric Line is drawn as shown.

It represents all stoichiometric $\text{CH}_3\text{OH} + \text{O}_2$ mixtures, with varying amounts of inert nitrogen



Flammability Diagram

Limiting or Minimum Oxygen Concentration

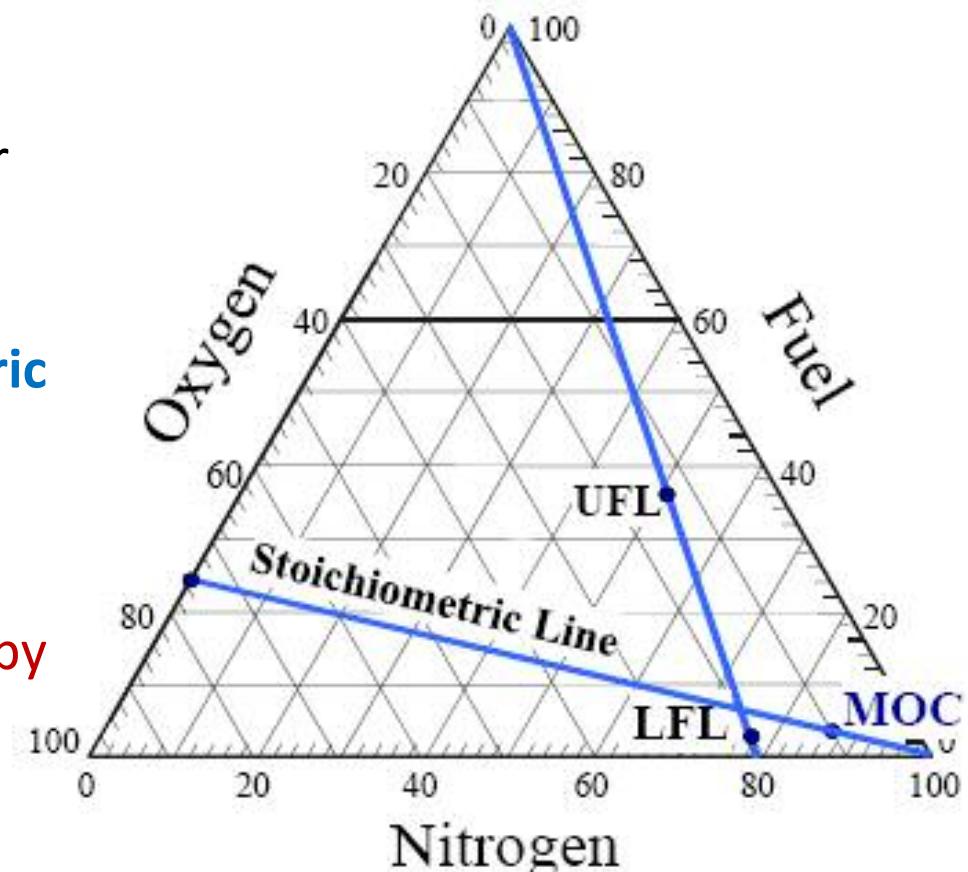
On Table 6-2 of the text, the MOC for ethylene is given as 10 vol.% oxygen.

It is plotted on the Stoichiometric Line

as shown.

Another way to estimate the LOC is by using the following approximation:

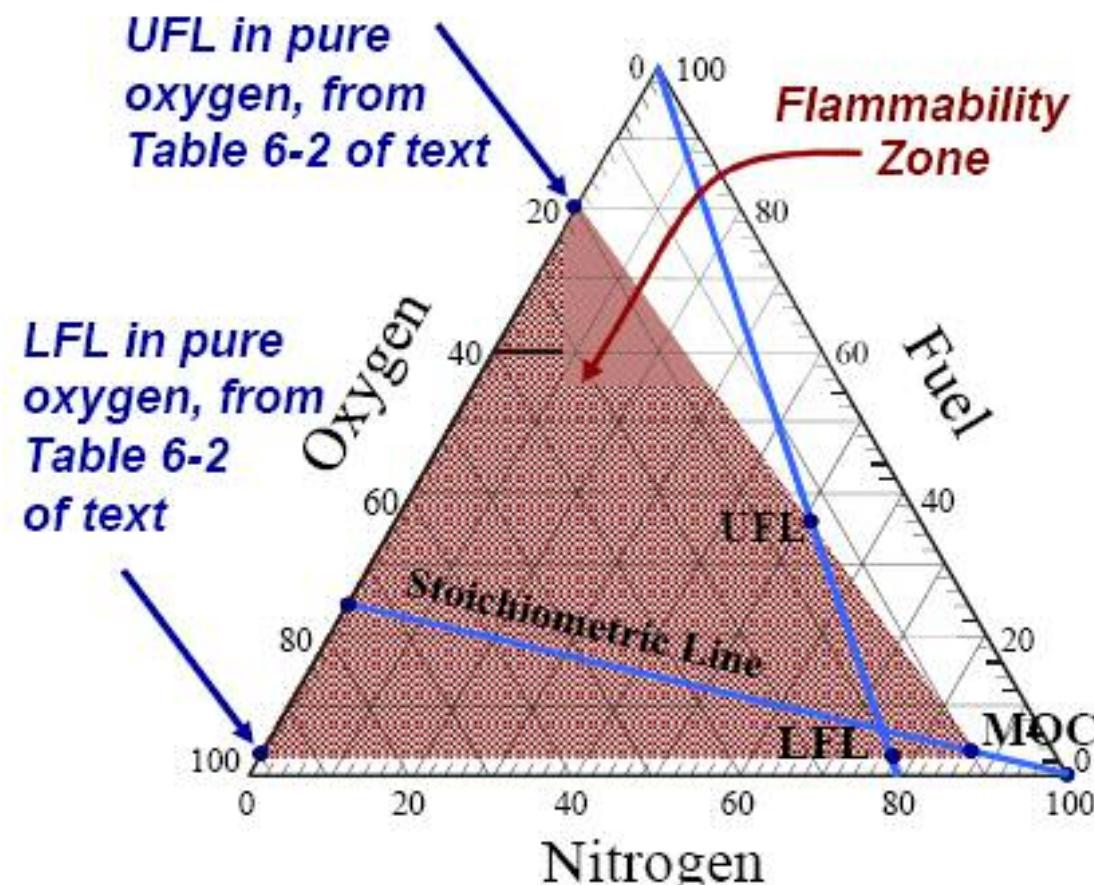
$$LOC = z(LFL).$$



Flammability Diagram

The general shape of the flammability boundary

This diagram reflects the fact that ethylene has relatively broad flammability limits; broader than typical alkane hydrocarbons.



Drawing an Approx. Diagram

1. Draw LFL and UFL on air line (% Fuel in air).
2. Draw stoichiometric line from combustion equation.
3. Plot intersection of LOC with stoichiometric line.
4. Draw LFL and UFL in pure oxygen, if known (% fuel in pure oxygen).
5. Connect the dots to get approximate diagram.

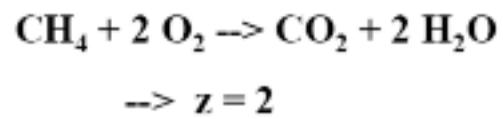
Example

Methane:

LFL: 5.3% fuel in air

UFL: 15% fuel in air

LOC: 12% oxygen

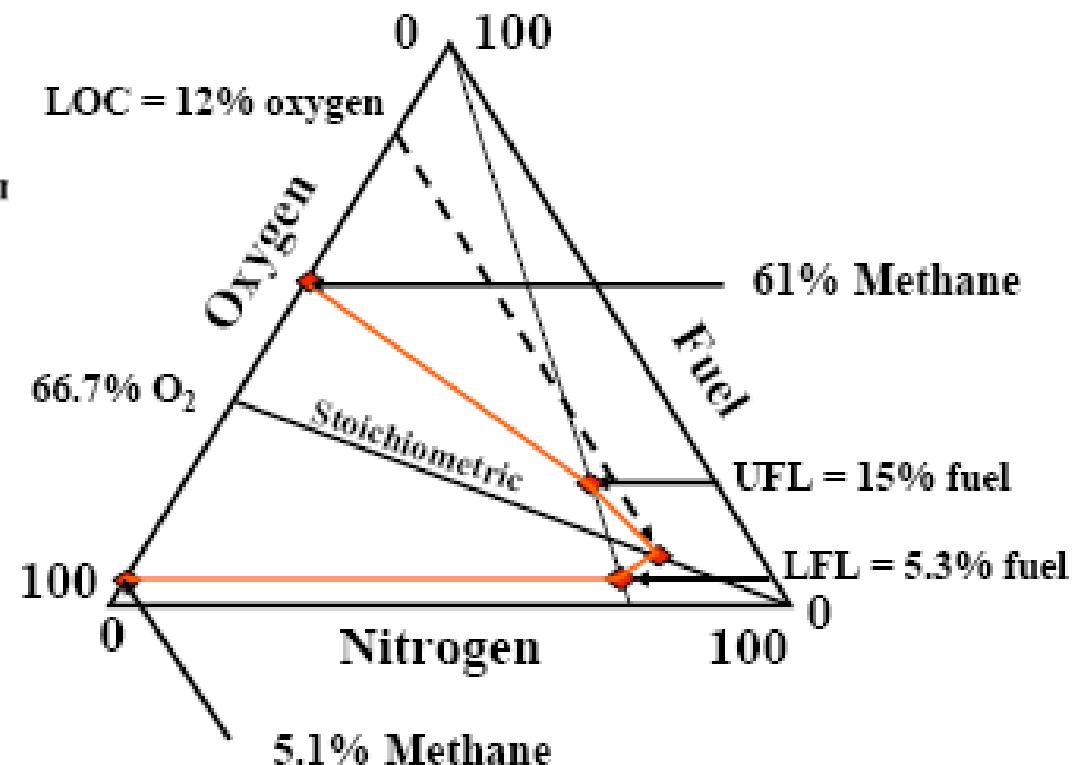


$$\left(\frac{z}{1+z} \right) * 100 = \left(\frac{2}{3} \right) * 100 = 66.7 \text{ \% oxygen}$$

Pure Oxygen:

LFL: 5.1% fuel in oxygen

UFL: 61% fuel in oxygen



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 in air:** 344 m/s, 1129 ft/s at ambient T, P.
- Deflagrations are the usual case with explosions involving flammable materials.

Comparison of Behavior

Deflagration:

Ignition X

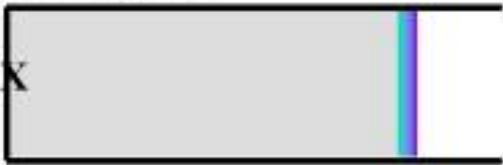


Reaction front moves at less than speed of sound.

Pressure wave moves away from reaction front at speed of sound.

Detonation:

Ignition X



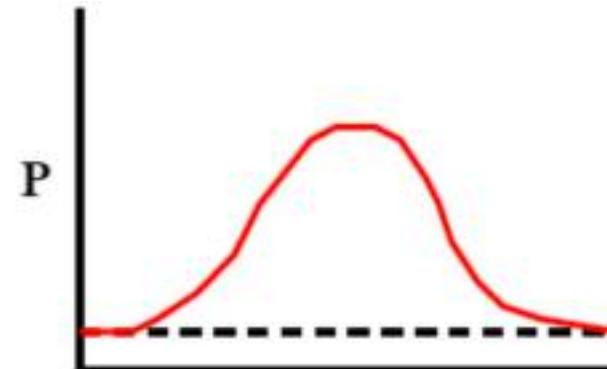
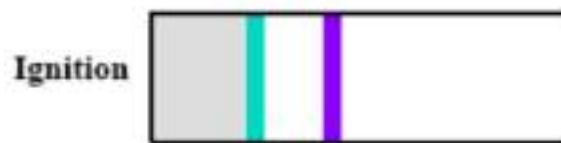
- Reacted gases
- Reaction / Flame Front
- Pressure Wave
- Unreacted gases

Reaction front moves greater than speed of sound.

Pressure wave is slightly ahead of reaction front moving at same speed.

Comparison of Behavior

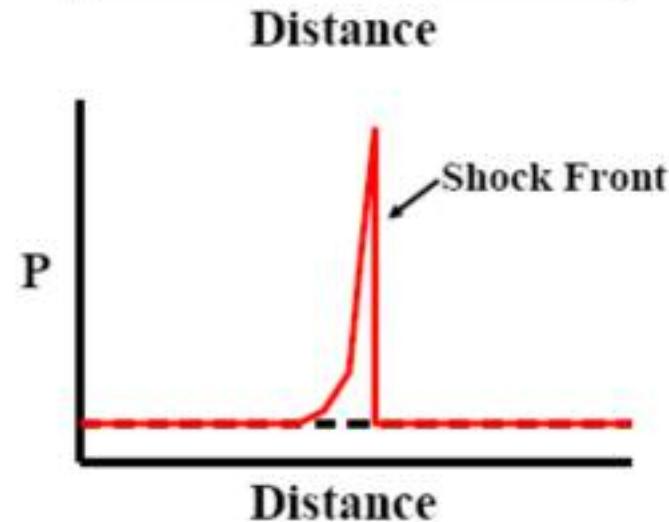
Deflagration:



Detonation:



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



Comparison of Behavior

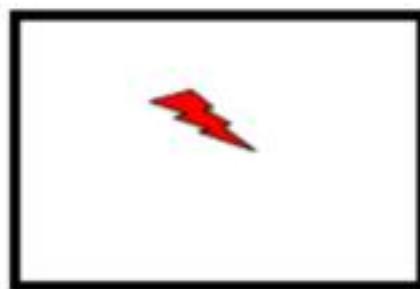
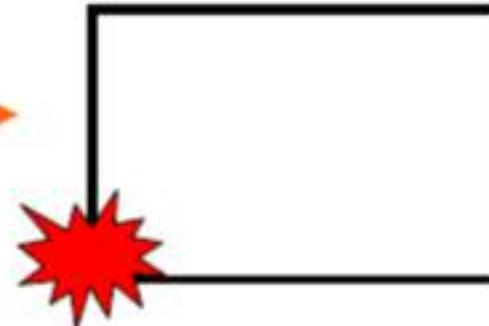


Detonation

Localized Damage

No wall thinning

Lots of pieces

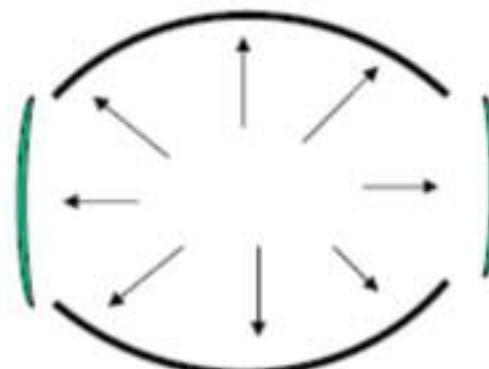


Deflagration

Damage all over

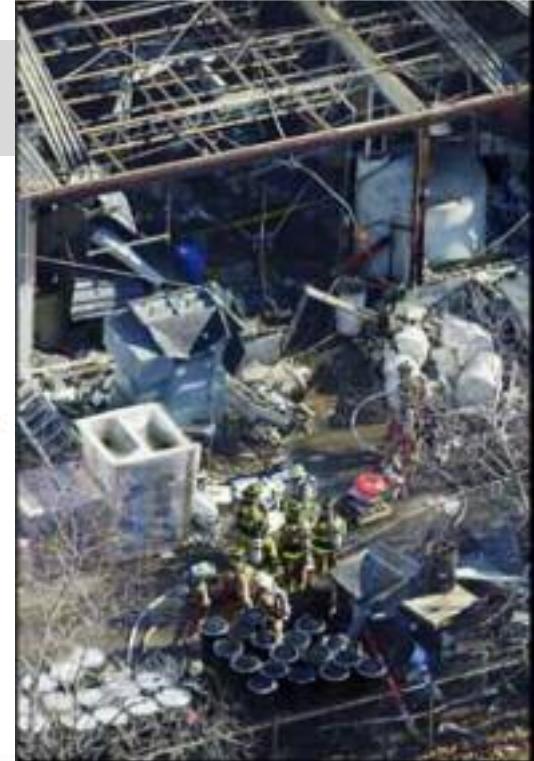
Wall thinning

A few pieces



Confined Explosions

Occurs in process or building. Almost all of the thermodynamic energy ends up in the pressure wave.



Cubic Law:
$$\left(\frac{dP}{dt} \right)_{\max} V^{1/3} = K_G, K_{St}$$

K Deflagration index (bar m/s)
 G gas
 St dust (Staub)

Deflagration index:

Measure of explosion robustness, higher value means more robust.
Depends on experimental conditions
Not a fundamental property.

Unconfined Explosions

- Occurs in the open. Only 2 to 10% of thermodynamic energy ends up in pressure wave. Use 2% for this class.



VCE: **Vapor Cloud Explosion**

- sudden release flammable vapor
- dispersion and mixing with air
- ignition vapor cloud

Prevention

- smaller inventories
- milder process conditions
- incipient leak detection
- automated block valves

Boiling Liquid Expanding Vapor Explosion

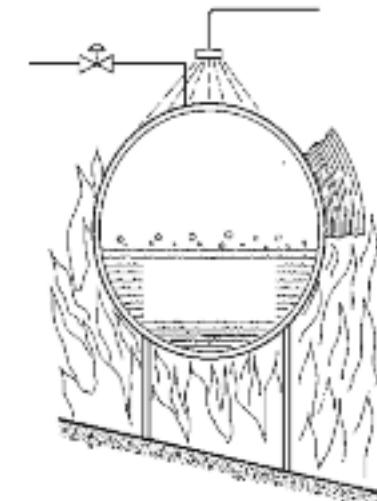
BLEVE: Boiling Liquid Expanding Vapor Explosion

- Release large amount of superheated liquid after vessel rupture (e.g. fire)

Effects: Blast + thermal



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.

Overpressures

Explosions result in a blast or pressure wave moving out from the explosion center at the speed of sound.

There are several ways to measure this pressure. The usual method is to measure the pressure at right angles to the pressure wave. This is called the Side-on Overpressure.

If the pressure is measured in a direction towards the blast, you get a higher value because of the deceleration of the moving gas as it impacts the pressure transducer.

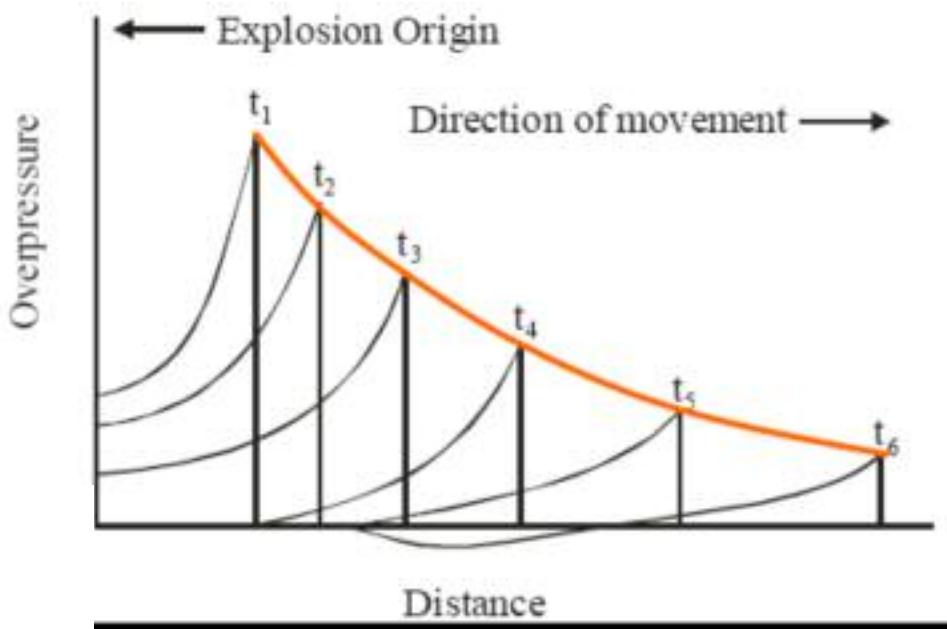
Batch Reactor Explosion Consequences



Peak Side-on Overpressures

Peak Side-on Overpressure (psig)	Consequence
0.03	Large glass panes shatter
0.15	Typical glass failure
0.7	Minor house damage
1.0	Partial house demolition
3	Steel frame building distorted
> 15	100% fatalities

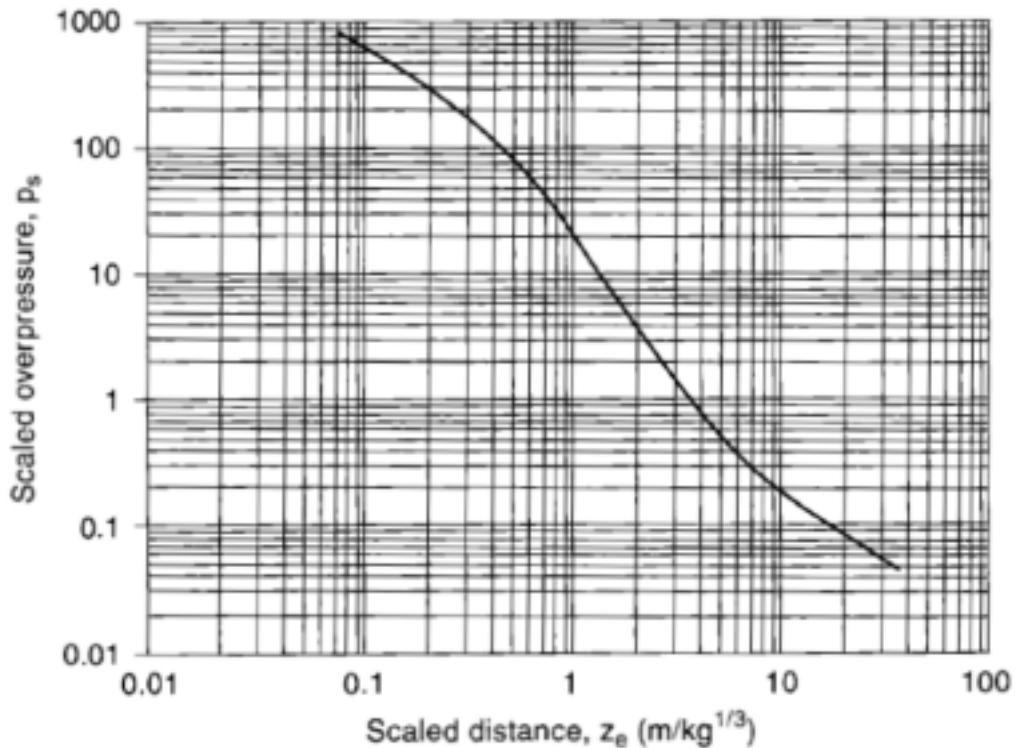
3 psig: Hazard zone for fatalities due to structure collapse.



Scaled overpressure versus scaled distance

The overpressure can be estimated using an equivalent mass of TNT, denoted m_{TNT} , and the distance from the ground-zero point of the explosion, denoted r .

$$z = \frac{r}{m_{TNT}^{1/3}}$$



The scaled overpressure p_s , is given by

$$\text{where } p_s = \frac{p_o}{p_a},$$

p_s is the scaled overpressure (unitless),
 p_o is the peak side-on overpressure, and
 p_a is the ambient pressure.

The data in Figure 6-23 are also represented by the empirical equation

$$\frac{p_o}{p_a} = \frac{1616 \left[1 + \left(\frac{z_e}{4.5} \right)^2 \right]}{\sqrt{1 + \left(\frac{z_e}{0.048} \right)^2} \sqrt{1 + \left(\frac{z_e}{0.32} \right)^2} \sqrt{1 + \left(\frac{z_e}{1.35} \right)^2}}.$$

Example 6-8

One kilogram of TNT is exploded. Compute the overpressure at a distance of 30 m from the explosion.

Solution

The value of the scaling parameter is determined using Equation 6-21:

$$\begin{aligned} z_e &= \frac{r}{m_{\text{TNT}}^{1/3}} \\ &= \frac{30 \text{ m}}{(1.0 \text{ kg})^{1/3}} = 30 \text{ m kg}^{-1/3}. \end{aligned}$$

From Figure 6-23 the scaled overpressure is 0.055. Thus, if the ambient pressure is 1 atm, then the resulting side-on overpressure is estimated at $(0.055)(101.3 \text{ kPa}) = 5.6 \text{ kPa}$ (0.81 psi). From Table 6-9 this overpressure will cause minor damage to house structures.

TNT Equivalency for VCEs

$$m_{TNT} = \frac{\eta m E_c}{E_{TNT}} = \frac{\text{Total Energy in Fuel}}{\text{Energy/mass of TNT}}$$

Where: m_{TNT} is the equivalent mass of TNT

η is the explosion efficiency

m is the total mass of fuel

E_c is the energy of explosion, or heat of comb.

E_{TNT} is the heat of combustion for TNT

(1120 cal/gm = 4686 kJ/kg = 2016 BTU/lb)

TNT Equiv. - Explosion Efficiency

$$m_{TNT} = \frac{\eta m E_c}{E_{TNT}}$$

$\eta \rightarrow 1$ for confined explosion

$\eta \rightarrow 0.02$ to 0.10 for unconfined explosion

Use a default value of 0.02, unless other information is available.

TNT Equivalency Procedure

Problem: Determine consequences at a specified location from an explosion.

1. Determine total mass of fuel involved.
2. Estimate explosion efficiency.
3. Look up energy of explosion (See Appendix B in text).
4. Apply Equation 6-24 to determine m_{TNT} .
5. Determine scaled distance.
$$z = \frac{r}{m_{TNT}^{1/3}}$$
6. Use Figure 6-23 or Equation 6-23 to determine overpressure.
7. Use Table 6-9 to estimate damage.

Example 6-9

One thousand kilograms of methane escapes from a storage vessel, mixes with air, and explodes. Determine (a) the equivalent amount of TNT and (b) the side-on peak overpressure at a distance of 50 m from the blast. Assume an explosion efficiency of 2%.

Solution

- Equation 6-24 applies. The energy of explosion for hexane is found in appendix B. Substituting into Equation 6-24, we obtain

$$m_{\text{TNT}} = \frac{\eta m \Delta H_c}{E_{\text{TNT}}} = \frac{(0.02)(1000 \text{ kg})(1 \text{ mol}/0.016 \text{ kg})(818.7 \text{ kJ/mol})}{4686 \text{ kJ/kg}} = 218 \text{ kg TNT.}$$

- Equation 6-21 is used to determine the scaled distance:

$$z_e = \frac{r}{m_{\text{TNT}}^{1/3}} = \frac{50 \text{ m}}{(218 \text{ kg})^{1/3}} = 8.3 \text{ m/kg}^{1/3}.$$

From Figure 6-23 (or Equation 6-23), the scaled overpressure is 0.25. Thus the overpressure is

$$p_o = p_s p_a = (0.25)(101.3 \text{ kPa}) = 25 \text{ kPa.}$$

This overpressure will demolish steel panel buildings.

HW

6-1

6-3d

6-6

6-7

6-8

6-17

Process Safety Engineering:

Toxic Release and Dispersion Models

Dr. Motasem Saidan

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Practical and Potential Releases

During an accident process equipment can release toxic materials very quickly

- Explosive rupture of a process vessel due to excess pressure
- Rupture of a pipeline with material under high pressure
- Rupture of tank with material above boiling point
- Rupture of a train or truck following an accident.

- ✓ **Identify the Design basis**

What process situations can lead to a release, and which are the worst situations

- ✓ **Source Model**

What are the process conditions and hence what will be the state of the release and rate of release

- ✓ **Dispersion Model**

Using prevailing conditions (or worst case) determine how far the materials could spread

Dispersion Models

What?

- Describe how vapors are transported downwind of a release.
Valid between 100 m to 10 km.
- Below 100 m use ventilation equations Chapt. 3.
- Above 10 km: almost unpredictable.

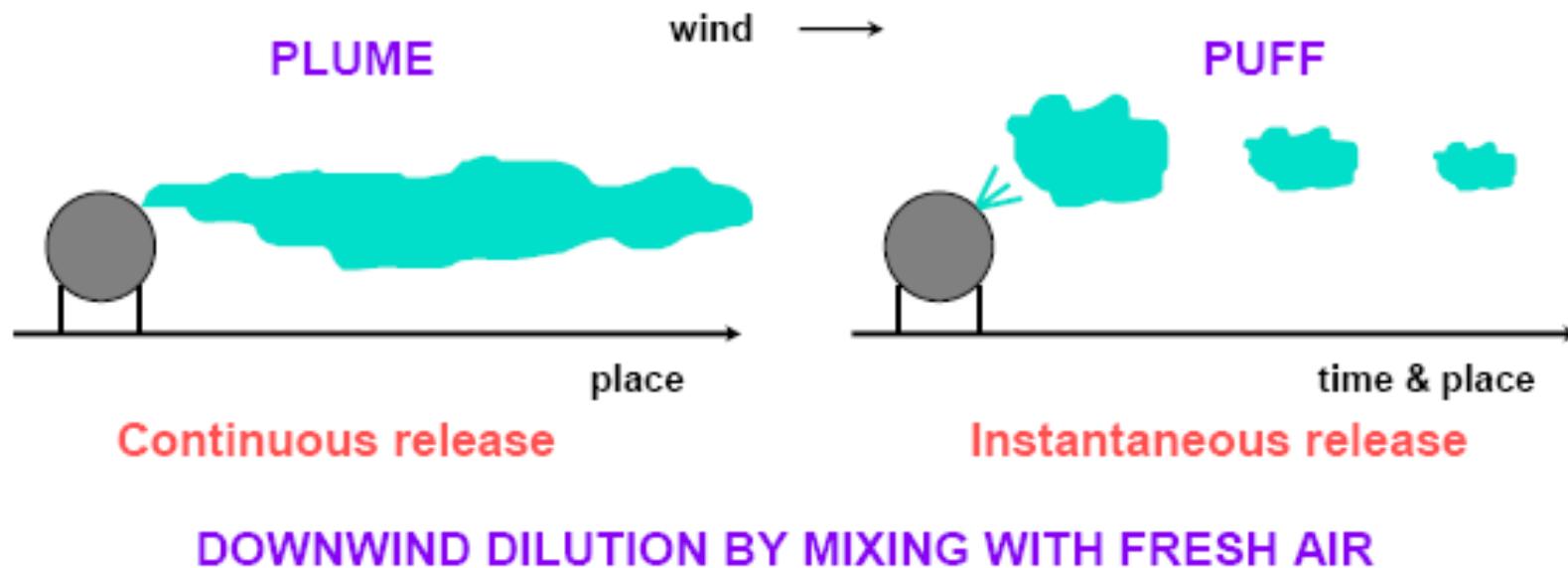
Why?

To determine the consequences.

Results:

- ✓ Downwind concentrations (x, y, z)
- ✓ Area affected
- ✓ Downwind evacuation distances

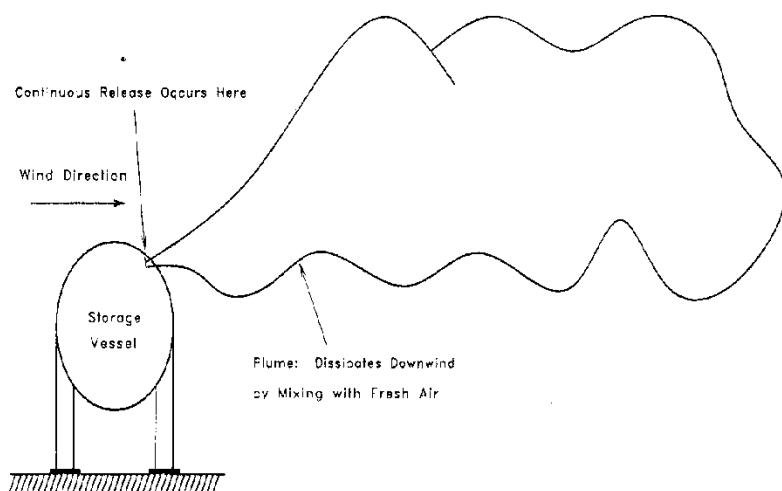
Dispersion



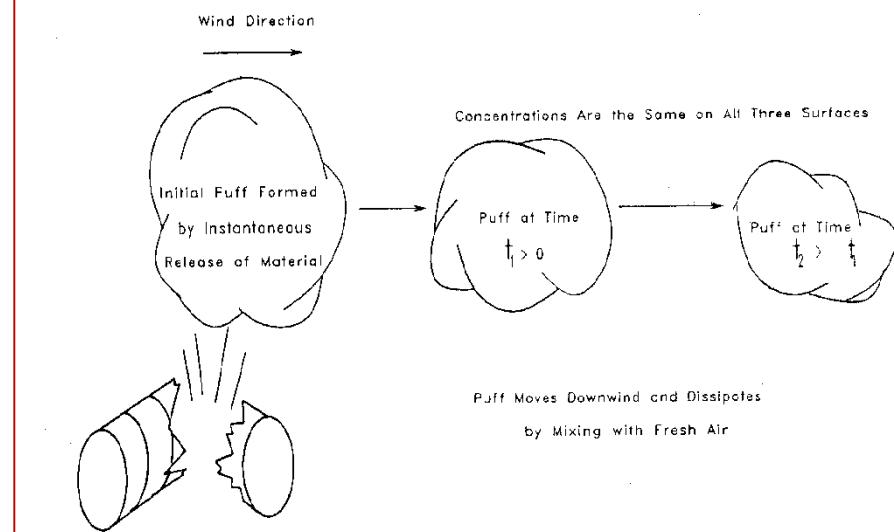
ATMOSPHERIC DISPERSION

- Wind speed
- Atmospheric stability: vertical temp. profile
- Roughness ground: buildings, structures, trees, water
- Height of release above ground level
- Momentum and buoyancy: effective height

- Plume models were originally developed for dispersion from a smoke stack.
- In an emergency if there is a leak in a large tank then a plume can develop.



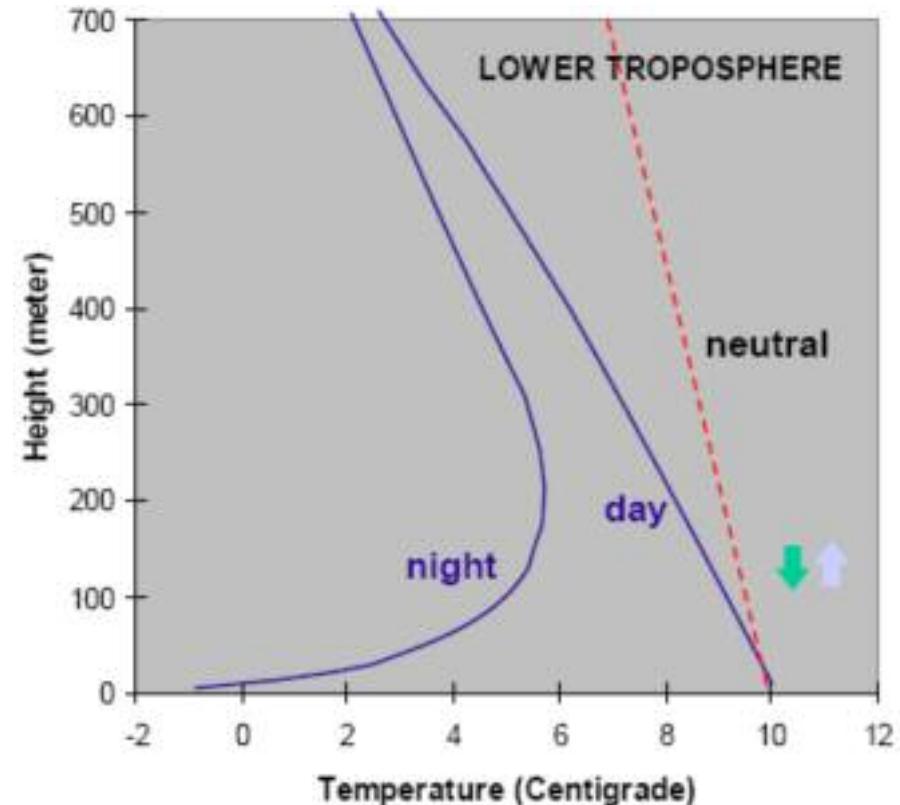
- Puff models are used when you have essentially an instantaneous release and the cloud is swept downwind.
- No significant plume develops



Atmospheric stability

MAINLY DETERMINED BY VERTICAL TEMPERATURE GRADIENT

- **Unstable** atmospheric conditions: Sun heats ground faster than heat can be removed so that air temperature near the ground is higher than the air temperature at higher elevations.
- **Neutral:** The air above the ground warms and the wind speed increases, reducing the effect of solar input.
- **Stable:** The sun cannot heat the ground as fast as the ground cools - temperature at ground is lower.



Atmospheric stability

STABILITY CLASSES A - F

- A Extremely unstable
- B Moderately unstable
- C Slightly unstable
- D Neutral
- E Slightly stable
- F Moderately stable

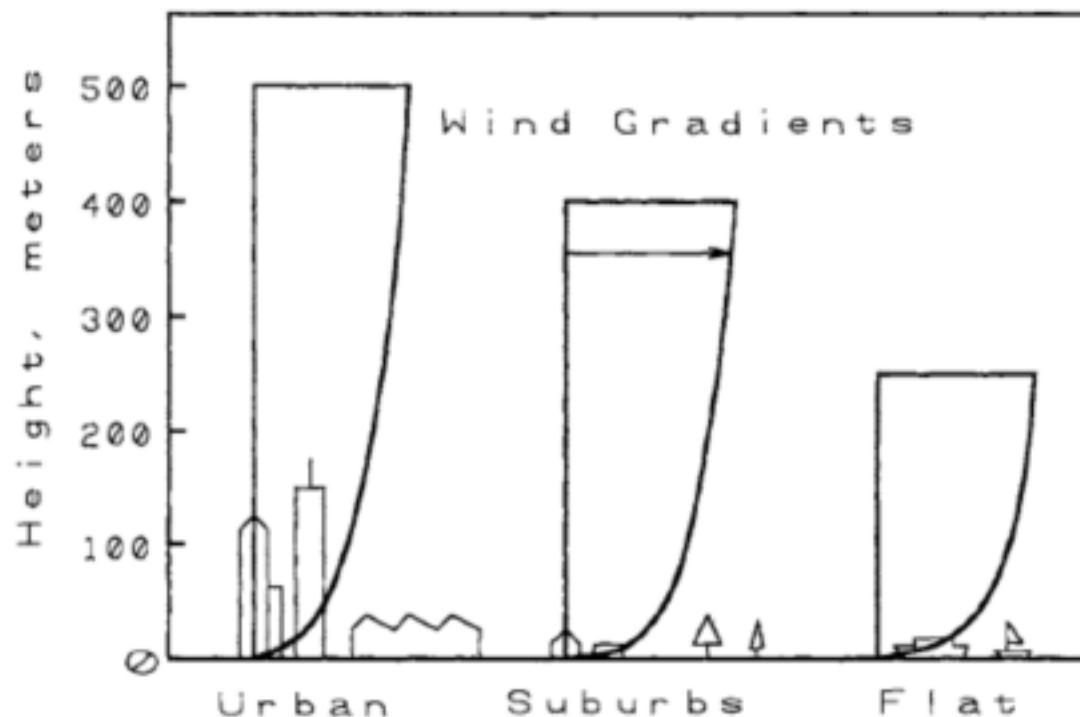
Table 5-1

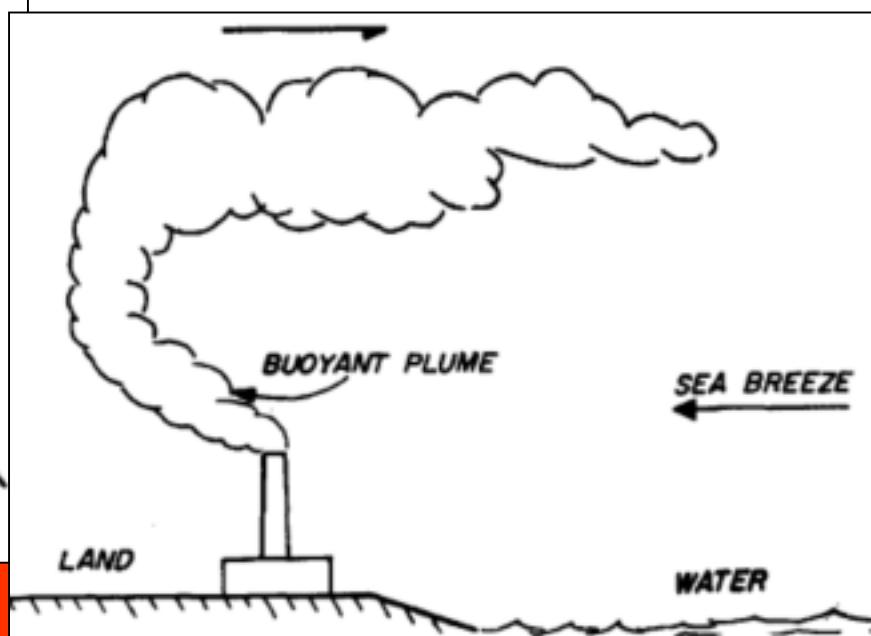
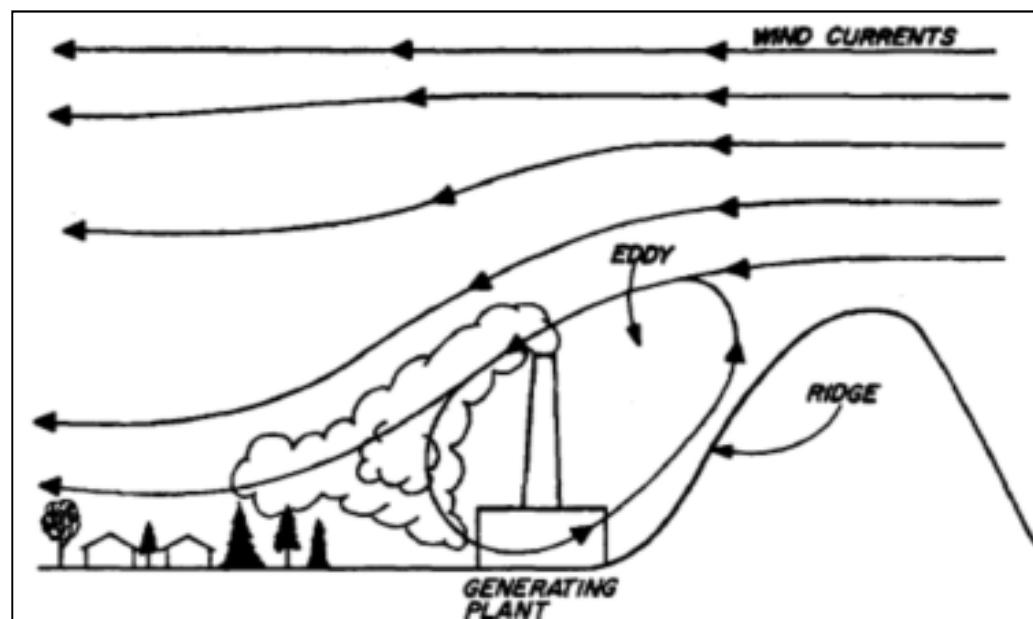
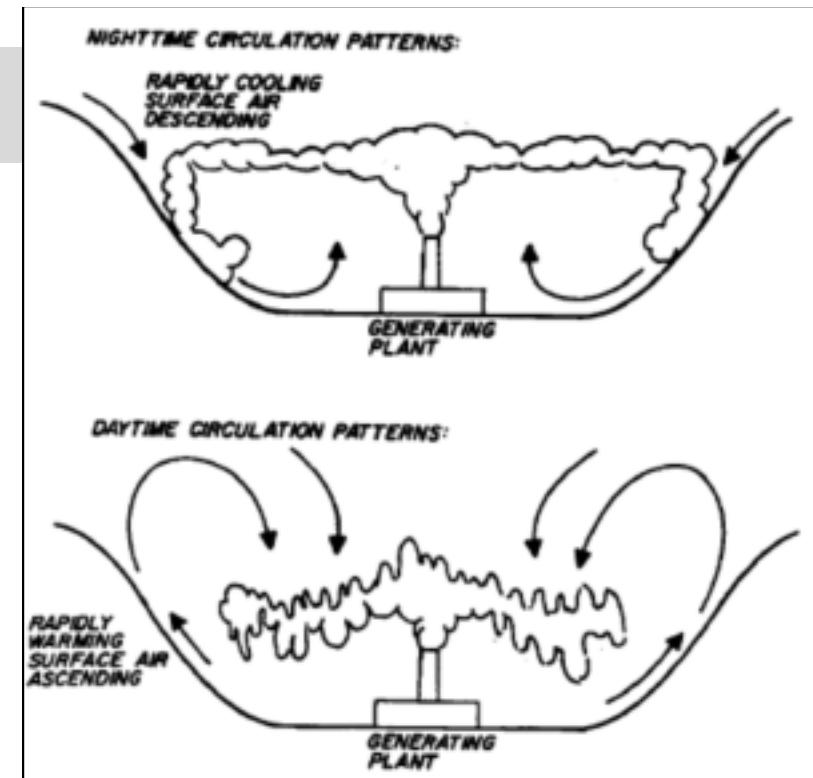
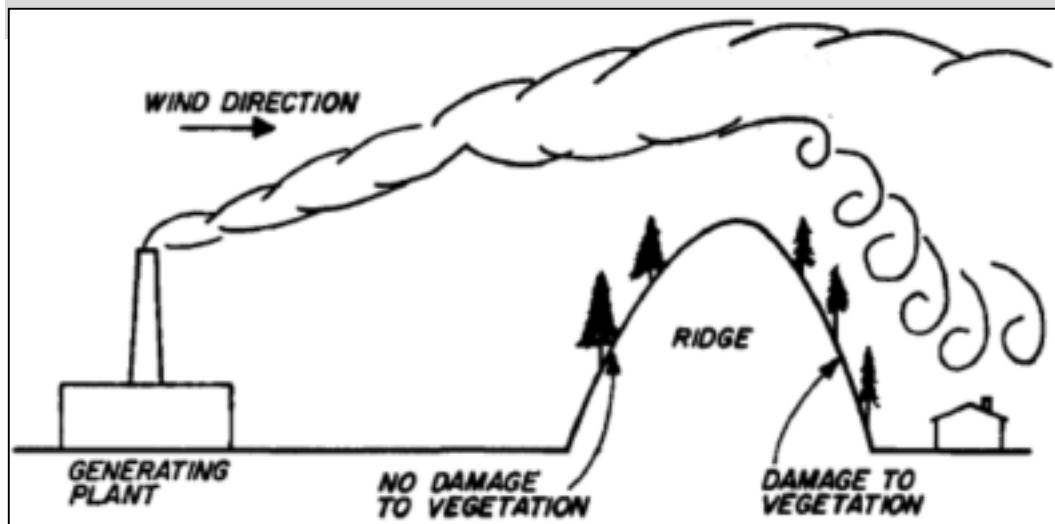
Table 5-1 Atmospheric Stability Classes for Use with the Pasquill-Gifford Dispersion Model^{1,2}

Surface wind speed (m/s)	Daytime insolation ³			Nighttime conditions ⁴	
	Strong	Moderate	Slight	Thin overcast or >4/8 low cloud	≤3/8 cloudiness
<2	A	A-B	B	F ⁵	F ⁵
2-3	A-B	B	C	E	F
3-4	B	B-C	C	D ⁶	E
4-6	C	C-D	D ⁶	D ⁶	D ⁶
>6	C	D ⁶	D ⁶	D ⁶	D ⁶

Ground conditions

- Ground conditions affect the mechanical mixing at the surface and the wind profile with height.
- Trees and buildings increase mixing, whereas lakes and open areas decrease it





Release Height Effect

- The release height significantly affects ground-level concentrations.
- As the release height increases, ground-level concentrations are reduced because the plume must disperse a greater distance vertically.

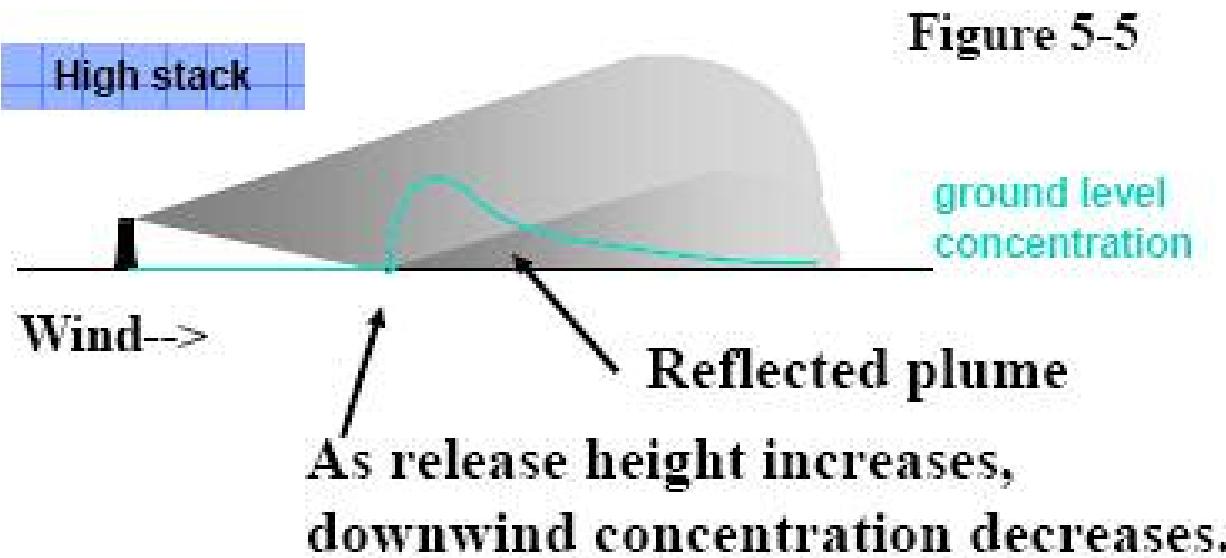
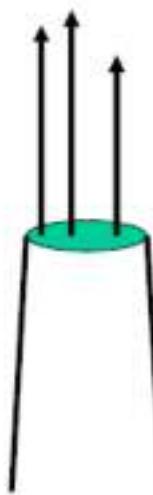


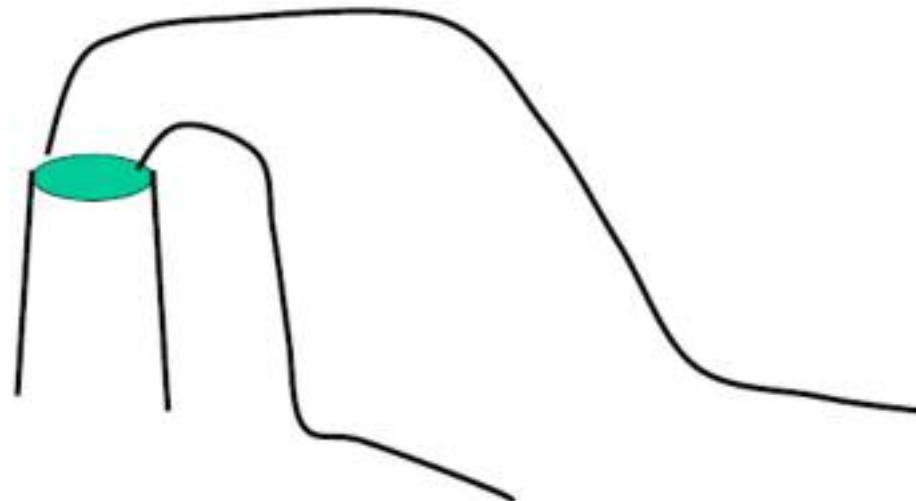
Figure 5-5

Release Momentum and Buoyancy



Jet Release

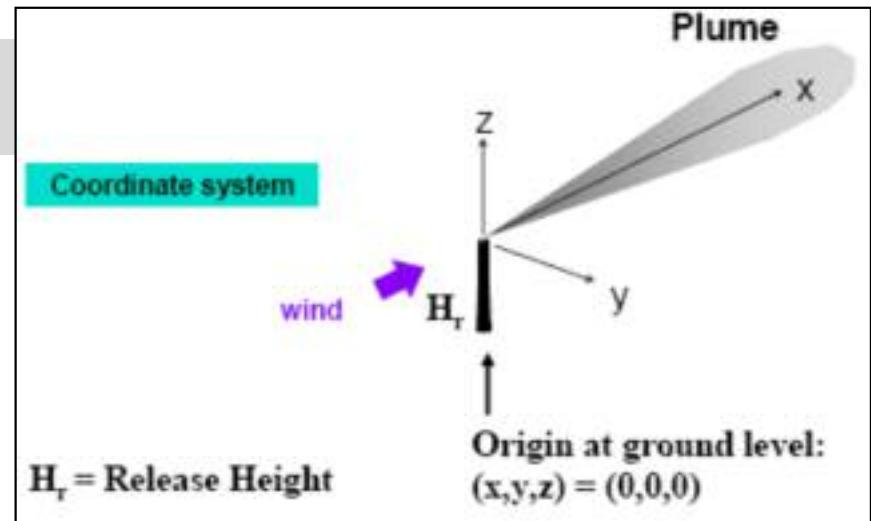
MW>29 --> Most hydrocarbons



Heavier than air. Gas becomes neutral downwind as it mixes with air.

Dispersion Models

- Dispersion models are based on a mass balance.
- Two approaches:



1. Use eddy diffusivities, K , to represent turbulence.

Advantage: nice tidy theoretical model.

Disadvantage: $K = K(x, y, z)$, and impossible to measure.

2. Use dispersion coefficients which represent the standard deviations in the concentration profiles.

Advantage: easy to measure and correlate.

Dispersion Models

- Practical and Potential Releases

$$\frac{\partial \langle C \rangle}{\partial t} + \langle u_j \rangle \frac{\partial \langle C \rangle}{\partial x_j} = \frac{\partial}{\partial x_j} \left(K_j \frac{\partial \langle C \rangle}{\partial x_j} \right)$$

Case 1 : Steady-State Continuous Point Release with No Wind

- constant mass release rate ($Q_m = \text{constant}$),
- no wind ($\langle u_j \rangle = 0$),
- steady state ($\partial \langle C \rangle / \partial t = 0$), and
- constant eddy diffusivity ($K_j = K^*$ in all directions).

$$\langle C \rangle(r) = \frac{Q_m}{4\pi K^* r}.$$

$$\langle C \rangle(x, y, z) = \frac{Q_m}{4\pi K^* \sqrt{x^2 + y^2 + z^2}}.$$

Case 2: Puff with No Wind

- puff release, that is, instantaneous release of a fixed mass of material Q_m^* (with units of mass),
- no wind ($\langle u_i \rangle = 0$), and
- constant eddy diffusivity ($K_j = K^*$ in all directions).

$$\langle C \rangle(r, t) = \frac{Q_m^*}{8(\pi K^* t)^{3/2}} \exp\left(-\frac{r^2}{4K^* t}\right),$$

$$\langle C \rangle(x, y, z, t) = \frac{Q_m^*}{8(\pi K^* t)^{3/2}} \exp\left[-\frac{(x^2 + y^2 + z^2)}{4K^* t}\right].$$

Case 3: Non-Steady-State Continuous Point Release with No Wind

- constant mass release rate ($Q_m = \text{constant}$),
- no wind ($\langle u_j \rangle = 0$), and
- constant eddy diffusivity ($K_j = K^*$ in all directions).

$$\langle C \rangle(r, t) = \frac{Q_m}{4\pi K^* r} \operatorname{erfc}\left(\frac{r}{2\sqrt{K^* t}}\right),$$

$$\langle C \rangle(x, y, z, t) = \frac{Q_m}{4\pi K^* \sqrt{x^2 + y^2 + z^2}} \operatorname{erfc}\left(\frac{\sqrt{x^2 + y^2 + z^2}}{2\sqrt{K^* t}}\right).$$

Case 4: Steady-State Continuous Point Source Release with Wind

- continuous release ($Q_m = \text{constant}$),
- wind blowing in x direction only ($\langle u_j \rangle = \langle u_x \rangle = u = \text{constant}$), and
- constant eddy diffusivity ($K_j = K^*$ in all directions).

$$\langle C \rangle(x, y, z) = \frac{Q_m}{4\pi K^* x} \exp\left[-\frac{u}{4K^* x}(y^2 + z^2)\right].$$

Along the centerline of this plume, $y = z = 0$, and

$$\langle C \rangle(x) = \frac{Q_m}{4\pi K^* x}.$$

Case 5: Puff with No Wind and Eddy Diffusivity Is a Function of Direction

- puff release ($Q_m^* = \text{constant}$),
- no wind ($\langle u_j \rangle = 0$), and
- each coordinate direction has a different but constant eddy diffusivity (K_x , K_y , and K_z).

$$(C)(x, y, z, t) = \frac{Q_m^*}{8(\pi t)^{3/2} \sqrt{K_x K_y K_z}} \exp \left[-\frac{1}{4t} \left(\frac{x^2}{K_x} + \frac{y^2}{K_y} + \frac{z^2}{K_z} \right) \right].$$

Case 6: Steady-State Continuous Point Source Release with Wind and Eddy Diffusivity Is a Function of Direction

- continuous release ($Q_m = \text{constant}$),
- steady-state ($\partial(C)/\partial t = 0$),
- wind blowing in x direction only ($\langle u_j \rangle = \langle u_x \rangle = u = \text{constant}$),
- each coordinate direction has a different but constant eddy diffusivity (K_x, K_y , and K_z)

$$\langle C \rangle(x, y, z) = \frac{Q_m}{4\pi x \sqrt{K_x K_y}} \exp\left[-\frac{u}{4x} \left(\frac{y^2}{K_y} + \frac{z^2}{K_z} \right) \right].$$

Along the centerline of this plume, $y = z = 0$, and the average concentration is given by

$$\langle C \rangle(x) = \frac{Q_m}{4\pi x \sqrt{K_y K_z}}. \quad (1)$$

Case 7: Puff with Wind

- puff release ($Q_m^* = \text{constant}$),
- wind blowing in x direction only ($\langle u_j \rangle = \langle u_x \rangle = u = \text{constant}$), and
- each coordinate direction has a different but constant eddy diffusivity (K_x , K_y , and K_z).

$$\langle C \rangle(x, y, z, t) = \frac{Q_m^*}{8(\pi t)^{3/2} \sqrt{K_x K_y K_z}} \exp \left\{ -\frac{1}{4t} \left[\frac{(x - ut)^2}{K_x} + \frac{y^2}{K_y} + \frac{z^2}{K_z} \right] \right\}.$$

Case 8: Puff with No Wind and with Source on Ground

$$\langle C \rangle(x, y, z, t) = \frac{Q_m^*}{4(\pi t)^{3/2} \sqrt{K_x K_y K_z}} \exp \left[-\frac{1}{4t} \left(\frac{x^2}{K_x} + \frac{y^2}{K_y} + \frac{z^2}{K_z} \right) \right].$$

Case 9: Steady-State Plume with Source on Ground

$$\langle C \rangle(x, y, z) = \frac{Q_m}{2\pi x \sqrt{K_x K_y}} \exp \left[-\frac{u}{4x} \left(\frac{y^2}{K_y} + \frac{z^2}{K_z} \right) \right].$$

Case 10: Continuous Steady-State Source with Source at Height H , above the Ground

$$\begin{aligned} \langle C \rangle(x, y, z) &= \frac{Q_m}{4\pi x \sqrt{K_y K_z}} \exp\left(-\frac{uy^2}{4K_y x}\right) \\ &\times \left\{ \exp\left[-\frac{u}{4K_z x}(z - H_r)^2\right] + \exp\left[-\frac{u}{4K_z x}(z + H_r)^2\right] \right\}. \end{aligned}$$

Gaussian form of plume equation

$$\langle C \rangle(x, y, z) = \frac{Q_m}{2\pi\sigma_y\sigma_z u} \exp\left(-\frac{y^2}{2\sigma_y^2}\right) \times \left\{ \exp\left[-\frac{(z - H_r)^2}{2\sigma_z^2}\right] + \exp\left[-\frac{(z + H_r)^2}{2\sigma_z^2}\right] \right\}$$



Top View of plume

--> **Wind**

$\langle C \rangle(x, y, z)$ = Ave. conc. (20-30 min ave)

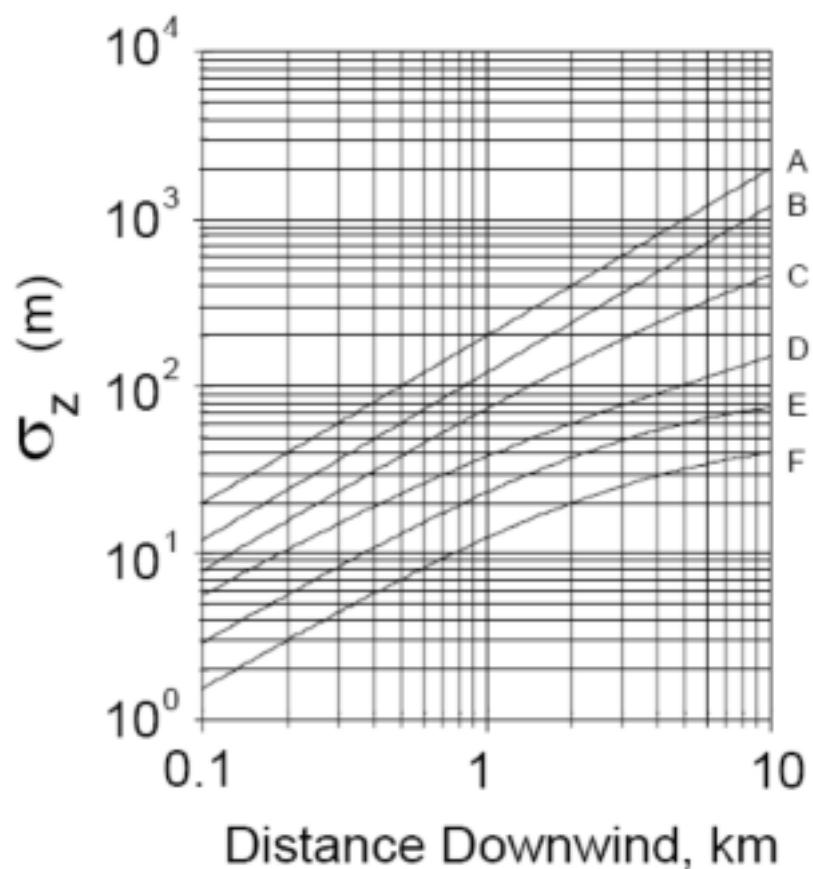
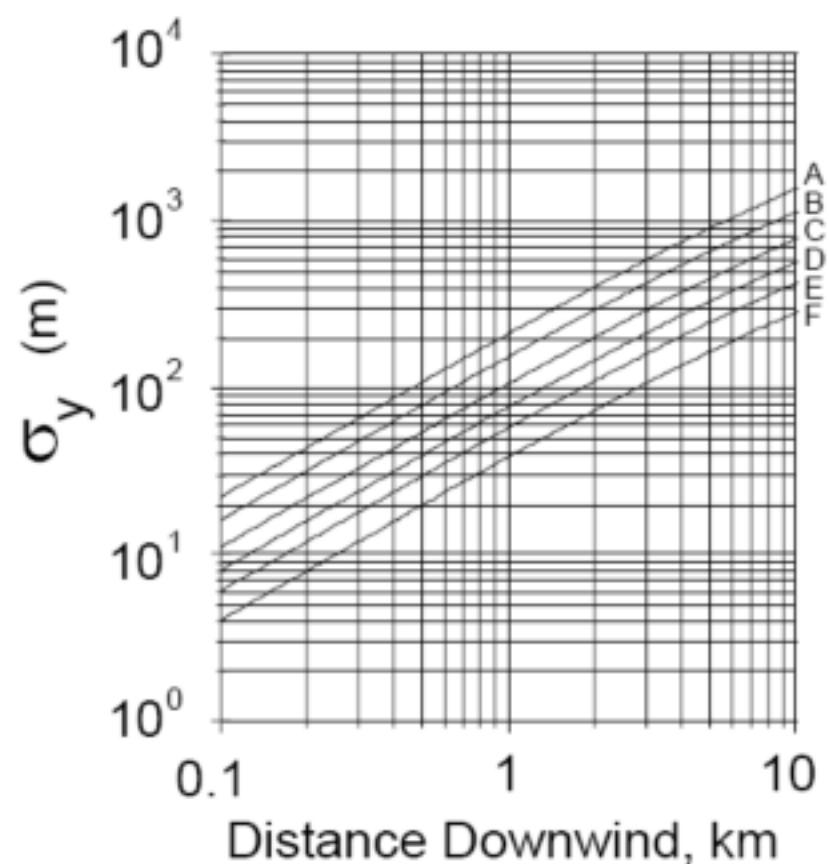
Q_m = Release rate (mass/time)

σ_y, σ_z = Dispersion coefficients = f(stability class, downwind distance)

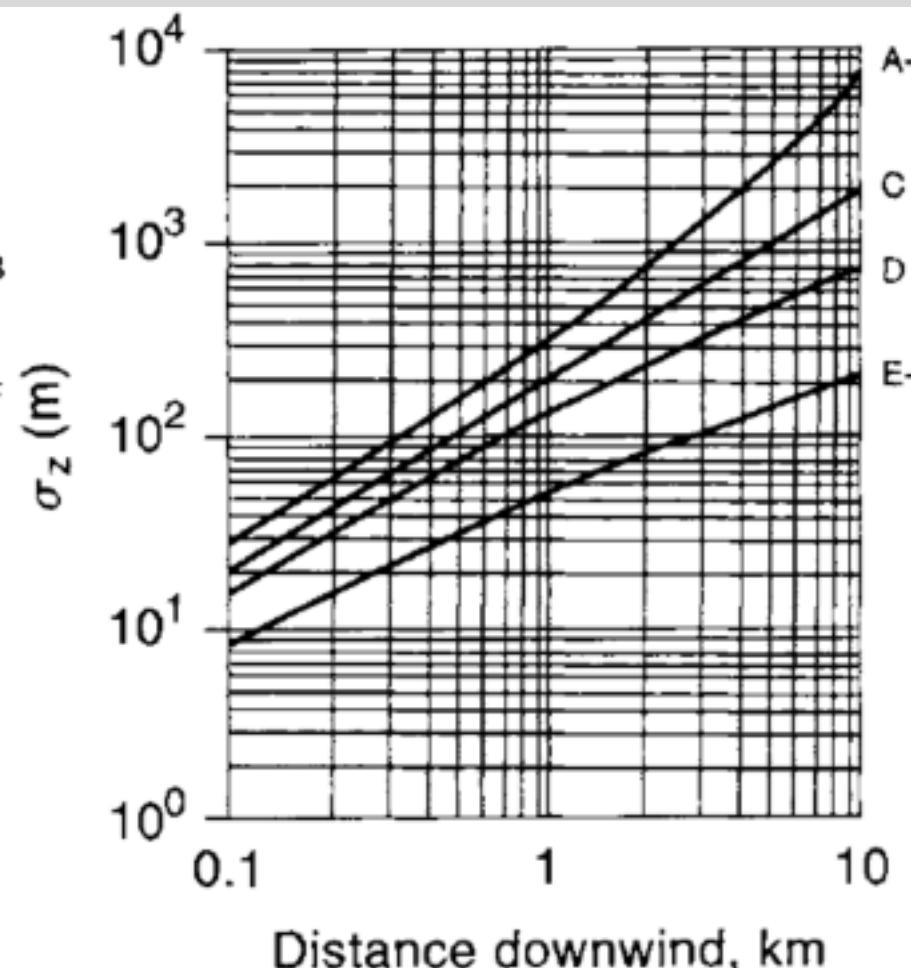
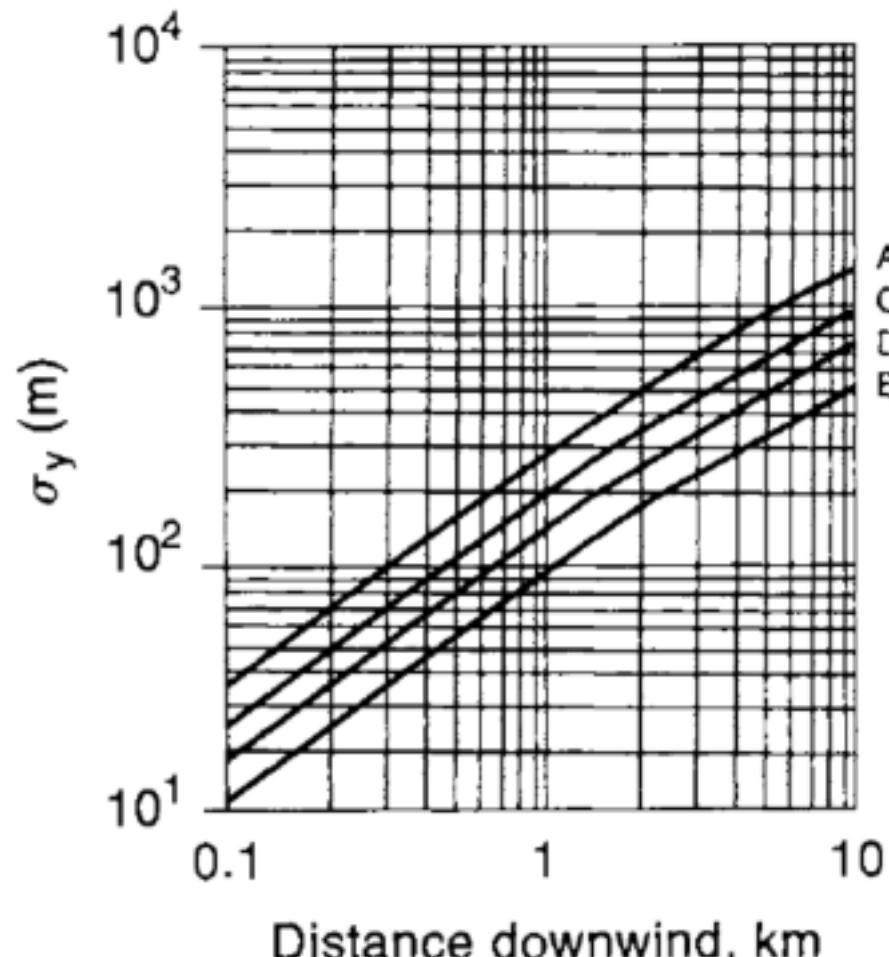
u = Wind speed (length/time)

y, z = Coordinates (length)

H_r = Release height (length)



Dispersion coefficients for plume model for rural releases.



Dispersion coefficients for plume model for urban releases.

Table 5-2 Recommended Equations for Pasquill-Gifford Dispersion Coefficients for Plume Dispersion^{1,2} (the downwind distance x has units of meters)

Pasquill-Gifford stability class	σ_y (m)	σ_z (m)
Rural conditions		
A	$0.22x(1 + 0.0001x)^{-1/2}$	$0.20x$
B	$0.16x(1 + 0.0001x)^{-1/2}$	$0.12x$
C	$0.11x(1 + 0.0001x)^{-1/2}$	$0.08x(1 + 0.0002x)^{-1/2}$
D	$0.08x(1 + 0.0001x)^{-1/2}$	$0.06x(1 + 0.0015x)^{-1/2}$
E	$0.06x(1 + 0.0001x)^{-1/2}$	$0.03x(1 + 0.0003x)^{-1}$
F	$0.04x(1 + 0.0001x)^{-1/2}$	$0.016x(1 + 0.0003x)^{-1}$
Urban conditions		
A-B	$0.32x(1 + 0.0004x)^{-1/2}$	$0.24x(1 + 0.0001x)^{+1/2}$
D	$0.22x(1 + 0.0004x)^{-1/2}$	$0.20x$
D	$0.16x(1 + 0.0004x)^{-1/2}$	$0.14x(1 + 0.0003x)^{-1/2}$
E-F	$0.11x(1 + 0.0004x)^{-1/2}$	$0.08x(1 + 0.0015x)^{-1/2}$

A-F are defined in Table 5-1.

Table 5-1 Atmospheric Stability Classes for Use with the Pasquill-Gifford Dispersion Model^{1,2}

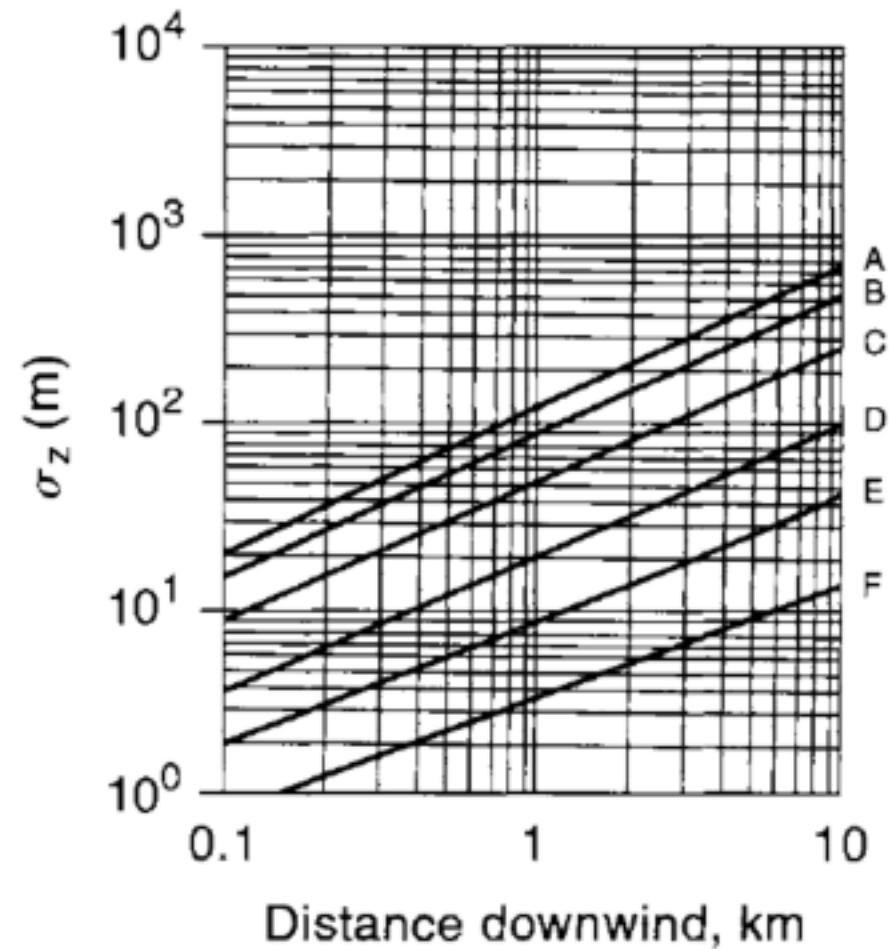
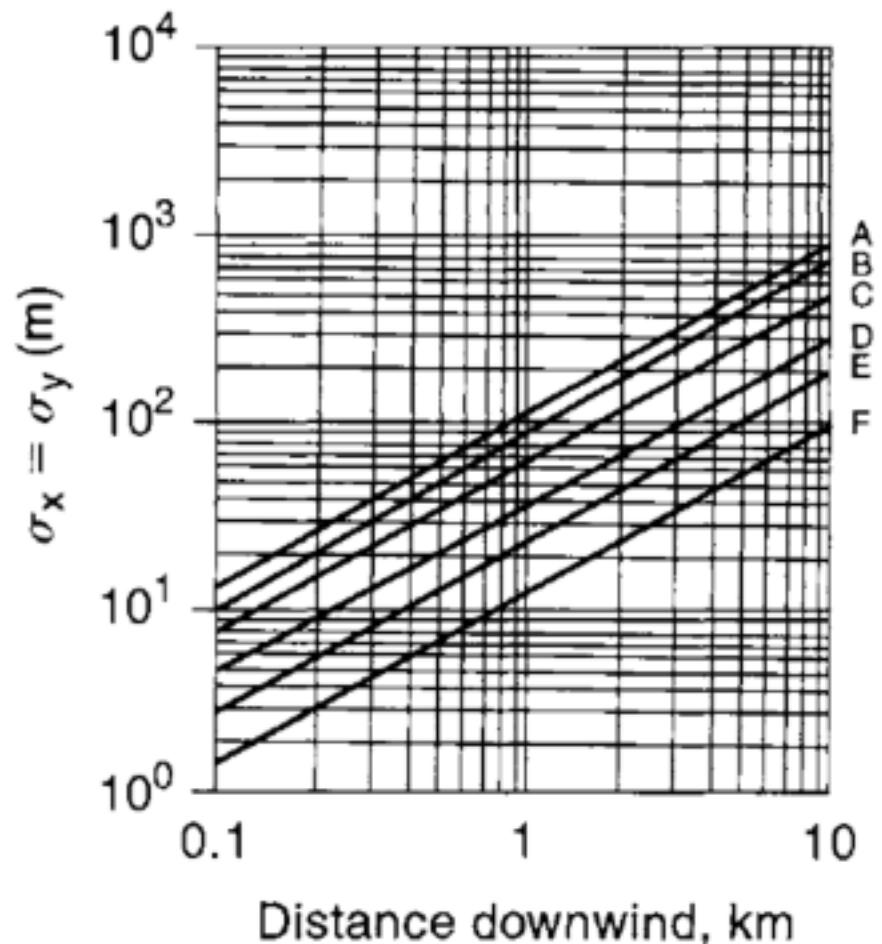
Surface wind speed (m/s)	Daytime insolation ³			Nighttime conditions ⁴	
	Strong	Moderate	Slight	Thin overcast or >4/8 low cloud	≤3/8 cloudiness
<2	A	A-B	B	F ⁵	F ⁵
2-3	A-B	B	C	E	F
3-4	B	B-C	C	D ⁶	E
4-6	C	C-D	D ⁶	D ⁶	D ⁶
>6	C	D ⁶	D ⁶	D ⁶	D ⁶

Stability classes:

- A, extremely unstable
- B, moderately unstable
- C, slightly stable
- D, neutrally stable
- E, slightly stable
- F, moderately stable

³Strong insolation corresponds to a sunny midday in midsummer in England. Slight insolation to similar conditions in midwinter.

⁴Night refers to the period 1 hour before sunset and 1 hour after dawn.



Dispersion coefficients for Pasquill-Gifford puff model.

Table 5-3 Recommended Equations for Pasquill-Gifford Dispersion Coefficients for Puff Dispersion^{1,2} (the downwind distance x has units of meters)

Pasquill-Gifford stability class	σ_y (m) or σ_x (m)	σ_z (m)
A	$0.18x^{0.92}$	$0.60x^{0.75}$
B	$0.14x^{0.92}$	$0.53x^{0.73}$
C	$0.10x^{0.92}$	$0.34x^{0.71}$
D	$0.06x^{0.92}$	$0.15x^{0.70}$
E	$0.04x^{0.92}$	$0.10x^{0.65}$
F	$0.02x^{0.89}$	$0.05x^{0.61}$

A–F are defined in Table 5-1.

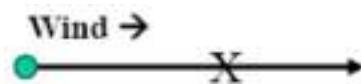
¹R. F. Griffiths, "Errors in the Use of the Briggs Parameterization for Atmospheric Dispersion Coefficients," *Atmospheric Environment* (1994), 28(17): 2861–2865.

²G. A. Briggs, *Diffusion Estimation for Small Emissions*, Report ATDL-106 (Washington, DC: Air Resources, Atmospheric Turbulence, and Diffusion Laboratory, Environmental Research Laboratories, 1974).

Simplified Cases - Plume

The ground-level concentration is found by setting $z = 0$:

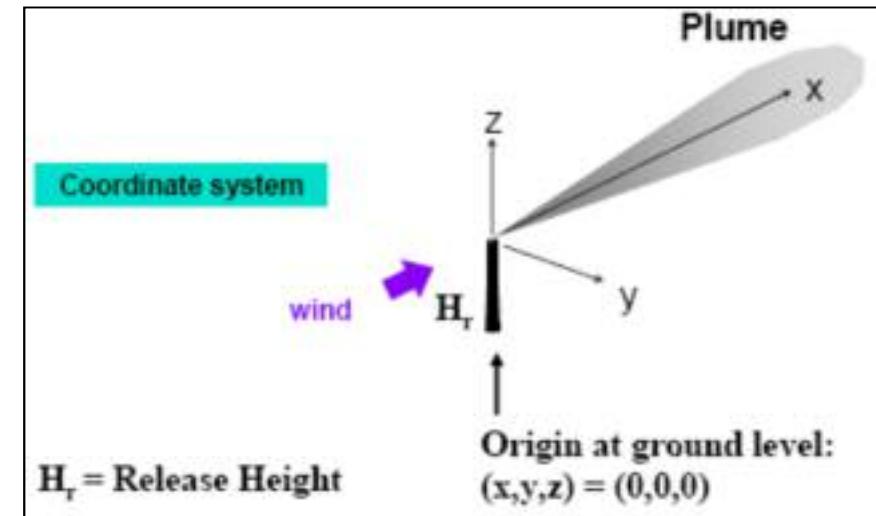
$$\langle C \rangle(x, y, 0) = \frac{Q_m}{\pi\sigma_y\sigma_z u} \exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2 - \frac{1}{2}\left(\frac{H_r}{\sigma_z}\right)^2\right].$$

Ground Centerline Concentration: 

$$\langle C \rangle(x, 0, 0) = \frac{Q_m}{\pi\sigma_y\sigma_z u} \exp\left[-\frac{1}{2}\left(\frac{H_r}{\sigma_z}\right)^2\right]$$

Ground, centerline, release height $H_r = 0$

$$\langle C \rangle(x, 0, 0) = \frac{Q_m}{\pi\sigma_y\sigma_z u}$$



X is implicit in the dispersion coefficients!

Maximum Concentrations - Plume

- Always occurs at release point.
- The distance downwind at which the maximum ground-level concentration occurs:

$$(\sigma_z)_{x,\max} = \frac{H_r}{\sqrt{2}}$$

- For releases above ground, max. concentration on ground occurs

downwind: $\langle C \rangle_{\max} = \frac{2Q_m}{e\pi u H_r^2} \left(\frac{\sigma_z}{\sigma_y} \right)$

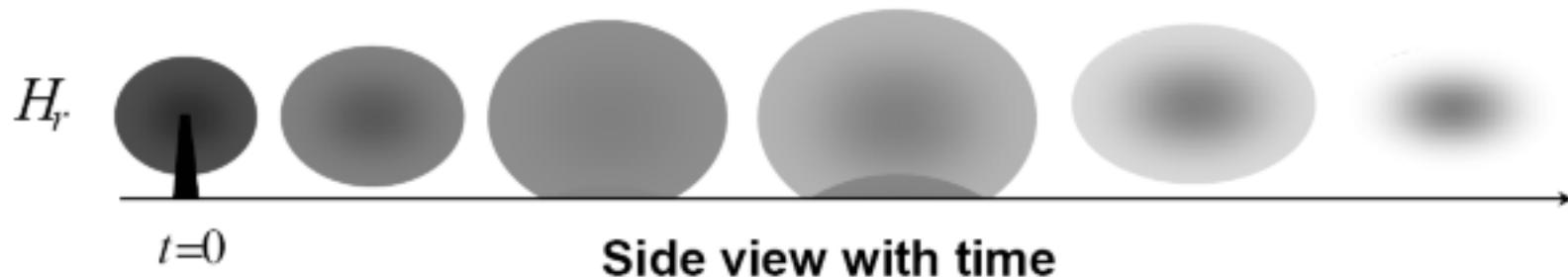
$$(\sigma_z)_{x,\max} = \frac{H_r}{\sqrt{2}}$$

$$\langle C \rangle_{\max} = \frac{2Q_m}{e\pi u H_r^2} \left(\frac{\sigma_z}{\sigma_y} \right)$$

1. Use left equation to determine σ_z
2. Use Figures 5-10 or 5-11 to get x .
3. Determine σ_y from Figures 5-10 or 5-11.
4. Calculate $\langle C \rangle$ from right equation.

Puff

$$\langle C \rangle(x, y, z, t) = \frac{Q_m^*}{\sqrt{2\pi^{3/2}} \sigma_x \sigma_y \sigma_z} \exp\left[\frac{1}{2} \left(\frac{y}{\sigma_y}\right)^2\right] \times \left\{ \exp\left[-\frac{1}{2} \left(\frac{z - H_r}{\sigma_z}\right)^2\right] + \exp\left[-\frac{1}{2} \left(\frac{z + H_r}{\sigma_z}\right)^2\right] \right\}$$



u, t not explicit in equation

x is implicit thru dispersion coefficients

Coordinate system moves with puff center at $x=ut$

Assume $\sigma_x = \sigma_y$

Simplified Cases - Puff

Concentration on ground below puff center

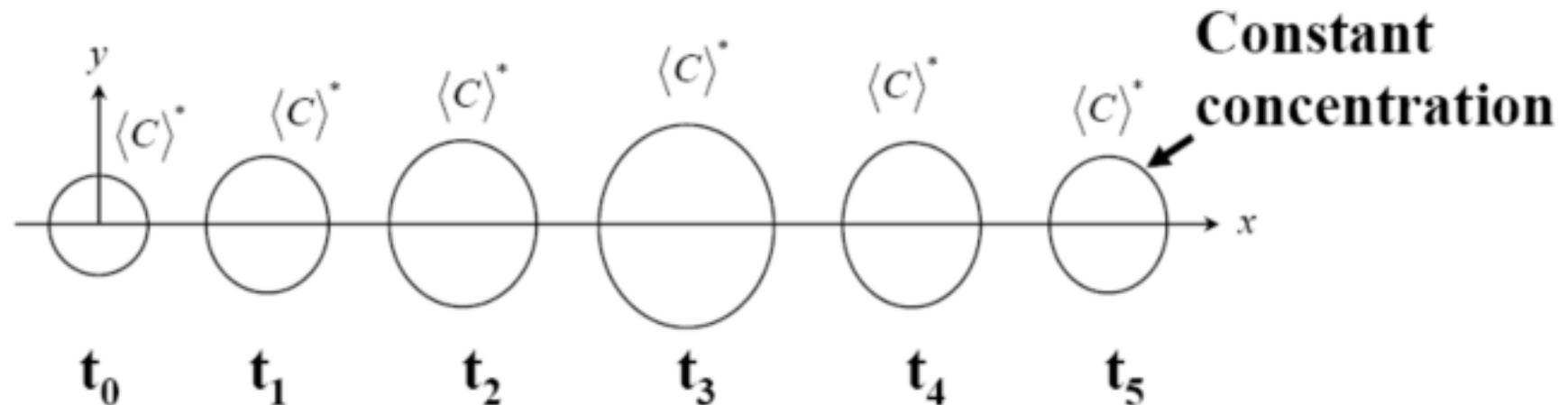
$$\langle C \rangle (0,0,0) = \frac{Q_m^*}{\sqrt{2\pi^{3/2}} \sigma_x \sigma_y \sigma_z} \exp\left[-\frac{1}{2} \left(\frac{H_r}{\sigma_z}\right)^2\right] \quad (5-56)$$

Same as above, with $H_r = 0$. Puff center on ground.

$$\langle C \rangle (0,0,0) = \frac{Q_m^*}{\sqrt{2\pi^{3/2}} \sigma_x \sigma_y \sigma_z} \quad (5-41)$$

Puff center always at release height.

Location of Puff

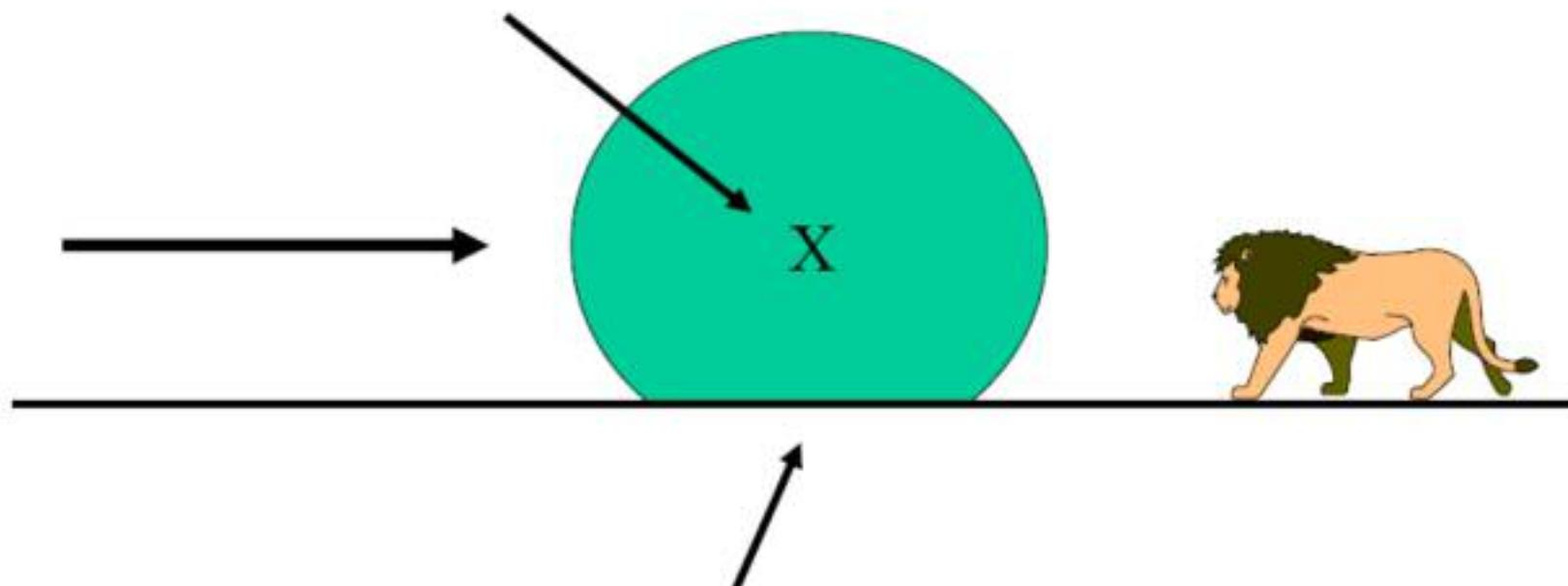


----> **Wind = constant at u**

Center of puff located at: $x = u t$

Maximum Concentration - Puff

Always at puff center



**On ground, max. concentration
always occurs directly below puff
center.**

Example 1:

10 kg/s of H_2S is released 100 m off of ground. Estimate the concentration 1 km downwind on ground? It is a clear, sunny day, 1 PM, wind speed = 3.5 m/s. Assume rural conditions.

Plume, due to continuous nature of release!

From Table 5-1, Stability Class B.

From Figure 5-10, $\sigma_y = 130$ m

From Figure 5-10, $\sigma_z = 120$ m

Use Equation 5-51 for a plume.

Example: Apply Equation 5-51

Applies to ground concentration directly downwind of release:

$$\langle C \rangle(x, 0, 0) = \frac{Q_m}{\pi \sigma_y \sigma_z u} \times \exp \left[-\frac{1}{2} \left(\frac{H_r}{\sigma_z} \right)^2 \right]$$

$$\langle C \rangle(x, 0, 0) = \frac{10.0 \text{ kg/s}}{(3.14)(130 \text{ m})(120 \text{ m})(3.5 \text{ m/s})} \times \exp \left[-\frac{1}{2} \left(\frac{100 \text{ m}}{120 \text{ m}} \right)^2 \right]$$

$$\langle C \rangle(x, 0, 0) = 41.2 \times 10^{-6} \text{ kg/m}^3 = 41.2 \text{ mg/m}^3$$

Use Equation 2-7 to get 29.7 ppm. TLV-TWA is 10 ppm.

Example: Where is max. concentration?

Use Equation 5-53:

$$(\sigma_z)_{x,\max} = \frac{H_r}{\sqrt{2}} = \frac{100 \text{ m}}{1.414} = 70.7 \text{ m}$$

Use equation in Table 5-3 to determine downwind distance:

$$\sigma_z = 0.12x$$

$$70.7 \text{ m} = 0.12x$$

$$x = 590 \text{ m}$$

At this location, from Figure 5-10:

$$\sigma_y = 92 \text{ m}$$

Use Equation 5-52 to calculate max. concentration:

$$\langle C \rangle_{\max} = \frac{2Q_m}{e\pi u H_r^2} \left(\frac{\sigma_z}{\sigma_y} \right) = \frac{(2)(100 \text{ kg/s})}{(2.718)(3.14)(3.5 \text{ m/s})(100 \text{ m})^2} \left(\frac{70.7 \text{ m}}{92 \text{ m}} \right)$$

$$\langle C \rangle_{\max} = 5.14 \times 10^{-4} \text{ kg/m}^3 = 514 \text{ mg/m}^3 = 370 \text{ ppm}$$

Example: What is max. discharge to result in 10 ppm?

Maximum will occur at same location: $(\sigma_z)_{x,\max} = \frac{H_r}{\sqrt{2}}$

10 ppm = 13.9 mg/m³ (Equation 2-7)

Substitute into Equation 5-52:

$$\langle C \rangle_{\max} = \frac{2Q_m}{e\pi u H_r^2} \left(\frac{\sigma_z}{\sigma_y} \right)$$

$$13.9 \times 10^{-6} \text{ kg/m}^3 = \frac{2Q_m}{(2.71)(3.14)(3.5 \text{ m/s})(100 \text{ m})^2} \left(\frac{70.71 \text{ m}}{92 \text{ m}} \right)$$

$Q_m = 2.7 \text{ kg/s}$ **Not very much!**

Example 2:

10 kg of H₂S is released instantly on the ground. What is concentration at fenceline 100 m away? Same conditions as before.

From Table 5-1, stability class is B.

At x = 0.1 km, from Figure 5-12: $\sigma_y = 10 \text{ m}$ $\sigma_z = 16 \text{ m}$

Use Equation 5-41 for a ground release, centerline conc.:

$$\langle C \rangle (0, 0, 0) = \frac{Q_m^*}{\sqrt{2\pi}^{3/2} \sigma_x \sigma_y \sigma_z}$$

Assume $\sigma_x = \sigma_y$

$$Q_m^* = 10 \text{ kg} = 10 \times 10^6 \text{ mg}$$

$$\langle C \rangle = 79.4 \text{ mg/m}^3 = 571 \text{ ppm}$$

How long does it take for puff to reach fenceline?

$$x = ut$$

$$t = \frac{x}{u} = \frac{100 \text{ m}}{3.5 \text{ m/s}} = 28.6 \text{ s after release.}$$

Very little time for an emergency response!

What size release will result in 10 ppm at fenceline?

Same procedure as for plume. Answer is 0.175 kg = 175 gm.

Not very much! Better to contain chemicals than to mitigate after a release!

! Exercises & HW

Examples

5.1

5.2

HW:

5.4

5.9

5.12

Integrated Dose

- When a person is standing in a fixed location (x, y, z) and a puff passes over, he/she receives a dose that is the time integral of the concentration.

$$D_{tid}(x, y, z) = \int_0^{\infty} \langle C \rangle(x, y, z, t) dt$$

- For person on ground at distance y crosswind, Eq. 5-43

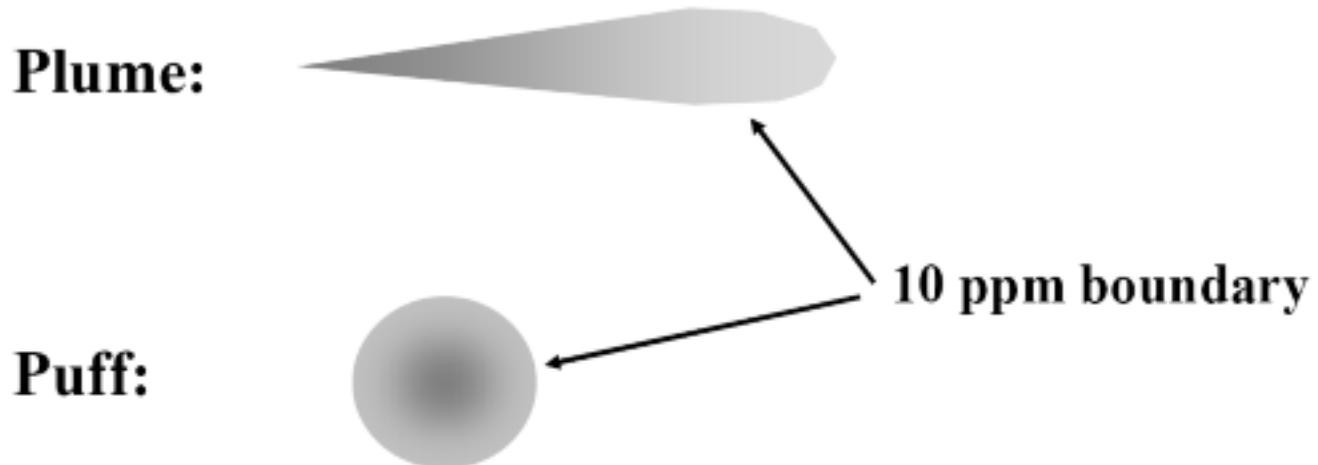
$$D_{tid}(x, y, 0) = \frac{Q_m}{\pi \sigma_y \sigma_z u} \exp\left(-\frac{1}{2} \frac{y^2}{\sigma_y^2}\right)$$

- For person on ground at centerline of flow, Eq. 5-44

$$D_{tid}(x, 0, 0) = \frac{Q_m}{\pi \sigma_y \sigma_z u}$$

Isopleths

- The cloud boundary defined by a fixed concentration
- Lines of constant concentration



Determining Isopleths: Plume and Puff

$$y = \sigma_y \sqrt{2 \ln \left(\frac{< C > (x, 0, 0, t)}{< C > (x, y, 0, t)} \right)} \quad (5-45)$$

↓
Downwind, ground centerline conc. Isopleth conc.

The ground-level concentration is given at $z = 0$:

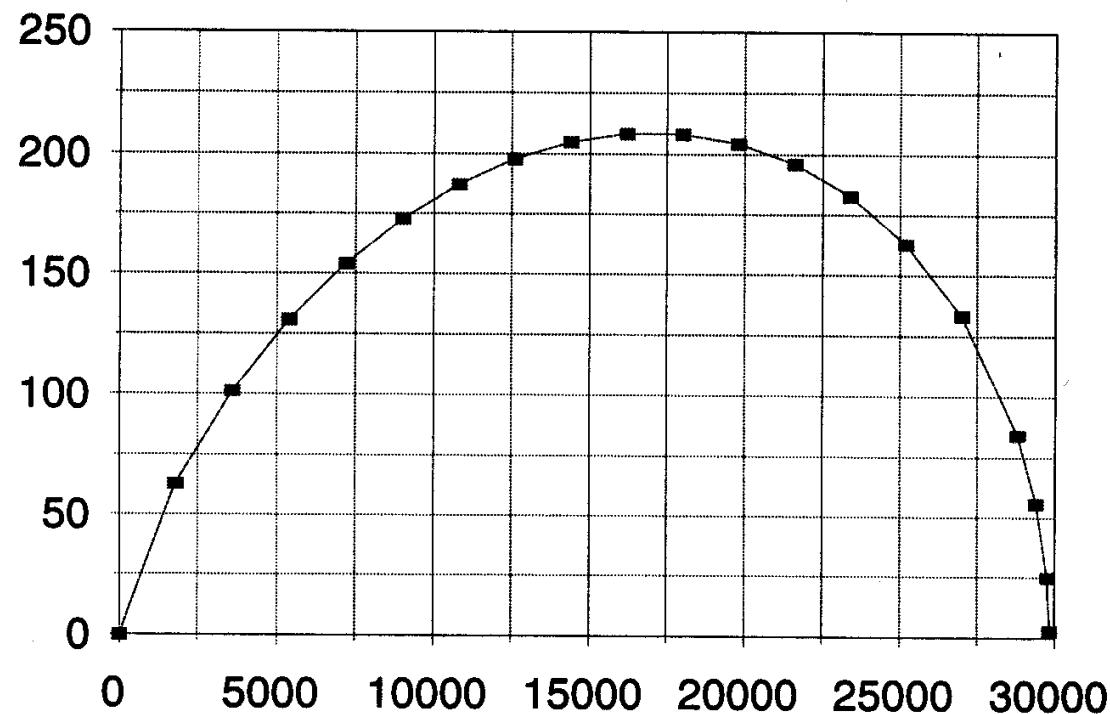
$$\langle C \rangle (x, y, 0, t) = \frac{Q_m^*}{\sqrt{2\pi}^{3/2} \sigma_x \sigma_y \sigma_z} \exp \left\{ -\frac{1}{2} \left[\left(\frac{x - ut}{\sigma_x} \right)^2 + \frac{y^2}{\sigma_y^2} \right] \right\}.$$

The ground-level concentration along the x axis is given at $y = z = 0$:

$$\langle C \rangle (x, 0, 0, t) = \frac{Q_m^*}{\sqrt{2\pi}^{3/2} \sigma_x \sigma_y \sigma_z} \exp \left[-\frac{1}{2} \left(\frac{x - ut}{\sigma_x} \right)^2 \right].$$

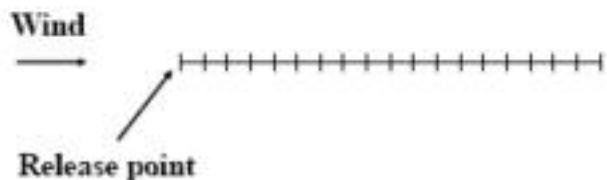
Equation 5-45 makes more sense if you write it as follows

$$y = \sigma_y \sqrt{2 \ln \left(\frac{\langle C \rangle(x, 0, 0, t)_{centerline}}{\langle C \rangle(x, y, 0, t)_{desired}} \right)}$$



Procedure to Determine Isopleths - 1

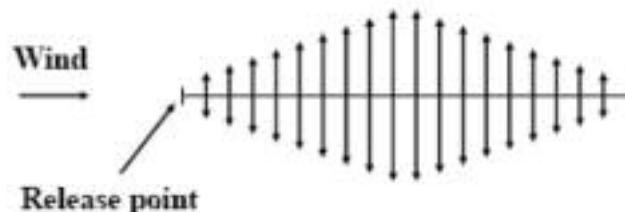
1. Determine concentrations along centerline at fixed points downwind.



2. Use equation (5-45) to find y at each fixed point.

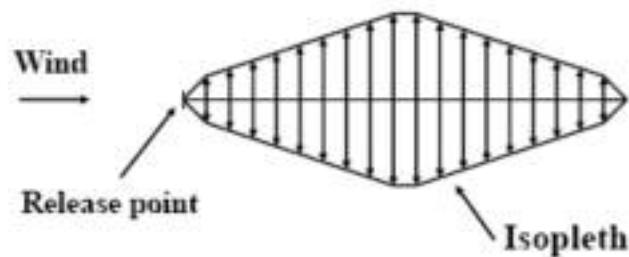
Procedure to Determine Isopleths - 2

3. Plot $+y$ and $-y$ at each fixed point.



Procedure to Determine Isopleths - 3

4. Connect the points.



Toxic Effect Criteria

ERPG: Emergency Response Planning Guideline

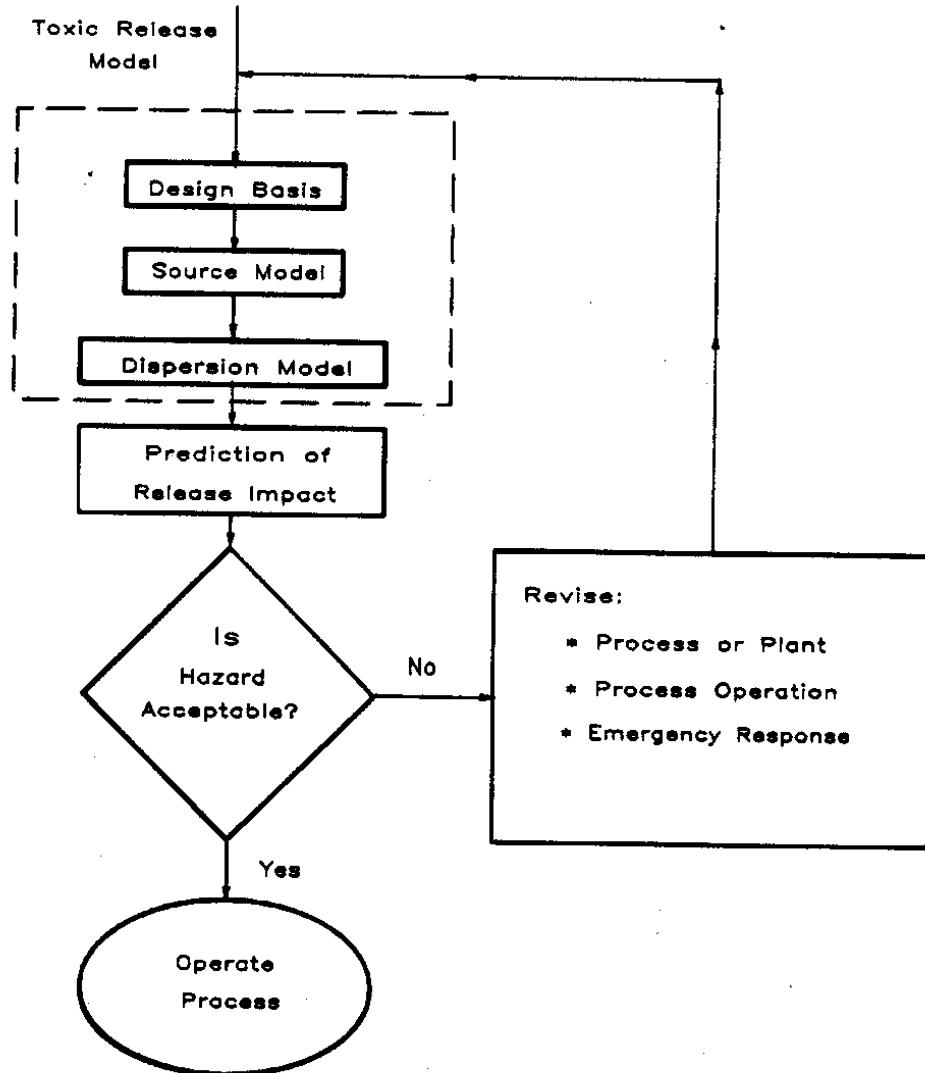
- **ERPG-1:** max. airborne concentration below which it is believed nearly all individuals can be exposed for up to 1-hr without experiencing effects other than mild transient adverse health effects or perceiving a clearly defined objectionable odor.
- **ERPG-2:** max. airborne conc. below which it is believed nearly all individuals can be exposed up to 1-hr without experiencing or developing irreversible or other serious health effects or symptoms that could impair their ability to take protective action.
- **ERPG-3:** max. airborne concentration below which it is believed nearly all individuals can be exposed for up to 1-hour without experiencing or developing life-threatening health effects.

Table 5-6

	<u>ERPG-1</u>	<u>ERPG-2</u>	<u>ERPG-3</u>
Ammonia	25 ppm	200 ppm	1000 ppm
Chlorine	1 ppm	3 ppm	20 ppm
Monomethylamine	10 ppm	100 ppm	500 ppm
Toluene	50 ppm	300 ppm	1000 ppm

Release Mitigation

- Utilize toxic release models as a tool for release mitigation.
- Make changes in process, operations or emergency response scenarios according to results.



Release Mitigation

- Inherent Safety
 - Inventory reduction
 - Chemical substitution
 - Process attenuation
- Engineering Design
 - Process integrity
 - Emergency control
 - Spill containment
- Management
 - Policies and procedures
 - Training for vapor release
 - Audits & inspections
 - Equipment testing
 - Routine maintenance
 - Management of change
 - Security

Process Safety Engineering:

Industrial Hygiene

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Industrial Hygiene: Definition

- **Industrial hygiene** is a science devoted to the identification, evaluation, and control of occupational conditions that cause sickness and injury
- **Industrial hygiene** is concerned with predicting, recognizing, assessing, controlling, and preventing workplace environmental stressors that can cause sickness or serious discomfort to workers.
 - An environmental stressor is any factor that can cause enough discomfort to result in lost time or illness.
 - *Gases, fumes, vapors, dusts, mists, noise, and radiation.*

Industrial Hygiene Phases

1. **Identification:** determination of the presence or possibility of workplace exposures.
2. **Evaluation:** determination of the magnitude of the exposure.
3. **Control:** application of appropriate technology to reduce workplace exposures to acceptable levels.

What Is an Industrial Hygienist?

- A person who by study, training, and experience can:

- ✓ Anticipate
- ✓ Recognize
- ✓ Evaluate
- ✓ Control

ANTICIPATION	Expectation of hazard existence
IDENTIFICATION	Presence of workplace exposure
EVALUATION	Magnitude of exposure
CONTROL	Reduction to acceptable levels

workplace environmental hazards

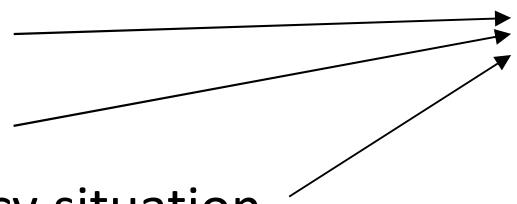
- ✓ **Anticipation/recognition** of potential or actual hazards through knowledge of:
 - Materials
 - Operations
 - Processes
 - Conditions
- ✓ **Evaluation** of environmental factors through:
 - Measurement of exposure intensity
 - Determination of exposure frequency, and duration
 - Comparison with regulatory, professional, and internal standards
 - Judgment: weigh all factors

- ✓ **Control** by employing of methods to eliminate or reduce exposure resulting in elimination or reduction of the occurrence of occupational disease through:
 - Engineering (including process) interventions
 - Administrative/programmatic measures
 - Personal protective equipment

OSHA: Process Safety Management

- **Process safety management (PSM)** was developed after the Bhopal accident (1985), to prevent similar accidents.
- Activities undertaken in Emergency management:

- Before the emergency situation
- During the emergency situation
- Immediately After the emergency situation



PSM

- Emergency management is a part of PSM (in chemical-related industries)

Purpose Of PSM

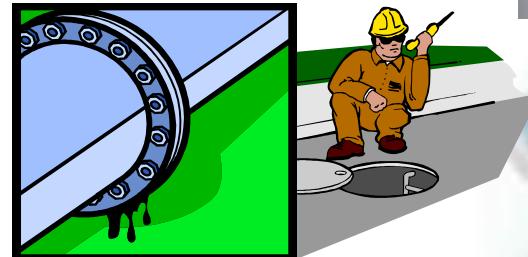
- **Proactive** and **systematic** Preventing or minimizing the consequences of catastrophic release of toxic, flammable, reactive or explosive chemicals



The PSM standard major sections



- Process safety Information (PSI)
- Employee participation
- Process Hazard Analysis (PHA)
- Operating procedure
- Training
- contractors safety
- Pre-Start-up Safety Review (PSSR)
- Mechanical Integrity
- Nonroutine work authorization (Hot Work Permits)
- Management of Change
- Emergency Planning and Response
- Incident Investigation
- Audit of PSM
- Trade secrets



EPA: Risk Management Plan (RMP)

- The RMP regulation is aimed at decreasing the number and magnitude of accidental releases of toxic and flammable substances.
- Although the RMP is similar to the PSM regulation in many respects, the RMP is designed to protect off-site people and the environment, whereas PSM is designed to protect on-site people.

➤ The RMP has the following elements:

- ✓ hazard assessment,
- ✓ prevention program,
- ✓ emergency response program,
- ✓ documentation that is maintained on the site and submitted to authorities. This information is also shared with the local community.

Industrial Hygiene: Identification

- In order to safely handle many hazardous chemicals on a daily basis within chemical plants, **all potential hazards must be identified and controlled.**
- **The identification step requires a thorough study of** the chemical process, operating conditions, and operating procedures.
- The sources of information include: process design descriptions, operating instructions, safety reviews, equipment vendor descriptions, information from chemical suppliers, and information from operating personnel.
- The quality of this identification step is often a function of the number of resources used and the quality of the questions asked.

Potential hazards

CHEMICAL PROCESS

OPERATING CONDITIONS

OPERATING PROCEDURES

- Process design
- Operating instructions
- Safety reviews
- Equipment description
- Chemical properties **MSDS's**



Data Useful for Health identification

- Threshold limit values (TLVs)
- Odor threshold for vapors
- Physical state
- Vapor pressure of liquids
- Sensitivity of chemical to temperature or impact
- Rates and heats of reaction
- Hazardous by-products
- Reactivity with other chemicals
- Explosive concentrations of chemicals, dusts, and vapors
- Noise levels of equipment
- Types and degree of radiation

Potential hazards	
Liquids	Noise
Vapors	Radiation
Dusts	Temperature
Fumes	Mechanical
Entry mode of toxicants	
Inhalation	Ingestion
Body absorption (skin or eyes)	Injection
Potential damage	
Lungs	Skin
Ears	Eyes
Nervous system	Liver
Kidneys	Reproductive organs
Circulatory system	Other organs

¹Olishfski, *Fundamentals of Industrial Hygiene*, pp. 24–26.

RISK ASSESSMENT: potential for hazard to result in an accident

Industrial Hygiene: Evaluation

- The evaluation phase determines the extent and degree of employee exposure to toxicants and physical hazards in the workplace environment.
- The various types of existing control measures and their effectiveness are also studied in the evaluation phase.
- Sudden exposures to high concentrations: ready access to a clean environment is important.
- Chronic effects arise from repeated exposures to low concentrations: preventing and controlling through continuous or frequent and periodic sampling and analysis.
- After the exposure data are obtained, it is necessary to compare actual exposure levels to acceptable occupational health standards to identify the potential hazards requiring better or more control measures.

Evaluating Exposures to Volatile Toxicants by Monitoring

- Continuously monitoring the air concentrations of toxicants on-line in a work environment (the monitoring depends on equipment availability)

$$\text{TWA} = \frac{1}{8} \int_0^{t_*} C(t) dt,$$

where,

- $C(t)$ is the concentration (in ppm or mg/m^3) of the chemical in the air and
- t , is the worker shift time in hours.

- **For one chemical**, if we assume that the concentration C_i is fixed (or averaged) over the period of time T_i , the TWA concentration is computed by

$$\text{TWA} = \frac{C_1 T_1 + C_2 T_2 + \dots + C_n T_n}{8 \text{ hr}}.$$

- The combined exposures from multiple toxicants with different TLV-TWAs is determined from the equation:

$$\sum_{i=1}^n \frac{C_i}{(\text{TLV-TWA})_i},$$

where

n is the total number of toxicants,

C_i is the concentration of chemical i with respect to the other toxicants, and

$(\text{TLV-TWA})_i$ is the TLV-TWA for chemical species i .

If the sum in the above Equation exceeds 1, then the workers are overexposed

The mixture TLV-TWA can be computed from

$$(\text{TLV-TWA})_{\text{mix}} = \frac{\sum_{i=1}^n C_i}{\sum_{i=1}^n \frac{C_i}{(\text{TLV-TWA})_i}}.$$

If the sum of the concentrations of the toxicants in the mixture exceeds this amount,

$$(\text{TLV-TWA})_{\text{mix}} < \sum_{i=1}^n C_i$$

then the workers are overexposed.

Example

Air contains 5 ppm of diethylamine (TLV-TWA of 10 ppm), 20 ppm of cyclohexanol (TLV-TWA of 50 ppm), and 10 ppm of propylene oxide (TLV-TWA of 20 ppm). What is the mixture TLV-TWA and has this level been exceeded?

Solution

From Equation 3-4,

$$\begin{aligned}(\text{TLV-TWA})_{\text{mix}} &= \frac{5 + 20 + 10}{\frac{5}{10} + \frac{20}{50} + \frac{10}{20}} \\ &= 25 \text{ ppm.}\end{aligned}$$

The total mixture concentration is $5 + 20 + 10 = 35$ ppm. The workers are overexposed under these circumstances.

An alternative approach is to use Equation 3-3:

$$\sum_{i=1}^3 \frac{C_i}{(\text{TLV-TWA})_i} = \frac{5}{10} + \frac{20}{50} + \frac{10}{20} = 1.40.$$

Because this quantity is greater than 1, the TLV-TWA has been exceeded.

Evaluation of Worker Exposures to Dusts

Dust evaluation calculations are performed in a manner identical to that used for volatile vapors. Instead of using ppm as a concentration unit, **mg/m³** or **mppcf** (millions of particles per cubic foot) is more convenient.

$$(\text{TLV-TWA})_{\text{mix}} = \frac{\sum_{i=1}^n C_i}{\sum_{i=1}^n \frac{C_i}{(\text{TLV-TWA})_i}}.$$

Example 3-5

Determine the TLV for a uniform mixture of dusts containing the following particles:

Type of dust	Concentration (wt.%)	TLV (mppcf)
Nonasbestiform talc	70	20
Quartz	30	2.7

Solution

From Equation 3-4:

$$\begin{aligned}\text{TLV of mixture} &= \frac{1}{\frac{C_1}{\text{TLV}_1} + \frac{C_2}{\text{TLV}_2}} \\ &= \frac{1}{\frac{0.70}{20} + \frac{0.30}{2.7}} \\ &= 6.8 \text{ mppcf.}\end{aligned}$$

Special control measures will be required when the actual particle count (of the size range specified in the standards or by an industrial hygienist) exceeds 6.8 mppcf.

Evaluating Worker Exposures to Noise

Noise evaluation calculations are performed identically to calculations for vapors, except that dBA is used instead of ppm and hours of exposure is used instead of concentration

$$\text{TLV-TWA}_{\text{mix}} = \frac{\sum_{i=1}^n C_i}{\sum_{i=1}^n \frac{C_i}{(\text{TLV-TWA})_i}},$$

Table 3-8 Permissible Noise Exposures¹

Sound level (dBA)	Maximum exposure (hr)
90	8
92	6
95	4
97	3
100	2
102	1.5
105	1
110	0.5
115	0.25

¹B. A. Plog, ed., *Fundamentals of Industrial Hygiene*, 3d ed. (Chicago: National Safety Council, 1988), p. 176.

Example 3-6

Determine whether the following noise level is permissible with no additional control features:

Noise level (dBA)	Duration (hr)	Maximum allowed (hr)
85	3.6	no limit
95	3.0	4
110	0.5	0.5

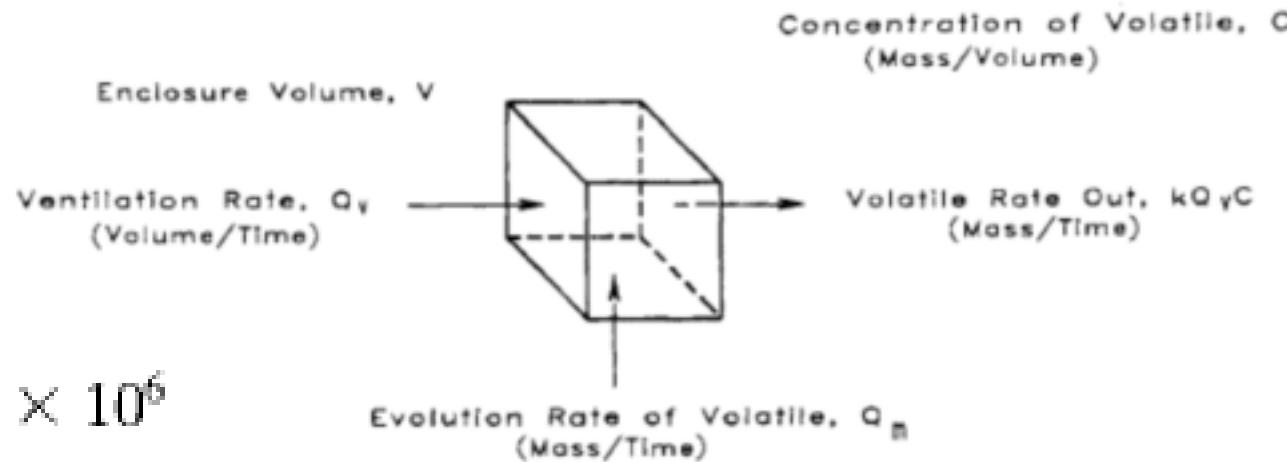
Solution

From Equation 3-3:

$$\sum_{i=1}^3 \frac{C_i}{(\text{TLV-TWA})_i} = \frac{3.6}{\text{no limit}} + \frac{3}{4} + \frac{0.5}{0.5} = 1.75.$$

Because the sum exceeds 1.0, employees in this environment are immediately required to wear ear protection. On a longer-term basis, noise reduction control methods should be developed for the specific pieces of equipment with excessive noise levels.

Estimating Worker Exposures to Toxic Vapors



$$C_{\text{ppm}} = \frac{Q_m R_g T}{k Q_v P M} \times 10^6$$

C be the concentration of volatile vapor in the enclosure (mass/volume),

V be the volume of the enclosure (volume),

Q_v be the ventilation rate (volume/time),

k be the nonideal mixing factor (unitless), and

Q_m be the evolution rate of volatile material (mass/time).

R_g is the ideal gas constant,

T is the absolute ambient temperature,

P is the absolute pressure, and

M is the molecular weight of the volatile species.

- ✓ A steady-state condition is assumed
- ✓ The K varies from 0.1 to 0.5 for most practical situation. For perfect mixing $k = 1$.

Example 3-7

An open toluene container in an enclosure is weighed as a function of time, and it is determined that the average evaporation rate is 0.1 g/min. The ventilation rate is 100 ft³/min. The temperature is 80°F and the pressure is 1 atm. Estimate the concentration of toluene vapor in the enclosure, and compare your answer to the TLV for toluene of 50 ppm.

Solution

Because the value of k is not known directly, it must be used as a parameter. From Equation 3-9

$$kC_{\text{ppm}} = \frac{Q_m R_g T}{Q_v P M} \times 10^6.$$

From the data provided

$$Q_m = 0.1 \text{ g/min} = 2.20 \times 10^{-4} \text{ lb}_m/\text{min},$$

$$R_g = 0.7302 \text{ ft}^3 \text{ atm/lb-mol}^{\circ}\text{R},$$

$$T = 80^{\circ}\text{F} = 540^{\circ}\text{R},$$

$$Q_v = 100 \text{ ft}^3/\text{min},$$

$$M = 92 \text{ lb}_m/\text{lb-mol},$$

$$P = 1 \text{ atm}.$$

Substituting into the equation for kC_{ppm} :

$$\begin{aligned} kC_{\text{ppm}} &= \frac{(2.20 \times 10^{-4} \text{ lb}_m/\text{min})(0.7302 \text{ ft}^3 \text{ atm/lb-mol}^{\circ}\text{R})(540^{\circ}\text{R})}{(100 \text{ ft}^3/\text{min})(1 \text{ atm})(92 \text{ lb}_m/\text{lb-mol})} \times 10^6 \\ &= 9.43 \text{ ppm.} \end{aligned}$$

Because k varies from 0.1 to 0.5, the concentration is expected to vary from 18.9 ppm to 94.3 ppm. Actual vapor sampling is recommended to ensure that the TLV is not exceeded.

Estimating the Vaporization Rate of a Liquid

- The vaporization rate is proportional to the difference between the saturation vapor pressure and the partial pressure of the vapor in the stagnant air;

$$Q_m \propto (P^{\text{sat}} - p),$$

Where,

P^{sat} is the saturation vapor pressure of the pure liquid at the temperature of the liquid
 p is the partial pressure of the vapor in the bulk stagnant gas above the liquid.

$$Q_m = \frac{MKA(P^{\text{sat}} - p)}{R_g T_L},$$

$$Q_m = \frac{MKAP^{\text{sat}}}{R_g T_L}.$$

When $P^{\text{sat}} \gg p$

Q_m is the evaporation rate (mass/time),

M is the molecular weight of the volatile substance,

K is a mass transfer coefficient (length/time) for an area A ,

R_g is the ideal gas constant, and

T_L is the absolute temperature of the liquid.

- The vaporization rate of volatile from an open vessel or from a spill of liquid
- to estimate the concentration (in ppm) of a volatile in an enclosure resulting from evaporation of a liquid

$$C_{\text{ppm}} = \frac{K A T P^{\text{sat}}}{k Q_v P T_L} \times 10^6.$$

- For most situations $T = T_L$

$$C_{\text{ppm}} = \frac{K A P^{\text{sat}}}{k Q_v P} \times 10^6.$$

$$K = K_0 \left(\frac{M_0}{M} \right)^{1/3}.$$

- Water is most frequently used as a reference substance; it has a mass transfer coefficient (K_0) of 0.83 cm/s.

Industrial Hygiene: Control

- This requires the application of appropriate technology for reducing workplace exposures.
- During the design process, the designer must pay particular attention to ensure that the newly designed control technique provides the desired control
- The two major control techniques are:
 - ✓ The Environmental controls and
 - ✓ Personal protection
- Respirators
- Ventilation

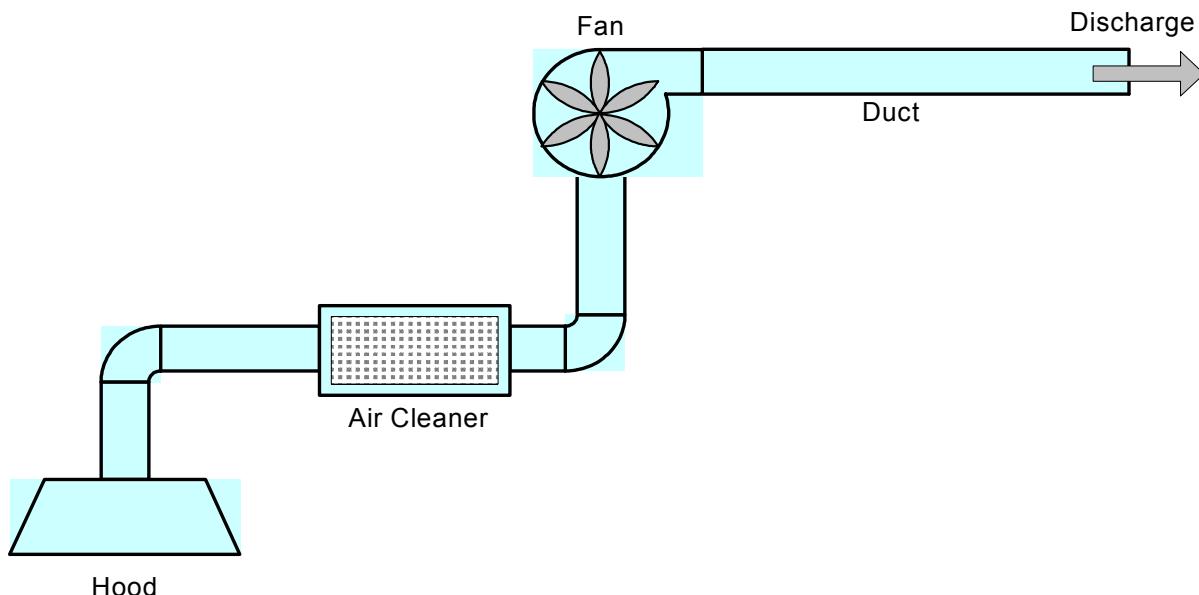
Type and explanation	Typical techniques
Enclosures	
Enclose room or equipment and place under negative pressure.	<ul style="list-style-type: none"> Enclose hazardous operations such as sample points. Seal rooms, sewers, ventilation, and the like. Use analyzers and instruments to observe inside equipment. Shield high-temperature surfaces. Pneumatically convey dusty material.
Local ventilation	
Contain and exhaust hazardous substances.	<ul style="list-style-type: none"> Use properly designed hoods. Use hoods for charging and discharging. Use ventilation at drumming station. Use local exhaust at sample points. Keep exhaust systems under negative pressure.
Dilution ventilation	
Design ventilation systems to control low-level toxics.	<ul style="list-style-type: none"> Design locker rooms with good ventilation and special areas or enclosures for contaminated clothing. Design ventilation to isolate operations from rooms and offices. Design filter press rooms with directional ventilation.
Wet methods	
Use wet methods to minimize contamination with dusts.	<ul style="list-style-type: none"> Clean vessels chemically vs. sandblasting. Use water sprays for cleaning. Clean areas frequently. Use water sprays to shield trenches or pump seals.
Good housekeeping	
Keep toxicants and dusts contained.	<ul style="list-style-type: none"> Use dikes around tanks and pumps. Provide water and steam connections for area washing. Provide lines for flushing and cleaning. Provide well-designed sewer system with emergency containment.
Personal protection	
As last line of defense.	<ul style="list-style-type: none"> Use safety glasses and face shields. Use aprons, arm shields, and space suits. Wear appropriate respirators; airline respirators are required when oxygen concentration is less than 19.5%.

Ventilation

- Ventilation can quickly remove dangerous concentrations of flammable and toxic materials.
- Ventilation can be highly localized, reducing the quantity of air moved and the equipment size.
- Ventilation equipment is readily available and can be easily installed.
- Ventilation equipment can be added to an existing facility
- Ventilation is based on two principles: (1) dilute the contaminant below the target concentration, and (2) remove the contaminant before workers are exposed.

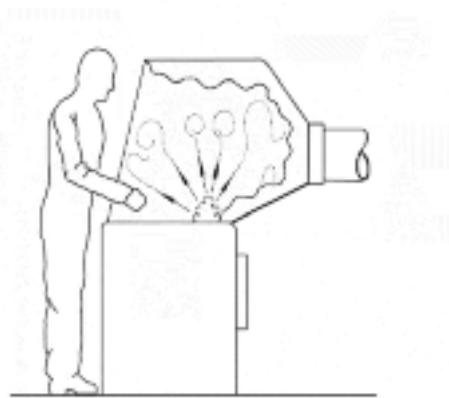
➤ The major disadvantage of ventilation is the operating cost.

- Ventilation systems are composed of fans and ducts.
- The fans produce a small pressure drop (less than 0.1 psi) that moves the air.
- The best system is a negative pressure system, with the fans located at the exhaust end of the system, pulling air out.

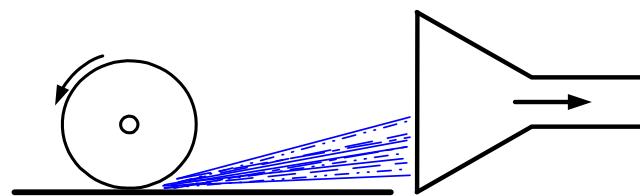


Local Ventilation

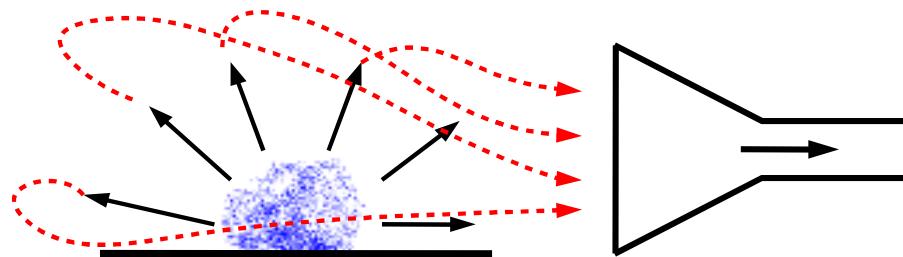
Enclosing (Contain and separate)



Receiving (Receive, contain & empty)



Capturing (Capture)



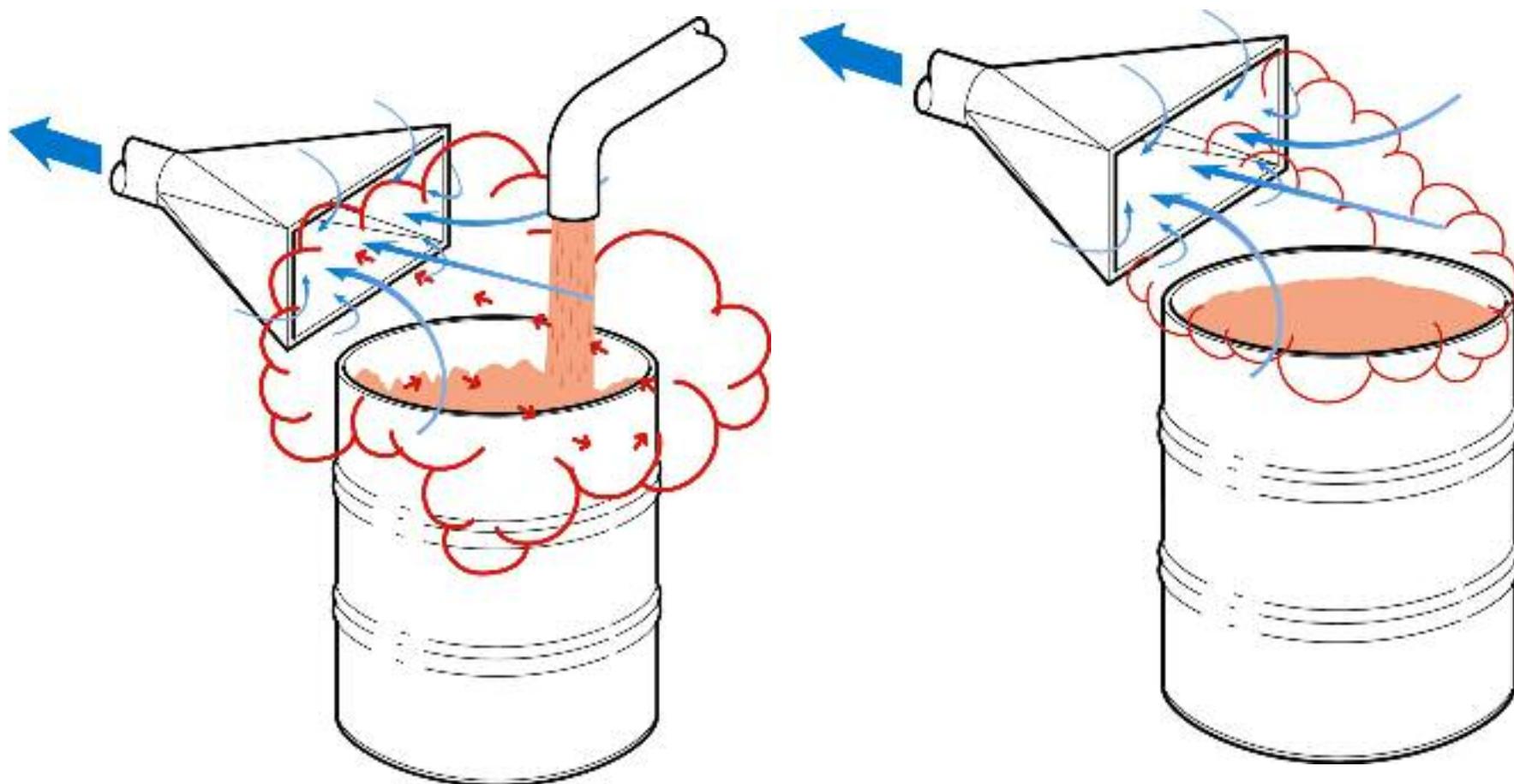
Source: HSE

Main reasons why systems fail to protect:

- Incorrect type of hood is chosen (and could never provide sufficient protection)
- The airborne contaminant isn't contained or captured.
- LEV hood design doesn't match the process and source(s)
- Insufficient airflow (various reasons).



Capturing Hoods



Air Cleaners - Filters



3.15

3.21

3.22

3.25